Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V

IUPAC Subcommittee on Gas Kinetic Data Evaluation
for Atmospheric Chemistry

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This paper updates and extends previous critical evaluations of the kinetics and photochemistry of gas-phase chemical reactions of neutral species involved in atmospheric chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984); **18**, 881 (1989); **21**, 1125 (1992)]. The work has been carried out by the authors under the auspices of the IUPAC Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry. Data sheets have been prepared for 658 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each reaction, a preferred value of the rate coefficient at 298 K is given together with a temperature dependence where possible. The selection of the preferred value is discussed and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. The data sheets are intended to provide the basic physical chemical data needed as input for calculations which model atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an appendix listing the available data on enthalpies of formation of the reactant and product species. We have also included for the first time in this series of evaluations a section on heterogeneous reactions of importance in atmospheric chemistry. © 1997 American Institute of Physics and American Chemical Society. [S0047-2689(97)00204-3]

Key words: air pollution; atmospheric chemistry; chemical kinetics; data evaluation; gas phase; heterogeneous atmospheric reactions; photoabsorption cross-section, photochemistry; quantum yield; rate coefficient.

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1. Preface

This paper is the fifth supplement to the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry, published by the CODATA Task Group on Gas Phase Chemical Kinetics in 1980¹ and subsequently updated by the first supplement in 1982,² and the second supplement in 1984.³ The original evaluation and the first two supplements were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude).

In 1985 the International Union of Pure and Applied Chemistry (IUPAC) set up a group to continue and enlarge upon the work initiated by CODATA. The Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry is chaired by J. A. Kerr and is part of the Commission on Chemical Kinetics (I.4) of the IUPAC Physical Chemistry Division.

This subcommittee produced the third supplement in 1989,⁴ and the fourth supplement in 1992,⁵ in which the original data base was extended and updated to include more reactions involved in tropospheric chemistry. Since it was not possible to cope with all of the very large number of chemical reactions involved in tropospheric chemistry, it was decided to limit the coverage to those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms. The present fifth supplement has continued this policy in considering the reactions of organic species.

Following the pattern of the fourth supplement,⁵ here we provide a data sheet for each of the reactions considered. For thermal reactions for which no new data have been published since the last data sheet was presented, we have summarized that data sheet by listing the **Preferred Values** together with

the *Comments on the Preferred Values*. For thermal reactions for which new data have subsequently appeared since the data sheet was last published, we have followed our previous practice of listing only the new data, together with updated Reviews and Evaluations. For photochemical reactions for which no new data have been published we have reproduced the data sheet from the last evaluation.⁵ Where new data have become available for existing photochemical reactions, we have listed only the new data. As in Supplement IV, we have also prepared a large number of data sheets for “new” thermal and photochemical reactions, which were not included in our previous evaluations.

For each reaction the data sheet includes the preferred rate coefficient with a statement of the error limits, a comment giving the basis for the recommendation, and a list of the relevant references. To the extent that this information suffices, the reader can use the present publication without need to refer to the previous publications in the series. However, it should be emphasized that in preparing the updated data sheets, we have not listed all of the previous data contained in the original evaluation¹ and the four supplements.^{2–5} Consequently for many reactions, to obtain the overall picture and background to the preferred rate parameters, it is essential that the present supplement be read in conjunction with its predecessors.^{1–5}

The following list of reactions, for which data sheets were prepared in previous evaluations, have now been omitted, on the grounds that they are unimportant in atmospheric chemistry:

These reactions are no longer included in the present Summary of Reactions and in referring to them in previous evaluations,¹⁻⁵ it should be kept in mind that the data sheets may not be up-to-date for any particular reaction.

In this evaluation we have included for the first time in our series of evaluations a consideration of heterogeneous reactions which are involved in atmospheric chemistry. In this context we have focused upon an assessment of data relating to uptake coefficients of gas phase species upon relevant surfaces. A summary table listing the heterogeneous reactions considered is also given after the summary table for the gas-phase reactions.

The cutoff point for literature searching for this supplement was May 1994. As in our previous evaluations, we also include data which were available to us in preprint form at that point.

2. Summary of Reactions and Preferred Rate Data

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
<i>O_x Reactions</i>						
550	$O + O_2 + M \rightarrow O_3 + M$	$6.0 \times 10^{-34} [O_2]$	± 0.05	$6.0 \times 10^{-34} (T/300)^{-2.8} [O_2]$	100–300	$\Delta n = \pm 0.5$
550	$O + O_3 \rightarrow 2O_2$	$5.6 \times 10^{-34} [N_2]$	± 0.05	$5.6 \times 10^{-34} (T/300)^{-2.8} [N_2]$	100–300	$\Delta n = \pm 0.5$
551	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	8.0×10^{-15}	± 0.08	$8.0 \times 10^{-12} \exp(-2060/T)$	200–400	± 200
551	$O(^1D) + O_3 \rightarrow O_2 + 2O(^3P)$	4.0×10^{-11}	± 0.05	$3.2 \times 10^{-11} \exp(67/T)$	200–350	± 100
	$\rightarrow 2O_2(^3\Sigma_g^-)$	1.2×10^{-10}	± 0.1	2.4×10^{-10}	100–400	$\Delta \log k = \pm 0.05$
		1.2×10^{-10}	± 0.1			
552	$O_2^* + O_3 \rightarrow O + 2O_2$		See data sheet			
552	$O_2(^3\Sigma_g^-, v') + M \rightarrow O_2(^3\Sigma_g^-, v'') + M$	1.6×10^{-18}	See data sheet			
553	$O_2(^1\Delta_g) + M \rightarrow O_2(^3\Sigma_g^-) + M$	$\leq 1.4 \times 10^{-19}$	± 0.2	$3.0 \times 10^{-18} \exp(-200/T)$	100–450	± 200
		5×10^{-18}	± 0.3			
		$\leq 2 \times 10^{-20}$				
553	$O_2(^1\Delta_g) + O_3 \rightarrow 2O_2 + O$	3.8×10^{-15}	± 0.10	$5.2 \times 10^{-11} \exp(-2840/T)$	280–360	± 500
554	$O_2(^1\Sigma_g^+) + M \rightarrow O_2(^3\Sigma_g^-) + M$	4.0×10^{-17}	± 0.3		200–350	± 200
	$\rightarrow O_2(^1\Delta_g) + M$	2.0×10^{-15}	± 0.10	2.0×10^{-15}		
		8.0×10^{-14}	± 0.3			
		4.0×10^{-12}	± 0.3			
		4.1×10^{-13}	± 0.10	4.1×10^{-13}	245–360	± 200
555	$O_2(^1\Sigma_g^+) + O_3 \rightarrow 2O_2 + O$	2.2×10^{-11}	± 0.06	2.2×10^{-11}	295–360	± 300
	$\rightarrow O_2(^1\Delta_g) + O_3$					
	$\rightarrow O_2(^3\Sigma_g^-) + O_3$					
556	$O_2 + h\nu \rightarrow$ products	See data sheet				
557	$O_3 + h\nu \rightarrow$ products	See data sheet				
<i>HO_x Reactions</i>						
560	$H + HO_2 \rightarrow H_2 + O_2$	5.6×10^{-12}	± 0.5	5.6×10^{-12}	245–300	$\Delta \log k = \pm 0.5$
	$\rightarrow 2HO$	7.2×10^{-11}	± 0.1	7.2×10^{-11}	245–300	$\Delta \log k = \pm 0.1$
	$\rightarrow H_2O + O$	2.4×10^{-12}	± 0.5	2.4×10^{-12}	245–300	$\Delta \log k = \pm 0.5$
560	$H + O_2 + M \rightarrow HO_2 + M$	$5.4 \times 10^{-32} [N_2]$	± 0.2	$5.4 \times 10^{-32} (T/300)^{-1.8} [N_2]$	200–600	$\Delta n = \pm 0.6$
		7.5×10^{-11}	± 0.3	7.5×10^{-11}	200–300	$\Delta n = \pm 0.6$
		$F_c = 0.55$	$\Delta F_c = \pm 0.15$	$F_c = \exp(-T/498)$	200–300	
561	$O + HO \rightarrow O_2 + H$	3.3×10^{-11}	± 0.1	$2.3 \times 10^{-11} \exp(110/T)$	220–500	± 100
562	$O + HO_2 \rightarrow HO + O_2$	5.8×10^{-11}	± 0.08	$2.7 \times 10^{-11} \exp(224/T)$	200–400	± 100
562	$O + H_2O_2 \rightarrow HO + HO_2$	1.7×10^{-15}	± 0.3	$1.4 \times 10^{-12} \exp(-2000/T)$	250–390	± 1000
563	$O(^1D) + H_2 \rightarrow HO + H$	1.1×10^{-10}	± 0.1	1.1×10^{-10}	200–350	± 100
563	$O(^1D) + H_2O \rightarrow 2HO$	2.2×10^{-10}	± 0.1	2.2×10^{-10}	200–350	± 100
564	$HO + H_2 \rightarrow H_2O + H$	6.7×10^{-15}	± 0.1	$7.7 \times 10^{-12} \exp(-2100/T)$	200–450	± 200
564	$HO + HO \rightarrow H_2O + O$	1.9×10^{-12}	± 0.15	$7.9 \times 10^{-14} (T/298)^{2.6} \exp(945/T)$	200–500	± 250

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/$ K
565	$\text{HO} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$6.9 \times 10^{-31} [\text{N}_2]$ 2.6×10^{-11} $F_c=0.5$	(k_0) (k_∞) ± 0.1 ± 0.2	$6.9 \times 10^{-31} (T/300)^{-0.8} [\text{N}_2]$ 2.6×10^{-11}	200–400 200–300	$\Delta n = \pm 0.5$ $\Delta \log k_\infty = \pm 0.2$
566	$\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.1×10^{-10}	± 0.1	$4.8 \times 10^{-11} \exp(250/T)$	250–400	± 200
566	$\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	1.7×10^{-12}	± 0.1	$2.9 \times 10^{-12} \exp(-160/T)$	240–460	± 100
567	$\text{HO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	6.7×10^{-14}	± 0.15	$1.9 \times 10^{-12} \exp(-1000/T)$	220–450	± 300
567	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.6×10^{-12}	± 0.15	$2.2 \times 10^{-13} \exp(600/T)$	230–420	± 200
567	$\text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M}$	$5.2 \times 10^{-32} [\text{N}_2]$ $4.5 \times 10^{-32} [\text{O}_2]$ See data sheet for effect of H_2O	± 0.15 ± 0.15	$1.9 \times 10^{-33} [\text{N}_2] \exp(980/T)$	230–420	± 300
568	$\text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$	2.0×10^{-15}	± 0.2	$1.4 \times 10^{-14} \exp(-600/T)$	250–350	+500 –100
569	$\text{H}_2\text{O} + h\nu \rightarrow \text{products}$	See data sheet				
569	$\text{H}_2\text{O}_2 + h\nu \rightarrow \text{products}$	See data sheet				
<i>NO_x Reactions</i>						
571	$\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$1.0 \times 10^{-31} [\text{N}_2]$ 3.0×10^{-11} $F_c=0.85$	(k_0) (k_∞) ± 0.1 ± 0.3	$1.0 \times 10^{-31} (T/300)^{-1.6} [\text{N}_2]$ $3.0 \times 10^{-11} (T/300)^{0.3}$ $F_c = \exp(-T/1850)$	200–300 200–1500 200–300	$\Delta n = \pm 0.3$ $\Delta n = \pm 0.3$
572	$\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$	9.7×10^{-12}	± 0.06	$6.5 \times 10^{-12} \exp(120/T)$	230–350	± 120
572	$\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{NO}_3 + \text{M}$	$9.0 \times 10^{-32} [\text{N}_2]$ 2.2×10^{-11} $F_c=0.8$	(k_0) (k_∞) ± 0.10 ± 0.2	$9.0 \times 10^{-32} (T/300)^{-2.0} [\text{N}_2]$ 2.2×10^{-11} $F_c = \exp(-T/1300)$	200–400 200–400 200–400	$\Delta n = \pm 1$ $\Delta n = \pm 0.5$
573	$\text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_2$	1.7×10^{-11}	± 0.3			
573	$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2$	2.6×10^{-11}	± 0.1	$1.8 \times 10^{-11} \exp(107/T)$	200–350	± 100
574	$\text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$	4.4×10^{-11}	± 0.1	4.4×10^{-11}	200–350	± 100
574	$\rightarrow 2\text{NO}$	7.2×10^{-11}	± 0.1	7.2×10^{-11}	200–350	± 100
574	$\text{HO} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2$	1.6×10^{-13}	± 0.1	$3.5 \times 10^{-12} \exp(-925/T)$	230–450	± 200
575	$\text{HO} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	6.5×10^{-12}	± 0.15	$2.7 \times 10^{-12} \exp(260/T)$	250–400	± 260
576	$\text{HO} + \text{HONO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	1.5×10^{-13}	(1 bar) ± 0.1	See data sheet		
576	$\text{HO} + \text{HO}_2\text{NO}_2 \rightarrow \text{products}$	5.0×10^{-12}	± 0.2	$1.5 \times 10^{-12} \exp(360/T)$	240–340	+300 –600
577	$\text{HO} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M}$	$7.4 \times 10^{-31} [\text{N}_2]$ 4.5×10^{-11} $F_c=0.9$	(k_0) (k_∞) ± 0.10 ± 0.2	$7.4 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2]$ 4.5×10^{-11}	200–400 200–400	$\Delta n = \pm 0.5$ $\Delta \log k = \pm 0.2$
578	$\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$2.6 \times 10^{-30} [\text{N}_2]$ 6.7×10^{-11} $F_c=0.43$	(k_0) (k_∞) ± 0.1 ± 0.10	$2.6 \times 10^{-30} (T/300)^{-2.9} [\text{N}_2]$ $6.7 \times 10^{-11} (T/300)^{-0.6}$	200–400 200–400	$\Delta n = \pm 0.3$ $\Delta n = \pm 0.5$
580	$\text{HO} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2$	2.0×10^{-11}	± 0.3			
580	$\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$	8.3×10^{-12}	± 0.1	$3.7 \times 10^{-12} \exp(240/T)$	230–500	± 100
581	$\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M}$	$1.8 \times 10^{-31} [\text{N}_2]$ 4.7×10^{-12} $F_c=0.6$	(k_0) (k_∞) ± 0.10 ± 0.2	$1.8 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2]$ 4.7×10^{-12}	200–300 200–300	$\Delta n = \pm 1$ $\Delta n = \pm 1$

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
582	$\text{HO}_2\text{NO}_2 + \text{M} \rightarrow \text{HO}_2 + \text{NO}_2 + \text{M}$	$1.3 \times 10^{-20} [\text{N}_2]$ (k_0/s^{-1}) 0.34 (k_∞/s^{-1}) $F_c = 0.6$	± 0.3 ± 0.5	$5 \times 10^{-6} (-10000/T) [\text{N}_2]$ $2.6 \times 10^{15} \exp(-10900/T)$	260–300 260–300	± 500 ± 500
583	$\text{HO}_2 + \text{NO}_3 \rightarrow \text{O}_2 + \text{HNO}_3$ $\rightarrow \text{HO} + \text{NO}_2 + \text{O}_2$	4.0×10^{-12}	± 0.2			
584	$\text{NH}_2 + \text{O}_2 \rightarrow \text{products}$	$< 6 \times 10^{-21}$				
584	$\text{NH}_2 + \text{O}_3 \rightarrow \text{products}$	1.7×10^{-13}	± 0.5	$4.9 \times 10^{-12} \exp(-1000/T)$	250–380	± 500
585	$\text{NH}_2 + \text{NO} \rightarrow \text{products}$	1.6×10^{-11}	± 0.2	$1.6 \times 10^{-11} (T/298)^{-1.5}$	210–500	$\Delta n = \pm 0.5$
586	$\text{NH}_2 + \text{NO}_2 \rightarrow \text{products}$	2.0×10^{-11}	± 0.2	$2.0 \times 10^{-11} (T/298)^{-2.0}$	250–500	$\Delta n = \pm 0.7$
586	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	2.0×10^{-38} (cm ⁶ molecule ⁻² s ⁻¹)	± 0.1	$3.3 \times 10^{-39} \exp(530/T)$	273–600	± 400
586	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	1.8×10^{-14}	± 0.08	$1.8 \times 10^{-12} \exp(-1370/T)$	195–304	± 200
587	$\text{NO} + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_3 + \text{M}$	$3.1 \times 10^{-34} [\text{N}_2]$ (k_0) 7.9×10^{-12} (k_∞)	± 0.3 ± 0.3	$3.1 \times 10^{-34} (T/300)^{-1.7} [\text{N}_2]$ $7.9 \times 10^{-12} (T/300)^{1.4}$	208–300 208–300	$\Delta n = \pm 1$ $\Delta n = \pm 0.5$
588	$\text{N}_2\text{O}_3 + \text{M} \rightarrow \text{NO} + \text{NO}_2 + \text{M}$	$F_c = 0.6$ $1.6 \times 10^{-14} [\text{N}_2]$ (k_0/s^{-1})	± 0.4	$1.9 \times 10^{-7} (T/300)^{-8.7}$ $\times \exp(-4880/T) [\text{N}_2]$ $4.7 \times 10^{15} (T/300)^{0.4} \exp(-4880/T)$	225–300 225–300	± 200 $\Delta n = \pm 1$ ± 100 $\Delta n = \pm 1$
589	$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	$F_c = 0.6$ 2.6×10^{-11}	± 0.1	$1.8 \times 10^{-11} \exp(110/T)$	220–400	± 100
590	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	3.2×10^{-17}	± 0.06	$1.2 \times 10^{-13} \exp(-2450/T)$	230–360	± 150
590	$\text{NO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$	$1.4 \times 10^{-33} [\text{N}_2]$ (k_0) 1.0×10^{-12} (k_∞)	± 0.3 ± 0.3	$1.4 \times 10^{-32} (T/300)^{-3.8} [\text{N}_2]$ 1.0×10^{-12}	300–500 250–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
592	$\text{N}_2\text{O}_4 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_2 + \text{M}$	$F_c = 0.40$ $6.1 \times 10^{-15} [\text{N}_2]$ (k_0/s^{-1})	± 0.3	$1.3 \times 10^{-5} (T/300)^{-3.8}$ $\times \exp(-6400/T) [\text{N}_2]$ $1.15 \times 10^{16} \exp(-6460/T)$	300–500 250–300	± 500 ± 500
593	$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	4.4×10^6 $F_c = 0.40$ $2.7 \times 10^{-30} [\text{N}_2]$ (k_0) 2.0×10^{-12} (k_∞)	± 0.10 ± 0.2	$2.7 \times 10^{-30} (T/300)^{-3.4} [\text{N}_2]$ $2.0 \times 10^{-12} (T/300)^{0.2}$	200–400 200–500	$\Delta n = \pm 0.5$ $\Delta n = \pm 0.6$
594	$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$F_c = 0.33$ $9.5 \times 10^{-20} [\text{N}_2]$ (k_0/s^{-1})	± 0.2	$F_c = [\exp(-7250) + \exp(-1050/T)]$ $1.0 \times 10^{-3} (T/300)^{-3.5}$ $\times \exp(-11000/T) [\text{N}_2]$ $9.7 \times 10^{14} (T/300)^{0.1}$ $\times \exp(-11080/T)$ $F_c = [\exp(-7250) + \exp(-1050/T)]$	200–500 200–400 200–300 200–300	$\Delta n = \pm 0.5$ $\Delta n = \pm 0.2$
595	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$F_c = 0.33$ $< 2 \times 10^{-21}$	± 0.3			
595	$\text{HONO} + h\nu \rightarrow \text{products}$	See data sheet				
596	$\text{HONO}_2 + h\nu \rightarrow \text{products}$	See data sheet				
599	$\text{HO}_2\text{NO}_2 + h\nu \rightarrow \text{products}$	See data sheet				
599	$\text{NO}_2 + h\nu \rightarrow \text{products}$	See data sheet				
601	$\text{NO}_3 + h\nu \rightarrow \text{products}$	See data sheet				
604	$\text{N}_2\text{O} + h\nu \rightarrow \text{products}$	See data sheet				
605	$\text{N}_2\text{O}_5 + h\nu \rightarrow \text{products}$	See data sheet				

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
<i>Organic Reactions</i>						
607	O + CH ₃ → products	1.4 × 10 ⁻¹⁰	± 0.1	1.4 × 10 ⁻¹⁰	200–900	± 100
607	O(¹ D) + CH ₄ → HO + CH ₃ → HCHO + H ₂	1.5 × 10 ⁻¹⁰	± 0.1	1.5 × 10 ⁻¹⁰	200–300	± 100
608	HO + CH ₄ → H ₂ O + CH ₃	6.2 × 10 ⁻¹⁵	± 0.08	2.3 × 10 ⁻¹² exp(–1765/T)	240–300	± 100
610	HO + C ₂ H ₆ + M → C ₂ H ₅ OH + M	5.0 × 10 ⁻³⁰ [N ₂] 9.0 × 10 ⁻¹³	± 0.1 ± 0.1	5 × 10 ⁻³⁰ (T/300) ^{-1.5} [N ₂] 9.0 × 10 ⁻¹³ (T/300) ²	200–300 200–300	$\Delta n = \pm 1.5$ $\Delta n = \pm 1$
611	HO + C ₂ H ₄ + M → C ₂ H ₄ OH + M	$F_c = 0.62$ 7 × 10 ⁻²⁹ [N ₂] 9 × 10 ⁻¹²	± 0.3 ± 0.3	7 × 10 ⁻²⁹ (T/300) ^{-3.1} [N ₂] 9 × 10 ⁻¹²	200–300 200–300	$\Delta n = \pm 2$ $\Delta n = \pm 0.5$
613	HO + C ₂ H ₆ → H ₂ O + C ₂ H ₅	2.5 × 10 ⁻¹³	± 0.10	7.9 × 10 ⁻¹² exp(–1030/T)	240–300	± 100
614	HO + C ₃ H ₈ + M → C ₃ H ₇ OH + M	8 × 10 ⁻²⁷ [N ₂] 3.0 × 10 ⁻¹¹	± 1.0 ± 0.1	8 × 10 ⁻²⁷ (T/300) ^{-3.5} [N ₂] 3.0 × 10 ⁻¹¹	200–300 200–300	$\Delta n = \pm 1$ $\Delta n = \pm 1$
615	HO + C ₃ H ₈ → H ₂ O + C ₃ H ₇	$F_c = 0.5$ 1.10 × 10 ⁻¹²	± 0.08	8.0 × 10 ⁻¹² exp(–590/T)	240–300	± 150
617	HO + CO → H + CO ₂	1.3 × 10 ⁻¹³ (1 + 0.6 P/bar)	± 0.1	1.3 × 10 ⁻¹³ (1 + 0.6 P/bar) × (300/T) ^{1.0}	200–300	$\Delta \log k = \pm 0.2$
618	HO + HCHO → H ₂ O + HCO	9.2 × 10 ⁻¹²	± 0.10	8.6 × 10 ⁻¹² exp(20/T)	240–300	± 150
619	HO + CH ₃ CHO → H ₂ O + CH ₃ CO	1.6 × 10 ⁻¹¹	± 0.10	5.6 × 10 ⁻¹² exp(310/T)	240–530	± 200
620	HO + C ₂ H ₅ CHO → products	2.0 × 10 ⁻¹¹	± 0.15			
620	HO + (CHO) ₂ → H ₂ O + CHOCO	1.1 × 10 ⁻¹¹	± 0.3			
621	HO + HOCH ₂ CHO → H ₂ O + HOCH ₂ CO → H ₂ O + HOCHCHO	8.0 × 10 ⁻¹²	± 0.3			
621	HO + CH ₃ COCHO → H ₂ O + CH ₃ COCO	2.0 × 10 ⁻¹²	± 0.2			
622	HO + CH ₃ COCH ₃ → H ₂ O + CH ₃ COCH ₂	1.5 × 10 ⁻¹¹	± 0.15			
622	HO + CH ₃ OH → H ₂ O + CH ₂ OH → H ₂ O + CH ₃ O	2.2 × 10 ⁻¹³	± 0.15			
623	HO + C ₂ H ₅ OH → H ₂ O + CH ₂ CH ₂ OH → H ₂ O + CH ₃ CHOH → H ₂ O + CH ₃ CH ₂ O	7.9 × 10 ⁻¹³ 1.4 × 10 ⁻¹³ 1.6 × 10 ⁻¹³ 2.9 × 10 ⁻¹² 1.6 × 10 ⁻¹³	± 0.15 ± 0.15 ± 0.15 ± 0.15 ± 0.15	2.8 × 10 ⁻¹² exp(–760/T) 3.1 × 10 ⁻¹² exp(–360/T) 4.1 × 10 ⁻¹² exp(–70/T)	240–300 240–300 270–340	± 200 ± 200 ± 200
625	HO + n-C ₃ H ₇ OH → products	5.5 × 10 ⁻¹²	± 0.2			
625	HO + i-C ₃ H ₇ OH → products	5.1 × 10 ⁻¹²	± 0.12	2.7 × 10 ⁻¹² exp(190/T)	270–340	± 200
626	HO + CH ₃ OCH ₃ → H ₂ O + CH ₃ OCH ₂	2.9 × 10 ⁻¹²	± 0.2	1.0 × 10 ⁻¹¹ exp(–370/T)	290–450	± 200
627	HO + CH ₃ COCH ₂ OH → products	3.0 × 10 ⁻¹²	± 0.3			
627	HO + CH ₃ OOH → H ₂ O + CH ₂ OOH → H ₂ O + CH ₃ OO	1.9 × 10 ⁻¹² 3.6 × 10 ⁻¹² 4.5 × 10 ⁻¹³	± 0.2 ± 0.2 ± 0.15	1.0 × 10 ⁻¹² exp(190/T) 1.9 × 10 ⁻¹² exp(190/T) 4.5 × 10 ⁻¹³	220–430 220–430 290–450	± 150 ± 150 ± 250
628	HO + HCOOH → products	8 × 10 ⁻¹³	± 0.3			
628	HO + CH ₃ COOH → products	1.2 × 10 ⁻¹²	± 0.2	1.2 × 10 ⁻¹²	290–450	± 300
629	HO + C ₂ H ₅ COOH → products	3.5 × 10 ⁻¹³	± 0.10	1.0 × 10 ⁻¹⁴ exp(1060/T) (1 bar)	290–400	± 500
629	HO + CH ₃ ONO ₂ → products					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/$ K
630	$\text{HO} + \text{C}_2\text{H}_5\text{ONO}_2 \rightarrow \text{products}$	4.9×10^{-13}	± 0.15	$4.4 \times 10^{-14} \exp(720/T)$ (1 bar)	290–380	± 500
630	$\text{HO} + n\text{-C}_3\text{H}_7\text{ONO}_2 \rightarrow \text{products}$	7.3×10^{-13}	± 0.15	7.3×10^{-13} (1 bar)	290–370	± 500
630	$\text{HO} + i\text{-C}_3\text{H}_7\text{ONO}_2 \rightarrow \text{products}$	4.9×10^{-13}	± 0.25			
631	$\text{HO} + \text{CH}_3\text{CO}_2\text{NO}_2 \rightarrow \text{products}$	1.1×10^{-13}	± 0.2	$9.5 \times 10^{-13} \exp(-650/T)$	270–300	± 400
631	$\text{HO} + \text{CH}_3\text{COCH}_2\text{ONO}_2 \rightarrow \text{products}$	$< 1 \times 10^{-12}$				
632	$\text{HO} + \text{HCN} \rightarrow \text{products}$	3×10^{-14}	± 0.5	$1.2 \times 10^{-13} \exp(-400/T)$ (1 bar)	290–440	± 300
632	$\text{HO} + \text{CH}_3\text{CN} \rightarrow \text{products}$	2.2×10^{-14}	± 0.15	$8.1 \times 10^{-13} \exp(-1080/T)$ (1 bar)	250–390	± 200
633	$\text{HO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{O}_2 + \text{CH}_3\text{O}_2\text{H}$	5.2×10^{-12}	± 0.3	$3.8 \times 10^{-13} \exp(780/T)$	225–580	± 500
633	$\text{HO}_2 + \text{HOCH}_2\text{O}_2 \rightarrow \text{O}_2 + \text{HOCH}_2\text{O}_2\text{H}$ $\rightarrow \text{O}_2 + \text{HCO}_2\text{H} + \text{H}_2\text{O}$	1.2×10^{-11}	± 0.3	$5.6 \times 10^{-15} \exp(2300/T)$	275–335	± 1500
634	$\text{HO}_2 + \text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{O}_2 + \text{C}_2\text{H}_5\text{O}_2\text{H}$	7.7×10^{-12}	± 0.2	$2.7 \times 10^{-13} \exp(1000/T)$	200–500	± 300
635	$\text{HO}_2 + \text{CH}_3\text{CO}_3 \rightarrow \text{O}_2 + \text{CH}_3\text{CO}_3\text{H}$ $\rightarrow \text{O}_3 + \text{CH}_3\text{CO}_2\text{H}$	1.0×10^{-11} 3.6×10^{-12}	± 0.3 ± 0.3	$4.3 \times 10^{-13} \exp(1040/T)$	250–370	± 500
636	$\text{HO}_2 + \text{HOCH}_2\text{CH}_2\text{O}_2 \rightarrow \text{products}$	1.0×10^{-11}	± 0.3			
636	$\text{HO}_2 + \text{CH}_3\text{OCH}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CH}_3\text{OCH}_2\text{O}_2\text{H}$ $\rightarrow \text{O}_2 + \text{CH}_3\text{OCHO} + \text{H}_2\text{O}$	See data sheet				
637	$\text{HO}_2 + \text{CH}_3\text{COCH}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CH}_3\text{COCH}_2\text{O}_2\text{H}$	9.0×10^{-12}	± 0.3	$9.7 \times 10^{-15} \exp(625/T)$	275–333	± 600
637	$\text{HO}_2 + \text{HCHO} \rightarrow \text{HOCH}_2\text{OO}$	7.9×10^{-14}	± 0.3	$2.4 \times 10^{-12} \exp(-7000/T)$	275–333	± 2000
638	$\text{HOCH}_2\text{OO} \rightarrow \text{HO}_2 + \text{HCHO}$	1.5×10^2				
639	$\text{NO}_3 + \text{CH}_4 \rightarrow \text{HNO}_3 + \text{CH}_3$	$< 1 \times 10^{-18}$				
639	$\text{NO}_3 + \text{C}_2\text{H}_2 \rightarrow \text{products}$	$< 1 \times 10^{-16}$	± 0.2	$3.3 \times 10^{-12} \exp(-2880/T)$	270–340	± 500
640	$\text{NO}_3 + \text{C}_2\text{H}_4 \rightarrow \text{products}$	2.1×10^{-16}	± 0.2	$4.6 \times 10^{-13} \exp(-1155/T)$	296–423	± 300
641	$\text{NO}_3 + \text{C}_2\text{H}_6 \rightarrow \text{HNO}_3 + \text{C}_2\text{H}_5$	$< 1 \times 10^{-17}$				
641	$\text{NO}_3 + \text{C}_3\text{H}_6 \rightarrow \text{products}$	9.5×10^{-15}	± 0.3			
642	$\text{NO}_3 + \text{C}_3\text{H}_8 \rightarrow \text{HNO}_3 + \text{C}_3\text{H}_7$	$< 7 \times 10^{-17}$	± 0.2	$1.4 \times 10^{-12} \exp(-1860/T)$	260–370	± 500
642	$\text{NO}_3 + \text{HCHO} \rightarrow \text{HNO}_3 + \text{HCO}$	5.8×10^{-16}	± 0.3	$1.3 \times 10^{-12} \exp(-2560/T)$	290–480	± 700
643	$\text{NO}_3 + \text{CH}_3\text{CHO} \rightarrow \text{HNO}_3 + \text{CH}_3\text{CO}$	2.7×10^{-15}	± 0.2			
643	$\text{NO}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{HNO}_3 + \text{CH}_3\text{COCH}_2$	$< 3 \times 10^{-17}$				
644	$\text{NO}_3 + \text{CH}_3\text{OH} \rightarrow \text{products}$	2.4×10^{-16}	± 0.5			
644	$\text{NO}_3 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{products}$	$< 2 \times 10^{-15}$				
644	$\text{NO}_3 + i\text{-C}_3\text{H}_7\text{OH} \rightarrow \text{products}$	$< 5 \times 10^{-15}$				
645	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	$1.0 \times 10^{-30} [\text{N}_2]$ 1.8×10^{-12}	± 0.2 ± 0.3	$1.0 \times 10^{-30} (T/300)^{-3.3} [\text{N}_2]$ $1.8 \times 10^{-12} (T/300)^{1.1}$	200–300 200–300	$\Delta n = \pm 1$ $\Delta n = \pm 1$
646	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$	$F_c = 0.27$ 3.8×10^{-15}	± 0.5			
646	$\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$	1.9×10^{-14} $5.9 \times 10^{-29} [\text{N}_2]$	± 0.5 ± 0.3	(1 bar air) (0.133 bar air)	200–300 200–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.2$
647	$n\text{-C}_3\text{H}_7 + \text{O}_2 + \text{M} \rightarrow n\text{-C}_3\text{H}_7\text{O}_2 + \text{M}$	7.8×10^{-12}	± 0.2	$5.9 \times 10^{-29} (T/300)^{-3.8} [\text{N}_2]$ 7.8×10^{-12}	200–300	$\Delta \log k = \pm 0.2$
647	$i\text{-C}_3\text{H}_7 + \text{O}_2 + \text{M} \rightarrow i\text{-C}_3\text{H}_7\text{O}_2 + \text{M}$	$F_c = 0.54$ 8×10^{-12} 1.1×10^{-11}	± 0.2 ± 0.3	$F_c = \{0.58 \exp(-T/1250) + 0.42 \exp(-T/183)\}$ 8×10^{-12} 1.1×10^{-11}	200–300 200–300	$\Delta \log k = \pm 0.2$ $\Delta \log k = \pm 0.3$

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
648	CH ₃ COCH ₂ + O ₂ + M → CH ₃ COCH ₂ O ₂ + M	1.5 × 10 ⁻¹²	± 0.5	(<i>k</i> _∞)		
648	HCO + O ₂ → CO + HO ₂	5.5 × 10 ⁻¹²	± 0.15		200–400	± 150
648	CH ₃ CO + O ₂ + M → CH ₃ CO ₂ + M	5.0 × 10 ⁻¹²	± 0.5	(<i>k</i> _∞)	200–300	Δ log <i>k</i> = ± 0.5
649	CH ₂ OH + O ₂ → HCHO + HO ₂	9.4 × 10 ⁻¹²	± 0.12			
649	CH ₃ CHOH + O ₂ → CH ₃ CHO + HO ₂	1.9 × 10 ⁻¹¹	± 0.3			
650	CH ₂ CH ₂ OH + O ₂ → products	3.0 × 10 ⁻¹²	± 0.3			
650	CH ₃ O + O ₂ → HCHO + HO ₂	1.9 × 10 ⁻¹⁵	± 0.2	7.2 × 10 ⁻¹⁴ exp(–1080/ <i>T</i>)	298–610	± 300
651	<i>n</i> -C ₃ H ₇ O + O ₂ → C ₂ H ₅ CHO + HO ₂	9.5 × 10 ⁻¹⁵	± 0.2	6.0 × 10 ⁻¹⁴ exp(–550/ <i>T</i>)	295–425	± 300
652	<i>i</i> -C ₃ H ₇ O + O ₂ → CH ₃ COCH ₃ + HO ₂	8 × 10 ⁻¹⁵	± 0.5			
652	CH ₃ OCH ₂ O + O ₂ → CH ₃ OCHO + HO ₂	8 × 10 ⁻¹⁵	± 0.3	1.5 × 10 ⁻¹⁴ exp(–200/ <i>T</i>)	290–390	± 200
652	CH ₃ OCH ₂ O + M → CH ₃ OCHO + H + M	See data sheet				
652	CH ₃ COCH ₂ O + O ₂ → CH ₃ COCHO + HO ₂	See data sheet				
652	CH ₃ COCH ₂ O + M → CH ₃ COCHO + HO ₂	2.5 × 10 ⁻¹²	± 0.3	5.1 × 10 ⁻¹² exp(–210/ <i>T</i>)	240–400	± 200
652	CH ₃ COCH ₂ O + M → CH ₃ CO + HCHO + M	1.6 × 10 ⁻²⁹ [N ₂]	± 0.1	1.6 × 10 ⁻²⁹ (7300) ^{-3.5} [N ₂]	200–400	Δ <i>n</i> = ± 0.5
653	CH ₃ + O ₃ → products	3.6 × 10 ⁻¹¹	± 0.5	3.6 × 10 ⁻¹¹ (7300) ^{-0.6}	200–400	Δ <i>n</i> = ± 0.5
653	CH ₃ O + NO + M → CH ₃ ONO + M	<i>F</i> _c = 0.6				
653	CH ₃ O + NO → HCHO + HNO	4 × 10 ⁻¹²		4 × 10 ⁻¹² (7300) ^{-0.7}	200–400	Δ <i>n</i> = ± 0.5
654	C ₂ H ₅ O + NO + M → C ₂ H ₅ ONO + M	4.4 × 10 ⁻¹¹	± 0.3	4.4 × 10 ⁻¹¹	200–300	Δ <i>n</i> = ± 0.5
654	C ₂ H ₅ O + NO → CH ₃ CHO + HNO	1.3 × 10 ⁻¹¹				
655	<i>i</i> -C ₃ H ₇ O + NO + M → <i>i</i> -C ₃ H ₇ ONO + M	3.4 × 10 ⁻¹¹	± 0.3	3.4 × 10 ⁻¹¹	200–300	Δ <i>n</i> = ± 0.5
655	<i>i</i> -C ₃ H ₇ O + NO → (CH ₃) ₂ CO + HNO	6.5 × 10 ⁻¹²	± 0.5			
655	CH ₃ O + NO ₂ + M → CH ₃ ONO ₂ + M	2.8 × 10 ⁻²⁹ [N ₂]	± 0.3	2.8 × 10 ⁻²⁹ (7300) ^{-4.5} [N ₂]	200–400	Δ <i>n</i> = ± 1
655		2.0 × 10 ⁻¹¹	± 0.3	2.0 × 10 ⁻¹¹	200–400	Δ <i>n</i> = ± 0.5
655		<i>F</i> _c = 0.44				
655	CH ₃ O + NO ₂ → HCHO + HONO	See data sheet				
656	C ₂ H ₅ O + NO ₂ + M → C ₂ H ₅ ONO ₂ + M	2.8 × 10 ⁻¹¹	± 0.3	2.8 × 10 ⁻¹¹	200–300	Δ <i>n</i> = ± 0.5
656	C ₂ H ₅ O + NO ₂ → CH ₃ CHO + HONO	See data sheet				
656	<i>i</i> -C ₃ H ₇ O + NO ₂ + M → <i>i</i> -C ₃ H ₇ ONO ₂ + M	3.5 × 10 ⁻¹¹	± 0.3	3.5 × 10 ⁻¹¹	200–300	Δ <i>n</i> = ± 0.5
656	<i>i</i> -C ₃ H ₇ O + NO ₂ → (CH ₃) ₂ CO + HONO	See data sheet				
657	CH ₃ O ₂ + NO → CH ₃ O + NO ₂	7.6 × 10 ⁻¹²	± 0.1	4.2 × 10 ⁻¹² exp(180/ <i>T</i>)	240–360	± 180
658	C ₂ H ₅ O ₂ + NO → C ₂ H ₅ O + NO ₂	8.7 × 10 ⁻¹²	± 0.2			
658	C ₂ H ₅ O ₂ + NO (+M) → C ₂ H ₅ ONO ₂ (+M)	≤ 1.2 × 10 ⁻¹³				
658	HOCH ₂ CH ₂ O ₂ + NO → HOCH ₂ CH ₂ O + NO ₂	9 × 10 ⁻¹²	± 0.5			
659	<i>n</i> -C ₃ H ₇ O ₂ + NO → <i>n</i> -C ₃ H ₇ O + NO ₂	4.9 × 10 ⁻¹²	± 0.3			
659	<i>n</i> -C ₃ H ₇ O ₂ + NO (+M) → <i>n</i> -C ₃ H ₇ ONO ₂ (+M)	1.0 × 10 ⁻¹³	± 0.5			
659	<i>i</i> -C ₃ H ₇ O ₂ + NO → <i>i</i> -C ₃ H ₇ O + NO ₂	4.8 × 10 ⁻¹²	± 0.3			
659	<i>i</i> -C ₃ H ₇ O ₂ + NO (+M) → <i>i</i> -C ₃ H ₇ ONO ₂ (+M)	2.1 × 10 ⁻¹³	± 0.5			
660	CH ₃ CO ₂ + NO → CH ₃ + CO ₂ + NO ₂	2.0 × 10 ⁻¹¹	± 0.2		280–325	± 600
661	C ₂ H ₅ CO ₂ + NO → C ₂ H ₅ + CO ₂ + NO ₂	2.0 × 10 ⁻¹¹	± 0.5			

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
661	CH ₃ O ₂ + NO ₂ + M → CH ₃ O ₂ NO ₂ + M	2.5 × 10 ⁻³⁰ [N ₂] (k ₀) 7.5 × 10 ⁻¹² (k _∞) F _c = 0.36	± 0.3 ± 0.3	2.5 × 10 ⁻³⁰ (T/300) ^{-5.5} [N ₂] 7.5 × 10 ⁻¹²	250–350 250–350	Δn = ± 1 Δn = ± 0.5
662	CH ₃ O ₂ NO ₂ + M → CH ₃ O ₂ + NO ₂ + M	6.8 × 10 ⁻¹⁹ [N ₂] (k ₀ /s ⁻¹) 4.5 (k _∞ /s ⁻¹) F _c = 0.36	± 0.3 ± 0.3	9 × 10 ⁻⁵ exp(-9690/T) [N ₂] 1.1 × 10 ⁻⁶ exp(-10560/T)	250–300 250–300	± 500 ± 500
663	C ₂ H ₅ O ₂ + NO ₂ + M → C ₂ H ₅ O ₂ NO ₂ + M	1.3 × 10 ⁻²⁹ [N ₂] (k ₀) 8.8 × 10 ⁻¹² (k _∞) F _c = 0.31	± 0.3 ± 0.3	1.3 × 10 ⁻²⁹ (T/300) ^{-6.2} [N ₂] 8.8 × 10 ⁻¹²	200–300 200–300	Δn = ± 1 Δlog k = ± 0.3
664	C ₂ H ₅ O ₂ NO ₂ + M → C ₂ H ₅ O ₂ + NO ₂ + M	1.4 × 10 ⁻¹⁷ [N ₂] (k ₀ /s ⁻¹) 5.4 (k _∞ /s ⁻¹) F _c = 0.31	± 0.5 ± 0.5	4.8 × 10 ⁻⁴ exp(-9285/T) [N ₂] 8.8 × 10 ⁻¹⁵ exp(-10440/T)	250–300 250–300	± 1000 ± 1000
664	CH ₃ CO ₃ + NO ₂ + M → CH ₃ CO ₃ NO ₂ + M	2.7 × 10 ⁻²⁸ [N ₂] (k ₀) 1.2 × 10 ⁻¹¹ (k _∞) F _c = 0.3	± 0.4 ± 0.2	2.7 × 10 ⁻²⁸ (T/300) ^{-7.1} [N ₂] 1.2 × 10 ⁻¹¹ (T/300) ^{-0.9}	250–300 250–300	Δn = ± 2 Δn = ± 1
665	CH ₃ CO ₃ NO ₂ + M → CH ₃ CO ₃ + NO ₂ + M	1.1 × 10 ⁻²⁰ [N ₂] (k ₀ /s ⁻¹) 3.8 × 10 ⁻⁴ (k _∞ /s ⁻¹) F _c = 0.3	± 0.4 ± 0.3	4.9 × 10 ⁻³ exp(-12100/T) [N ₂] 5.4 × 10 ⁻⁶ exp(-13830/T)	300–330 300–330	± 1000 ± 300
666	C ₂ H ₅ CO ₃ NO ₂ + M → C ₂ H ₅ CO ₃ + NO ₂ + M	4.4 × 10 ⁻⁴ (k _∞ /s ⁻¹) No recommendation (see data sheet)	± 0.4	2 × 10 ⁻⁵ exp(-12800/T)	300–315	± 500
667	CH ₃ O ₂ + NO ₂ → products CH ₃ O ₂ + CH ₃ O ₂ → CH ₃ OH + HCHO + O ₂ → 2CH ₃ O + O ₂ → CH ₃ OOCH ₃ + O ₂	3.7 × 10 ⁻¹³	± 0.12	1.1 × 10 ⁻¹³ exp(365/T)	200–400	± 200
669	CH ₃ O ₂ + CH ₃ CO ₃ → CH ₃ O + CH ₃ CO ₂ + O ₂ → HCHO + CH ₃ COCH ₂ OH + O ₂ → CH ₃ O + CH ₃ COCH ₂ O + O ₂	1.1 × 10 ⁻¹¹ 1.8 × 10 ⁻¹²	± 0.3 ± 0.5			
670	CH ₃ O ₂ + CH ₃ COCH ₂ O ₂ → CH ₃ OH + CH ₃ COCHO + O ₂ → HCHO + CH ₃ COCH ₂ OH + O ₂ → CH ₃ O + CH ₃ COCH ₂ O + O ₂	3.8 × 10 ⁻¹²	± 0.3			
670	HOCH ₂ O ₂ + HOCH ₂ O ₂ → HCOOH + CH ₂ (OH) ₂ + O ₂ → 2HOCH ₂ O + O ₂	7.0 × 10 ⁻¹³ 5.5 × 10 ⁻¹²	± 0.3 ± 0.3	5.7 × 10 ⁻¹⁴ exp(750/T)	275–325	± 750
671	C ₂ H ₅ O ₂ + C ₂ H ₅ O ₂ → C ₂ H ₅ OH + CH ₃ CHO + O ₂ → 2C ₂ H ₅ O + O ₂ → C ₂ H ₅ OOCC ₂ H ₅ + O ₂	6.4 × 10 ⁻¹⁴	± 0.12	6.4 × 10 ⁻¹⁴	250–450	+ 300 – 100
672	CH ₃ OCH ₂ O ₂ + CH ₃ OCH ₂ O ₂ → CH ₃ OCH ₂ OH + CH ₃ OCHO + O ₂ → 2CH ₃ OCH ₂ O + O ₂	7 × 10 ⁻¹³ 1.4 × 10 ⁻¹²	± 0.3 ± 0.3			
673	CH ₃ CO ₃ + CH ₃ CO ₃ → 2CH ₃ CO ₂ + O ₂	1.6 × 10 ⁻¹¹	± 0.5	2.8 × 10 ⁻¹² exp(530/T)	250–370	± 500
674	CH ₃ CO ₃ + CH ₃ COCH ₂ O ₂ → CH ₃ COOH + CH ₃ COCHO + O ₂ → CH ₃ + CO ₂ + CH ₃ COCH ₂ O + O ₂	5.0 × 10 ⁻¹²	± 0.3			

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
674	HOCH ₂ CH ₂ O ₂ + HOCH ₂ CH ₂ O ₂ → HOCH ₂ CH ₂ OH + HOCH ₂ CHO + O ₂ → 2HOCH ₂ CH ₂ O + O ₂	1.15 × 10 ⁻¹² 1.15 × 10 ⁻¹²	± 0.3 ± 0.3			
675	n -C ₃ H ₇ O ₂ + n -C ₃ H ₇ O ₂ → n -C ₃ H ₇ OH + C ₂ H ₅ CHO + O ₂ → 2 n -C ₃ H ₇ O + O ₂	3 × 10 ⁻¹³	± 0.5			
675	i -C ₃ H ₇ O ₂ + i -C ₃ H ₇ O ₂ → i -C ₃ H ₇ OH + (CH ₃) ₂ CO + O ₂ → 2 i -C ₃ H ₇ O + O ₂	4.4 × 10 ⁻¹⁶ 5.6 × 10 ⁻¹⁶	± 0.3 ± 0.3	1.6 × 10 ⁻¹² exp(-2200/T)	300–400	± 300
676	CH ₃ COCH ₂ O ₂ + CH ₃ COCH ₂ O ₂ → CH ₃ COCH ₂ OH + CH ₃ COCHO + O ₂ → 2CH ₃ COCH ₂ O + O ₂	2.0 × 10 ⁻¹² 6.0 × 10 ⁻¹²	0.5 0.3			
678	RCHO + H ₂ O → RCOOH + H ₂ O					
678	RCHO + NO ₂ → RCHO + NO ₃					
678	RCHO + SO ₂ → products					
678	RCHO + HCHO → products					
680	O ₃ + C ₂ H ₂ → products	1 × 10 ⁻²⁰	± 1.0			
681	O ₃ + C ₂ H ₄ → products	1.6 × 10 ⁻¹⁸	± 0.10	9.1 × 10 ⁻¹⁵ exp(-2580/T)	180–360	± 100
682	O ₃ + C ₃ H ₆ → products	1.0 × 10 ⁻¹⁷	± 0.10	5.5 × 10 ⁻¹⁵ exp(-1880/T)	230–370	± 200
684	HCHO + $h\nu$ → products	See data sheet				
685	CH ₃ CHO + $h\nu$ → products	See data sheet				
686	C ₂ H ₅ CHO + $h\nu$ → products	See data sheet				
687	(CHO) ₂ + $h\nu$ → products	See data sheet				
688	CH ₃ COCHO + $h\nu$ → products	See data sheet				
690	CH ₃ COCH ₃ + $h\nu$ → products	See data sheet				
691	CH ₃ OOH + $h\nu$ → products	See data sheet				
692	CH ₃ ONO ₂ + $h\nu$ → products	See data sheet				
693	C ₂ H ₅ ONO ₂ + $h\nu$ → products	See data sheet				
694	n -C ₃ H ₇ ONO ₂ + $h\nu$ → products	See data sheet				
694	i -C ₃ H ₇ ONO ₂ + $h\nu$ → products	See data sheet				
695	CH ₃ O ₂ NO ₂ + $h\nu$ → products	See data sheet				
696	CH ₃ CO ₃ NO ₂ + $h\nu$ → products	See data sheet				
<i>SO_x Reactions</i>						
698	O + CS → CO + S	2.1 × 10 ⁻¹¹	± 0.1	2.7 × 10 ⁻¹⁰ exp(-760/T)	150–300	± 250
698	O + CH ₃ SCH ₃ → CH ₃ SO + CH ₃	5.0 × 10 ⁻¹¹	± 0.1	1.3 × 10 ⁻¹¹ exp(409/T)	270–560	± 100
699	O + CS ₂ → products	3.6 × 10 ⁻¹²	± 0.2	3.2 × 10 ⁻¹¹ exp(-650/T)	200–500	± 100
700	O + CH ₃ SSCH ₃ → CH ₃ SO + CH ₃ S	1.3 × 10 ⁻¹⁰	± 0.3	5.5 × 10 ⁻¹¹ exp(250/T)	290–570	± 100
700	O + OCS → SO + CO	1.2 × 10 ⁻¹⁴	± 0.2	1.6 × 10 ⁻¹¹ exp(-2150/T)	220–500	± 150
701	O + SO ₂ + M → SO ₃ + M	1.4 × 10 ⁻³³ [N ₂]	± 0.3	4.0 × 10 ⁻³² exp(-1000/T)	200–400	± 200
701	S + O ₂ → SO + O	2.1 × 10 ⁻¹²	± 0.2	2.1 × 10 ⁻¹²	230–400	± 200
701	S + O ₃ → SO + O ₂	1.2 × 10 ⁻¹¹	± 0.3			
702	Cl + H ₂ S → HCl + HS	5.7 × 10 ⁻¹¹	± 0.3	5.7 × 10 ⁻¹¹	210–350	± 100
702	HO + H ₂ S → H ₂ O + HS	4.8 × 10 ⁻¹²	± 0.08	6.3 × 10 ⁻¹² exp(-80/T)	200–300	± 80

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/$ K
703	$\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$	$4.0 \times 10^{-31} [\text{N}_2]$ 2×10^{-12} $F_c = 0.45$	(k_0) ± 0.3 (k_∞) ± 0.3	$4.0 \times 10^{-31} (T/300)^{-3.3} [\text{N}_2]$ 2×10^{-12}	300–400 200–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
703	$\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$	4.3×10^{-13}	± 0.1	$1.3 \times 10^{-12} \exp(-330/T)$	290–420	± 200
704	$\text{HO} + \text{OCS} \rightarrow \text{products}$	2.0×10^{-15}	± 0.3	$1.1 \times 10^{-13} \exp(-1200/T)$	250–500	± 500
704	$\text{HO} + \text{CS}_2 + \text{M} \rightarrow \text{HOCS}_2 + \text{M}$	$8 \times 10^{-31} [\text{N}_2]$ 8×10^{-12} $F_c = 0.8$	(k_0) ± 0.5 (k_∞) ± 0.5	$8 \times 10^{-31} [\text{N}_2]$ 8×10^{-12}	270–300 250–300	$\Delta \log k = \pm 0.5$ $\Delta \log k = \pm 0.5$
704	$\text{HO} + \text{CS}_2 \rightarrow \text{HS} + \text{OCS}$	$< 2 \times 10^{-15}$				
705	$\text{HOCS}_2 + \text{M} \rightarrow \text{HO} + \text{CS}_2 + \text{M}$	$4.8 \times 10^{-14} [\text{N}_2]$ 4.8×10^5 $F_c = 0.8$	(k_0/s^{-1}) ± 0.5 (k_∞/s^{-1}) ± 0.5	$1.6 \times 10^{-6} \exp(-5160/T) [\text{N}_2]$ $1.6 \times 10^{13} \exp(-5160/T)$	250–300 250–300	± 500 ± 500
706	$\text{HOCS}_2 + \text{O}_2 \rightarrow \text{products}$	3.0×10^{-14}	± 0.3	3.0×10^{-14}	240–350	$\Delta \log k = \pm 0.3$
707	$\text{HO} + \text{CH}_3\text{SH} \rightarrow \text{products}$	3.3×10^{-11}	± 0.10	$9.9 \times 10^{-12} \exp(356/T)$	240–430	± 100
708	$\text{HO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{SCH}_3$ $\rightarrow \text{CH}_3\text{S(OH)CH}_3$	4.8×10^{-12} 1.7×10^{-12}	± 0.10 (1 bar air)	$1.13 \times 10^{-11} \exp(-254/T)$ See data sheet	250–400	± 150
709	$\text{HO} + \text{CH}_3\text{SSCH}_3 \rightarrow \text{products}$	2.3×10^{-10}	± 0.10	$7.0 \times 10^{-11} \exp(350/T)$	250–370	± 200
710	$\text{HO}_2 + \text{SO}_2 \rightarrow \text{products}$	$\leq 1 \times 10^{-18}$				
710	$\text{NO}_3 + \text{H}_2\text{S} \rightarrow \text{products}$	$< 1 \times 10^{-15}$				
711	$\text{NO}_3 + \text{CS}_2 \rightarrow \text{products}$	$< 1 \times 10^{-15}$				
711	$\text{NO}_3 + \text{OCS} \rightarrow \text{products}$	$< 1 \times 10^{-16}$				
711	$\text{NO}_3 + \text{SO}_2 \rightarrow \text{products}$	$< 1 \times 10^{-19}$				
712	$\text{NO}_3 + \text{CH}_3\text{SH} \rightarrow \text{products}$	9.2×10^{-13}	± 0.15	9.2×10^{-13}	250–370	± 400
712	$\text{NO}_3 + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	1.1×10^{-12}	± 0.15	$1.9 \times 10^{-13} \exp(520/T)$	250–380	± 200
713	$\text{NO}_3 + \text{CH}_3\text{SSCH}_3 \rightarrow \text{products}$	7×10^{-13}	± 0.3	7×10^{-13}	300–380	± 500
713	$\text{HS} + \text{O}_2 \rightarrow \text{products}$	$\leq 4 \times 10^{-19}$				
714	$\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$	3.7×10^{-12}	± 0.2	$9.5 \times 10^{-12} \exp(-280/T)$	290–450	± 250
714	$\text{HS} + \text{NO} + \text{M} \rightarrow \text{HSNO} + \text{M}$	$2.4 \times 10^{-31} [\text{N}_2]$ 2.7×10^{-11} $F_c = 0.6$	(k_0) ± 0.3 (k_∞) ± 0.5	$2.4 \times 10^{-31} (T/300)^{-2.5} [\text{N}_2]$ 2.7×10^{-11}	200–300 200–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.5$
715	$\text{HS} + \text{NO}_2 \rightarrow \text{HSO} + \text{NO}$	5.8×10^{-11}	± 0.3	$2.6 \times 10^{-11} \exp(240/T)$	220–450	± 200
715	$\text{HSO} + \text{O}_2 \rightarrow \text{products}$	$\leq 2.0 \times 10^{-17}$				
716	$\text{HSO} + \text{O}_3 \rightarrow \text{products}$	1.1×10^{-13}	± 0.3			
716	$\text{HSO} + \text{NO} \rightarrow \text{products}$	$\leq 1.0 \times 10^{-15}$				
717	$\text{HSO} + \text{NO}_2 \rightarrow \text{products}$	9.6×10^{-12}	± 0.3			
717	$\text{HSO}_2 + \text{O}_2 \rightarrow \text{products}$	3.0×10^{-13}	± 0.8			
717	$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$	7.6×10^{-17}	± 0.15	$1.6 \times 10^{-13} \exp(-2280/T)$	230–420	± 500
718	$\text{SO} + \text{O}_3 \rightarrow \text{SO}_2 + \text{O}_2$	8.9×10^{-14}	± 0.10	$4.5 \times 10^{-12} \exp(-1170/T)$	230–420	± 150
718	$\text{SO} + \text{NO}_2 \rightarrow \text{SO}_2 + \text{NO}$	1.4×10^{-11}	± 0.1	1.4×10^{-11}	210–360	± 100
719	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{products}$	$< 6 \times 10^{-15}$				
719	$\text{SO}_3 + \text{NH}_3 \rightarrow \text{products}$	6.9×10^{-11}	± 0.3			
720	$\text{CS} + \text{O}_2 \rightarrow \text{products}$	2.9×10^{-19}	± 0.6			
720	$\text{CS} + \text{O}_3 \rightarrow \text{OCS} + \text{O}_2$	3.0×10^{-16}	± 0.5			
720	$\text{CS} + \text{NO}_2 \rightarrow \text{OCS} + \text{NO}$	7.6×10^{-17}	± 0.5			
721	$\text{CH}_2\text{SH} + \text{O}_2 \rightarrow \text{products}$	6.6×10^{-12}	± 0.3			

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
721	CH ₃ SH + O ₃ → products	3.5 × 10 ⁻¹¹	± 0.3			
722	CH ₃ SH + NO → products	1.5 × 10 ⁻¹¹	± 0.3			
722	CH ₃ SH + NO ₂ → products	4.4 × 10 ⁻¹¹	± 0.5			
723	CH ₃ S + O ₂ + M → CH ₃ SOO + M	See data sheet				
724	CH ₃ SOO + M → CH ₃ S + O ₂ + M	See data sheet				
724	CH ₃ S + O ₃ → products	5.4 × 10 ⁻¹²	± 0.2	2.0 × 10 ⁻¹² exp(290/T)	290–360	± 200
725	CH ₃ S + NO + M → CH ₃ SNO + M	3.2 × 10 ⁻²⁹ [N ₂] (k ₀)	± 0.3	3.2 × 10 ⁻²⁹ (T/300) ⁻⁴ [N ₂]	250–450	Δn = ± 2
		4 × 10 ⁻¹¹ (k _∞)	± 0.5	4 × 10 ⁻¹¹	250–450	Δlog k = ± 0.5
726	CH ₃ S + NO ₂ → CH ₃ SO + NO	F _c = 0.60	± 0.15	F _c = exp(-T/580)	240–350	± 300
727	CH ₃ SO + O ₃ → products	5.8 × 10 ⁻¹¹	± 0.3	2.2 × 10 ⁻¹¹ exp(320/T)		
727	CH ₃ SO + NO ₂ → products	6.0 × 10 ⁻¹³	± 0.3			
728	CH ₃ SOO + O ₃ → products	1.2 × 10 ⁻¹¹	± 0.5			
728	CH ₃ SOO + NO → products	< 8 × 10 ⁻¹³ (228 K)				
729	CH ₃ SOO + NO ₂ → products					
729	CH ₃ SCH ₃ + O ₂ → CH ₃ SCH ₂ O ₂	5.7 × 10 ⁻¹²	± 0.4			
730	CH ₃ SCH ₂ O ₂ + NO → CH ₃ SCH ₂ O + NO ₂	1.9 × 10 ⁻¹¹	± 0.4			
730	CH ₃ SCH ₂ O ₂ + CH ₃ SCH ₂ O ₂ → products	≤ 8 × 10 ⁻¹²				
731	CH ₃ SS + O ₃ → products	4.6 × 10 ⁻¹²	± 0.3			
731	CH ₃ SS + NO ₂ → products	1.8 × 10 ⁻¹¹	± 0.3			
732	CH ₃ SSO + NO ₂ → products	4.5 × 10 ⁻¹²	± 0.3			
732	O ₃ + CH ₃ SCH ₃ → products	< 1 × 10 ⁻¹⁸				
733	OCS + hν → products	See data sheet				
734	CS ₂ + hν → products	See data sheet				
735	CH ₃ SSCH ₃ + hν → products	See data sheet				
735	CH ₃ SNO + hν → products	See data sheet				
<i>FO_x Reactions</i>						
737	O + FO → O ₂ + F	2.7 × 10 ⁻¹¹	± 0.3			
737	O + FO ₂ → O ₂ + FO	5 × 10 ⁻¹¹	± 0.7			
737	O(1D) + HF → HO + F → O(3P) + HF	1 × 10 ⁻¹⁰	± 0.5			
738	O(1D) + COF ₂ → CO ₂ + F ₂ → O(3P) + COF ₂	2.2 × 10 ⁻¹¹	± 0.2			
739	O(1D) + CH ₃ F → products	5.2 × 10 ⁻¹¹	± 0.2			
739	O(1D) + CH ₂ F ₂ → products	1.6 × 10 ⁻¹⁰	± 0.2			
739	O(1D) + CHF ₃ → products	5.1 × 10 ⁻¹¹	± 0.3			
739	O(1D) + CH ₃ CHF ₂ → products	9.8 × 10 ⁻¹²	± 0.3			
739	O(1D) + CH ₃ CF ₃ → products	2.6 × 10 ⁻¹⁰	± 0.3			
739	O(1D) + CH ₃ CHF ₂ → products	2.0 × 10 ⁻¹⁰	± 0.3			
739	O(1D) + CH ₂ FCF ₃ → products	1.0 × 10 ⁻¹⁰	± 0.3			
739	O(1D) + CHF ₂ CF ₃ → products	4.9 × 10 ⁻¹¹	± 0.3			
739	O(1D) + CHF ₂ CF ₃ → products	1.2 × 10 ⁻¹⁰	± 0.3			
740	F + H ₂ → HF + H	2.6 × 10 ⁻¹¹	± 0.1			
740	F + H ₂ O → HF + HO	1.4 × 10 ⁻¹¹	± 0.1			
				1.4 × 10 ⁻¹⁰ exp(-500/T)	200–375	± 200
				1.4 × 10 ⁻¹¹	240–370	± 200

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/$ K
741	$\text{F} + \text{O}_2 + \text{M} \rightarrow \text{FO}_2 + \text{M}$	$5.8 \times 10^{-33} [\text{N}_2]$ 1.2×10^{-10} $F_c \approx 0.5$	± 0.3 ± 0.3	$5.8 \times 10^{-33} (7/300)^{-1.7} [\text{N}_2]$ 1.2×10^{-10} $F_c \approx 0.5$	100–400 100–400 100–400	$\Delta n = \pm 0.5$ $\Delta \log k_c = \pm 0.3$
742	$\text{FO}_2 + \text{M} \rightarrow \text{F} + \text{O}_2 + \text{M}$	$1.5 \times 10^{-17} [\text{N}_2]$ 3.1×10^5	± 0.3 ± 0.3	(k_0) (k_∞) (k_0/s^{-1}) (k_∞/s^{-1})	315–420 315–420	± 500 $\Delta n = \pm 0.5$ ± 500 $\Delta n = \pm 0.5$
743	$\text{F} + \text{O}_3 \rightarrow \text{FO} + \text{O}_2$	$F_c \approx 0.5$	± 0.25	$F_c \approx 0.5$	315–420	$\Delta n = \pm 0.5$
744	$\text{F} + \text{HONO}_2 \rightarrow \text{HF} + \text{NO}_3$	1.0×10^{-11}	± 0.1	$2.2 \times 10^{-11} \exp(-230/T)$	250–365	± 200
744	$\text{F} + \text{CH}_4 \rightarrow \text{HF} + \text{CH}_3$	2.3×10^{-11}	± 0.2	$6.0 \times 10^{-12} \exp(400/T)$	260–320	± 200
745	$\text{HO} + \text{CH}_3\text{F} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{F}$	8.0×10^{-11}	± 0.15	$3.0 \times 10^{-10} \exp(-400/T)$	250–450	± 200
746	$\text{HO} + \text{CH}_2\text{F}_2 \rightarrow \text{H}_2\text{O} + \text{CHF}_2$	2.0×10^{-14}	± 0.10	$1.6 \times 10^{-12} \exp(-1305/T)$	240–300	± 200
747	$\text{HO} + \text{CHF}_3 \rightarrow \text{H}_2\text{O} + \text{CF}_3$	1.1×10^{-14}	± 0.2	$2.0 \times 10^{-12} \exp(-1545/T)$	240–300	± 300
748	$\text{HO} + \text{CF}_4 \rightarrow \text{HOF} + \text{CF}_3$	2.7×10^{-16}	± 0.2	$6.0 \times 10^{-13} \exp(-2295/T)$	240–300	± 300
749	$\text{HO} + \text{CH}_3\text{CH}_2\text{F} \rightarrow \text{products}$	$< 2 \times 10^{-18}$	± 0.2	$2.4 \times 10^{-12} \exp(-740/T)$	240–300	± 300
750	$\text{HO} + \text{CH}_3\text{CHF}_2 \rightarrow \text{products}$	2.0×10^{-13}	± 0.15	$1.0 \times 10^{-12} \exp(-990/T)$	240–300	± 300
751	$\text{HO} + \text{CH}_3\text{CF}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CF}_3$	3.6×10^{-14}	± 0.3	$1.05 \times 10^{-12} \exp(-1990/T)$	240–300	± 300
752	$\text{HO} + \text{CH}_2\text{FCH}_2\text{F} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{FCHF}$	1.3×10^{-15}	± 0.2	$3.3 \times 10^{-12} \exp(-1610/T)$	270–340	± 300
753	$\text{HO} + \text{CH}_2\text{FCHF}_2 \rightarrow \text{products}$	1.1×10^{-13}	± 0.2	$7.3 \times 10^{-13} \exp(-1540/T)$	240–300	± 300
754	$\text{HO} + \text{CH}_2\text{FCF}_3 \rightarrow \text{H}_2\text{O} + \text{CHF}_2\text{CF}_3$	1.5×10^{-14}	± 0.3	$5.9 \times 10^{-12} \exp(-1630/T)$	270–340	± 300
755	$\text{HO} + \text{CHF}_2\text{CHF}_2 \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{CHF}_2$	4.2×10^{-15}	± 0.2	$4.9 \times 10^{-13} \exp(-1655/T)$	240–300	± 300
756	$\text{HO} + \text{CHF}_2\text{CF}_3 \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{CF}_3$	5.9×10^{-15}	± 0.3	$2.1 \times 10^{-12} \exp(-1690/T)$	270–340	± 300
757	$\text{HO} + \text{CHF}_2\text{CF}_2\text{CF}_2\text{F} \rightarrow \text{products}$	1.9×10^{-15}	± 0.3	$1.1 \times 10^{-12} \exp(-1620/T)$	270–340	± 300
758	$\text{HO} + \text{CF}_3\text{CF}_2\text{CH}_2\text{F} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CF}_2\text{CHF}$	7.2×10^{-15}	± 0.3	$7.9 \times 10^{-13} \exp(-2305/T)$	270–463	± 300
759	$\text{HO} + \text{CF}_3\text{CH}_2\text{CHF}_2 \rightarrow \text{products}$	6×10^{-15}	± 0.2	$4.5 \times 10^{-13} \exp(-1675/T)$		
760	$\text{HO} + \text{CF}_3\text{CH}_2\text{CF}_3 \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CHFCF}_3$	4.8×10^{-15}	± 0.2			
761	$\text{HO} + \text{CF}_3\text{CHFCF}_3 \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CF}_2\text{CF}_3$	3.5×10^{-16}	± 0.2			
762	$\text{HO} + \text{CHF}_2\text{OCHF}_2 \rightarrow \text{H}_2\text{O} + \text{CHF}_2\text{OCF}_2$	1.6×10^{-15}	± 0.2			
762	$\text{HO} + \text{HCOF} \rightarrow \text{H}_2\text{O} + \text{FCO}$	2.9×10^{-15}	± 0.2			
763	$\text{HO} + \text{CHF}_2\text{CHO} \rightarrow \text{products}$	$< 1 \times 10^{-14}$	± 0.2			
763	$\text{HO} + \text{CF}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CO}$	1.6×10^{-12}	± 0.2			
764	$\text{HO} + \text{CF}_3\text{COOH} \rightarrow \text{products}$	6.0×10^{-13}	± 0.2			
765	$\text{HO}_2 + \text{CH}_2\text{FO}_2 \rightarrow \text{O}_2 + \text{CH}_2\text{FO}_2\text{H}$ $\rightarrow \text{O}_2 + \text{HCOF} + \text{H}_2\text{O}$	1.4×10^{-13} See data sheet	± 0.20		283–348	$\Delta \log k = \pm 0.20$
765	$\text{HO}_2 + \text{CF}_3\text{CHFO}_2$ $\rightarrow \text{O}_2 + \text{CF}_3\text{CHFO}_2\text{H}$ $\rightarrow \text{O}_2 + \text{CF}_3\text{COF} + \text{H}_2\text{O}$	3.8×10^{-12} No recommendation (see data sheet)	± 0.3		210–365	± 300
766	$\text{FO} + \text{O}_3 \rightarrow \text{products}$	2.2×10^{-11}	± 0.15		300–850	± 200
767	$\text{FO} + \text{NO} \rightarrow \text{F} + \text{NO}_2$	1.0×10^{-11}	± 0.2		298–435	± 250
767	$\text{FO} + \text{FO} \rightarrow \text{products}$	$< 3.4 \times 10^{-16}$	± 0.5			
768	$\text{FO}_2 + \text{O}_3 \rightarrow \text{products}$	1.5×10^{-12}	± 0.5			
768	$\text{FO}_2 + \text{NO} \rightarrow \text{FNO} + \text{O}_2$	1.0×10^{-13}	± 0.5			
769	$\text{FO}_2 + \text{NO}_2 \rightarrow \text{products}$	$< 5.1 \times 10^{-16}$				
769	$\text{FO}_2 + \text{CO} \rightarrow \text{products}$	$< 4.1 \times 10^{-15}$				
770	$\text{FO}_2 + \text{CH}_4 \rightarrow \text{products}$					

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
770	CF ₃ + O ₂ + M → CF ₃ O ₂ + M	1.9×10 ⁻²⁹ [N ₂] 1.0×10 ⁻¹¹ $F_c=0.6$	±0.2 ±0.3	1.9×10 ⁻²⁹ (T/300) ^{-4.7} [N ₂] 1.0×10 ⁻¹¹	200–300 200–400	$\Delta n = \pm 1$ $\Delta \log k_{\infty} = \pm 0.3$
*	CF ₃ O → COF ₂ + F	<10 ⁻⁵				
771	CF ₃ O + O ₂ → COF ₂ + FO ₂	<1×10 ⁻¹⁸		<1×10 ⁻¹⁰ exp(-5600/T)	250–370	
772	CF ₃ O + O ₃ → CF ₃ O ₂ + O ₂	2.5×10 ⁻¹⁴	±1	2×10 ⁻¹² exp(-1300/T)	250–370	±600
773	CF ₃ O + H ₂ O → CF ₃ OH + HO	<2×10 ⁻¹⁷		<3×10 ⁻¹² exp(-3600/T)	250–380	
773	CF ₃ O + NO → COF ₂ + FNO	5.4×10 ⁻¹¹	±0.1	3.7×10 ⁻¹¹ exp(110/T)	230–390	±100
774	CF ₃ O + CH ₄ → CF ₃ OH + CH ₃	2.1×10 ⁻¹⁴	±0.1	2.5×10 ⁻¹² exp(-1420/T)	230–380	±200
775	CF ₃ O + C ₂ H ₆ → CF ₃ OH + C ₂ H ₅	1.2×10 ⁻¹²	±0.1	4.7×10 ⁻¹² exp(-400/T)	230–360	±200
777	CH ₂ FO + O ₂ → HCOF + HO ₂					
777	CH ₂ FO + M → HCOF + H + M					
777	CH ₃ CF ₂ O + O ₂ → products	See data sheet				
777	CH ₃ CF ₂ O + M → CH ₃ + COF ₂ + M	See data sheet				
777	CH ₂ FCHFO + O ₂ → CH ₂ FCOF + HO ₂	See data sheet				
777	CH ₂ FCHFO + M → CH ₂ F + HCOF + M	See data sheet				
777	CF ₃ CHFO + O ₂ → CF ₃ COF + HO ₂	See data sheet				
777	CF ₃ CHFO + M → CF ₃ + HCOF + M	See data sheet				
777	CF ₃ CF ₂ O + O ₂ → products	See data sheet				
777	CF ₃ CF ₂ O + M → CF ₃ + COF ₂ + M	See data sheet				
781	CH ₂ FO ₂ + NO → CH ₂ FO + NO ₂	1.3×10 ⁻¹¹	±0.3			
781	CH ₂ FO ₂ + NO → CH ₂ FO + NO ₂	1.3×10 ⁻¹¹	±0.3			
781	CF ₃ O ₂ + NO → CF ₃ O + NO ₂	1.6×10 ⁻¹¹	±0.15	1.6×10 ⁻¹¹ (T/298) ^{-1.2}	230–430	$\Delta \log k = \pm 0.15$
781	CH ₂ FCHFO ₂ + NO → CH ₂ FCHFO + NO ₂	>9×10 ⁻¹²				
781	CHF ₂ CF ₂ O ₂ + NO → CHF ₂ CF ₂ O + NO ₂	>1×10 ⁻¹¹				
781	CF ₃ CHFO ₂ + NO → CF ₃ CHFO + NO ₂	1.3×10 ⁻¹¹	±0.3			
781	CF ₃ CF ₂ O ₂ + NO → CF ₃ CF ₂ O + NO ₂	>1×10 ⁻¹¹				
784	CF ₃ O ₂ + O ₃ → CF ₃ O + 2O ₂	<3×10 ⁻¹⁵				
785	CF ₃ O ₂ + NO ₂ + M → CF ₃ O ₂ NO ₂ + M	4.5×10 ⁻²⁹ [N ₂] 7.5×10 ⁻¹² $F_c=0.28$	±0.3 ±0.5	4.5×10 ⁻²⁹ (T/300) ^{-6.4} [N ₂] 7.5×10 ⁻¹² $F_c=0.28$	220–300 200–300 220–300	$\Delta \log n = \pm 1$ $\Delta \log k_{\infty} = \pm 0.5$
786	CF ₃ O ₂ NO ₂ + M → CF ₃ O ₂ + NO ₂ + M	3.6×10 ⁻¹⁹ [N ₂] $F_c=0.28$	±0.4	5×10 ⁻¹¹ (T/300) ⁻⁶ ×exp(-12460/T) [N ₂]	233–373	±500
786	CH ₂ FO ₂ + CH ₃ FO ₂ → CH ₂ FOH + HCOF + O ₂	5.6×10 ⁻² $F_c=0.28$	±0.5	1.2×10 ⁻¹⁷ exp(-12580/T)	233–373	±500
787	CHF ₂ O ₂ + CHF ₂ O ₂ → CHF ₂ OH + COF ₂ + O ₂	(2.0–4.0)×10 ⁻¹²		(2.0–4.0)×10 ⁻¹³ exp(700/T)	220–380	
788	CF ₃ O ₂ + CF ₃ O ₂ → 2CF ₃ O + O ₂	(2.5–5)×10 ⁻¹²	±0.2			
789	CF ₃ O ₂ + CF ₃ CHFO ₂ → CF ₃ OOCHFCF ₃ + O ₂	1.7×10 ⁻¹²				
790	CHF ₂ CF ₂ O ₂ + CHF ₂ CF ₂ O ₂ → CHF ₂ CF ₂ OOCHF ₂ + O ₂	8×10 ⁻¹²	±0.5			
	→ 2CHF ₂ CF ₂ O + O ₂	≤3×10 ⁻¹²				

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
791	CF ₃ CHFO ₂ + CF ₃ CHFO ₂ → CF ₃ CHFOH + CF ₃ COF + O ₂ → 2CF ₃ CHFO + O ₂	5.9 × 10 ⁻¹²	± 0.3	7.8 × 10 ⁻¹³ exp(605/T)	210–375	± 200
792	CF ₃ CF ₂ O ₂ + CF ₃ CF ₂ O ₂ → 2CF ₃ CF ₂ O + O ₂	≤ 2 × 10 ⁻¹²				
792	HCOF + <i>hν</i> → products	See data sheet				
794	COF ₂ + <i>hν</i> → products	See data sheet				
794	CF ₃ CHO + <i>hν</i> → products	See data sheet				
795	CF ₃ COF + <i>hν</i> → products	See data sheet				
<i>ClO_x Reactions</i>						
797	O + HOCl → HO + ClO	1.3 × 10 ⁻¹³	± 0.7	1.0 × 10 ⁻¹¹ exp(-1300/T)	200–300	± 1000
797	O + ClO → Cl + O ₂	3.8 × 10 ⁻¹¹	± 0.1	3.8 × 10 ⁻¹¹	200–300	± 250
798	O + OClO → O ₂ + ClO	1.0 × 10 ⁻¹³	± 0.3	2.4 × 10 ⁻¹² exp(-960/T)	240–400	± 300
798	O + OClO + M → ClO ₂ + M	1.8 × 10 ⁻³¹ [N ₂] (<i>k₀</i>) 3.1 × 10 ⁻¹¹ (7/298) ⁻¹ [N ₂] (<i>k_∞</i>)	± 0.3 ± 0.3	1.8 × 10 ⁻³¹ (7/298) ⁻¹ [N ₂] 3.1 × 10 ⁻¹¹ (7/298) ⁻¹	250–300 250–300	Δ <i>H</i> = ± 0.5 Δ <i>H</i> = ± 1
799	O + Cl ₂ O → ClO + ClO	<i>F_c</i> = 0.48 4.5 × 10 ⁻¹²	± 0.15	2.7 × 10 ⁻¹¹ exp(-530/T)	230–380	± 200
800	O + ClONO ₂ → products	2.0 × 10 ⁻¹³	± 0.1	3.0 × 10 ⁻¹² exp(-800/T)	213–295	± 200
800	O(1D) + CHF ₂ Cl → products	1.0 × 10 ⁻¹⁰	± 0.15	1.0 × 10 ⁻¹⁰	175–340	Δ log <i>k</i> = ± 0.15
800	O(1D) + CHFCl ₂ → products	1.9 × 10 ⁻¹⁰	± 0.2	1.9 × 10 ⁻¹⁰	175–340	Δ log <i>k</i> = ± 0.2
800	O(1D) + CH ₃ CF ₂ Cl → products	2.2 × 10 ⁻¹⁰	± 0.2			
800	O(1D) + CH ₃ CFCl ₂ → products	2.6 × 10 ⁻¹⁰	± 0.2			
800	O(1D) + CH ₂ ClCF ₃ → products	1.2 × 10 ⁻¹⁰	± 0.2			
800	O(1D) + CH ₂ ClCF ₂ Cl → products	1.6 × 10 ⁻¹⁰	± 0.3			
800	O(1D) + CHFCICF ₃ → products	8.6 × 10 ⁻¹¹	± 0.2			
800	O(1D) + CHCl ₂ CF ₃ → products	2.0 × 10 ⁻¹⁰	± 0.2			
801	O(1D) + CF ₂ Cl ₂ → products	1.4 × 10 ⁻¹⁰	± 0.1			
802	O(1D) + CFCl ₃ → products	2.3 × 10 ⁻¹⁰	± 0.1			
803	O(1D) + CCl ₄ → products	3.3 × 10 ⁻¹⁰	± 0.1			
803	O(1D) + COFCl → products	1.9 × 10 ⁻¹⁰	± 0.3			
803	O(1D) + COCl ₂ → products	3.6 × 10 ⁻¹⁰	± 0.3			
804	Cl + H ₂ → HCl + H	1.6 × 10 ⁻¹⁴	± 0.1			
805	Cl + HO ₂ → HCl + O ₂	3.2 × 10 ⁻¹¹	± 0.2	3.7 × 10 ⁻¹¹ exp(-2300/T)	200–300	± 200
805	→ ClO + HO	9.1 × 10 ⁻¹²	± 0.2	1.8 × 10 ⁻¹¹ exp(170/T)	250–420	± 250
805	Cl + H ₂ O ₂ → HCl + HO ₂	4.1 × 10 ⁻¹³	± 0.3	4.1 × 10 ⁻¹¹ exp(-450/T)	250–420	± 250
806	Cl + O ₂ + M → ClOO + M	1.4 × 10 ⁻³³ [N ₂] (<i>k₀</i>)	± 0.2	1.1 × 10 ⁻¹¹ exp(-980/T)	265–424	± 500
806	ClOO + M → Cl + O ₂ + M	1.6 × 10 ⁻³³ [O ₂] (<i>k₀</i>)	± 0.2	1.4 × 10 ⁻³³ (7/300) ^{-3.9} [N ₂] 1.6 × 10 ⁻³³ (7/300) ^{-2.9} [O ₂]	160–300	Δ <i>H</i> = ± 1
807	Cl + CO + M → ClCO + M	6.2 × 10 ⁻¹³ [N ₂] (<i>k₀</i>)	± 0.3	2.8 × 10 ⁻¹⁰ exp(-1820/T) [N ₂]	200–300	Δ <i>H</i> = ± 1
808	ClCO + M → Cl + CO + M	1.3 × 10 ⁻³³ [N ₂] (<i>k₀</i>)	± 0.3	1.3 × 10 ⁻³³ (7/300) ^{-3.8} [N ₂]	185–300	Δ <i>H</i> = ± 1
808	Cl + O ₃ → ClO + O ₂	2.0 × 10 ⁻¹⁴ [N ₂] (<i>k₀</i>)	± 0.4	4.1 × 10 ⁻¹⁰ exp(-2960/T) [N ₂]	185–300	± 200
809	Cl + HONO ₂ → HCl + NO ₃	1.2 × 10 ⁻¹¹	± 0.06	2.9 × 10 ⁻¹¹ exp(-260/T)	205–298	± 100
809	Cl + NO ₃ → ClO + NO ₂	< 2.0 × 10 ⁻¹⁶				
810	Cl + OClO → ClO + ClO	2.4 × 10 ⁻¹¹	± 0.2	2.4 × 10 ⁻¹¹	200–300	± 400
		5.8 × 10 ⁻¹¹	± 0.1	3.4 × 10 ⁻¹¹ exp(160/T)	298–450	± 200

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/$ K
810	$\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{Cl}_2 + \text{ClO}$	9.6×10^{-11}	± 0.1	$6.2 \times 10^{-11} \exp(130/T)$	233–373	± 130
811	$\text{Cl} + \text{Cl}_2\text{O}_2 \rightarrow \text{Cl}_2 + \text{ClOO}$	1.0×10^{-10}	± 0.3	1.0×10^{-10}	230–298	± 300
811	$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3$	1.2×10^{-11}	± 0.12	$6.8 \times 10^{-12} \exp(160/T)$	219–298	± 200
812	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	1.0×10^{-13}	± 0.08	$9.6 \times 10^{-12} \exp(-1350/T)$	200–300	± 250
813	$\text{Cl} + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{C}_2\text{H}_2\text{Cl} + \text{M}$	$5.7 \times 10^{-30} [\text{N}_2]$	± 0.3	$5.7 \times 10^{-30} (T/300)^{-3} [\text{N}_2]$	200–300	$\Delta n = \pm 1$
		2.3×10^{-10} (k_∞)	± 0.3	2.3×10^{-10}	200–400	$\Delta n = \pm 1$
814	$\text{Cl} + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_2\text{H}_4\text{Cl} + \text{M}$	$F_c = 0.6$				
		$1.6 \times 10^{-29} [\text{air}]$ (k_0)	± 0.5	$1.6 \times 10^{-29} (T/300)^{-3.5} [\text{air}]$	250–300	$\Delta n = \pm 1$
		3×10^{-10} (k_∞)	± 0.3	3×10^{-10}	250–300	$\Delta n = \pm 1$
814	$\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5$	5.9×10^{-11}	± 0.06	$8.1 \times 10^{-11} \exp(-95/T)$	220–600	± 100
815	$\text{Cl} + \text{C}_3\text{H}_8 \rightarrow \text{HCl} + \text{C}_3\text{H}_7$	1.4×10^{-10}	± 0.12	$1.2 \times 10^{-10} \exp(40/T)$	220–600	± 200
816	$\text{Cl} + \text{HCHO} \rightarrow \text{HCl} + \text{HCO}$	7.3×10^{-11}	± 0.06	$8.2 \times 10^{-11} \exp(-34/T)$	200–500	± 100
816	$\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{HCl} + \text{CH}_3\text{CO}$	7.2×10^{-11}	± 0.15	7.2×10^{-11}	210–340	± 300
817	$\text{Cl} + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{products}$	1.2×10^{-10}	± 0.3			
817	$\text{Cl} + \text{CH}_3\text{COCH}_3 \rightarrow \text{HCl} + \text{CH}_3\text{COCH}_2$	3.5×10^{-12}	± 0.3			
817	$\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{HCl} + \text{CH}_2\text{OH}$	5.5×10^{-11}	± 0.15	5.5×10^{-11}	200–573	± 200
818	$\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{products}$	9.4×10^{-11}	± 0.2			
818	$\text{Cl} + n\text{-C}_3\text{H}_7\text{OH} \rightarrow \text{products}$	1.5×10^{-10}	± 0.2			
819	$\text{Cl} + i\text{-C}_3\text{H}_7\text{OH} \rightarrow \text{products}$	8.4×10^{-11}	± 0.3			
819	$\text{Cl} + \text{CH}_3\text{OOH} \rightarrow \text{products}$	5.9×10^{-11}	± 0.5			
820	$\text{Cl} + \text{HCOOH} \rightarrow \text{products}$	2.0×10^{-13}	± 0.2			
820	$\text{Cl} + \text{CH}_3\text{COOH} \rightarrow \text{products}$	2.8×10^{-14}	± 0.3			
820	$\text{Cl} + \text{CH}_3\text{ONO}_2 \rightarrow \text{products}$	2.4×10^{-13}	± 0.3			
821	$\text{Cl} + \text{C}_2\text{H}_5\text{ONO}_2 \rightarrow \text{products}$	4.7×10^{-12}	± 0.2			
821	$\text{Cl} + n\text{-C}_3\text{H}_7\text{ONO}_2 \rightarrow \text{products}$	2.7×10^{-11}	± 0.2			
821	$\text{Cl} + i\text{-C}_3\text{H}_7\text{ONO}_2 \rightarrow \text{products}$	5.8×10^{-12}	± 0.3			
821	$\text{Cl} + \text{CH}_3\text{C(O)OONO}_2 \rightarrow \text{products}$	$< 2 \times 10^{-14}$				
822	$\text{Cl} + \text{CH}_3\text{CN} \rightarrow \text{products}$	$\leq 2 \times 10^{-15}$				
822	$\text{Cl} + \text{HC(O)Cl} \rightarrow \text{HCl} + \text{ClCO}$	7.8×10^{-13}	± 0.15	$1.2 \times 10^{-11} \exp(-815/T)$	265–325	± 300
823	$\text{Cl} + \text{CH}_3\text{F} \rightarrow \text{HCl} + \text{CH}_2\text{F}$	3.5×10^{-13}	± 0.15	$1.7 \times 10^{-11} \exp(-1160/T)$	273–368	± 500
823	$\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{HCl} + \text{CH}_2\text{Cl}$	4.9×10^{-13}	± 0.15	$3.3 \times 10^{-11} \exp(-1250/T)$	233–322	± 300
824	$\text{Cl} + \text{CH}_2\text{F}_2 \rightarrow \text{HCl} + \text{CHF}_2$	7.3×10^{-14}	± 0.5	$1.5 \times 10^{-11} \exp(-1580/T)$	281–368	± 500
825	$\text{Cl} + \text{CH}_2\text{FCl} \rightarrow \text{HCl} + \text{CHFCl}$	1.1×10^{-13}	± 0.3	$1.0 \times 10^{-11} \exp(-1340/T)$	273–368	± 500
825	$\text{Cl} + \text{CH}_2\text{Cl}_2 \rightarrow \text{HCl} + \text{CHCl}_2$	3.6×10^{-13}	± 0.15	$2.8 \times 10^{-11} \exp(-1300/T)$	270–370	± 300
826	$\text{Cl} + \text{CHF}_2\text{Cl} \rightarrow \text{HCl} + \text{CF}_2\text{Cl}$	1.9×10^{-15}	± 0.15			
827	$\text{Cl} + \text{CHFCl}_2 \rightarrow \text{HCl} + \text{CFCl}_2$	2.1×10^{-14}	± 0.3			
827	$\text{Cl} + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_3$	7.6×10^{-14}	± 0.3	$4.9 \times 10^{-12} \exp(-1240/T)$	240–330	± 400
828	$\text{Cl} + \text{CH}_3\text{CH}_2\text{F} \rightarrow \text{HCl} + \text{CH}_3\text{CHF}$	6.7×10^{-12}	± 0.5	$1.5 \times 10^{-11} \exp(-240/T)$	281–368	± 500
828	$\rightarrow \text{HCl} + \text{CH}_2\text{CH}_2\text{F}$	7.3×10^{-13}	± 0.5	$1.2 \times 10^{-11} \exp(-830/T)$	281–368	± 500
	$\text{Cl} + \text{CH}_3\text{CHF}_2 \rightarrow \text{HCl} + \text{CH}_3\text{CF}_2$	2.7×10^{-13}	± 0.15	$6.8 \times 10^{-12} \exp(-960/T)$	280–360	± 500
	$\rightarrow \text{HCl} + \text{CH}_2\text{CHF}_2$	2.5×10^{-15}	± 0.5	$7.6 \times 10^{-12} \exp(-2395/T)$	280–360	± 500
829	$\text{Cl} + \text{CH}_2\text{FCH}_2\text{F} \rightarrow \text{HCl} + \text{CHFCH}_2\text{F}$	7.7×10^{-13}	± 0.5	$2.7 \times 10^{-11} \exp(-1060/T)$	280–360	± 500
830	$\text{Cl} + \text{CH}_3\text{CF}_3 \rightarrow \text{HCl} + \text{CH}_2\text{CF}_3$	2.6×10^{-17}	± 0.5	$1.0 \times 10^{-11} \exp(-3830/T)$	281–368	± 500
830	$\text{Cl} + \text{CH}_2\text{FCF}_2 \rightarrow \text{HCl} + \text{CH}_2\text{FCF}_2$	2.5×10^{-14}	± 0.5	$4.8 \times 10^{-12} \exp(-1560/T)$	281–368	± 500
	$\rightarrow \text{HCl} + \text{CHFCHF}_2$	2.5×10^{-14}	± 0.5	$6.7 \times 10^{-12} \exp(-1670/T)$	281–368	± 500

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
831	Cl + CH ₃ CF ₂ Cl → HCl + CH ₂ CF ₂ Cl	4.0 × 10 ⁻¹⁶	± 0.15			
832	Cl + CH ₃ CFCl ₂ → HCl + CH ₂ CFCl ₂	2.3 × 10 ⁻¹⁵	± 0.1	1.0 × 10 ⁻¹² exp(-1800/T)	298–376	± 500
832	Cl + CH ₃ CCl ₃ → HCl + CH ₂ CCl ₃	< 4 × 10 ⁻¹⁴				
833	Cl + CH ₂ FCF ₃ → HCl + CHF ₂ CF ₃	1.5 × 10 ⁻¹⁵	± 0.1			
833	Cl + CHF ₂ CHF ₂ → HCl + CF ₂ CHF ₂	2.2 × 10 ⁻¹⁵	± 0.2	7.9 × 10 ⁻¹² exp(-2440/T)	280–360	± 500
834	Cl + CHF ₂ CF ₃ → HCl + CF ₂ CF ₃	2.4 × 10 ⁻¹⁶	± 0.2			
835	Cl + CHFClCF ₃ → HCl + CFClCF ₃	2.7 × 10 ⁻¹⁵	± 0.1	1.1 × 10 ⁻¹² exp(-1800/T)	276–376	± 500
835	Cl + CHCl ₂ CF ₃ → HCl + CCl ₂ CF ₃	1.2 × 10 ⁻¹⁴	± 0.1	4.4 × 10 ⁻¹² exp(-1750/T)	276–382	± 500
836	Cl + OCS → SCI + CO	< 1.0 × 10 ⁻¹⁶				
837	Cl + CS ₂ + O ₂ → products	≤ 4 × 10 ⁻¹⁵				
838	Cl + CH ₃ SCH ₃ → products	3.3 × 10 ⁻¹⁰	± 0.2		250–330	± 400
839	HO + Cl ₂ → HOCl + Cl	6.7 × 10 ⁻¹⁴	± 0.1	1.4 × 10 ⁻¹² exp(-900/T)	200–300	± 150
839	HO + HCl → H ₂ O + Cl	8.1 × 10 ⁻¹³	± 0.1	2.4 × 10 ⁻¹² exp(-330/T)	200–300	± 500
840	HO + HOCl → ClO + H ₂ O	5.0 × 10 ⁻¹³	± 0.5	3.0 × 10 ⁻¹² exp(-500/T)	200–300	± 500
840	HO + ClO → HO ₂ + Cl → HCl + O ₂	1.7 × 10 ⁻¹¹	± 0.2	1.1 × 10 ⁻¹¹ exp(120/T)	200–373	± 150
841	HO + OCIO → HOCl + O ₂	7.0 × 10 ⁻¹²	± 0.3	4.5 × 10 ⁻¹³ exp(800/T)	290–480	± 200
841	HO + ClNO ₂ → HOCl + NO ₂	3.6 × 10 ⁻¹⁴	± 0.3	2.4 × 10 ⁻¹² exp(-1250/T)	260–350	± 300
842	HO + ClONO ₂ → products	3.9 × 10 ⁻¹³	± 0.2	1.2 × 10 ⁻¹² exp(-330/T)	246–387	± 200
843	HO + CH ₃ Cl → H ₂ O + CH ₂ Cl	4.2 × 10 ⁻¹⁴	± 0.10	3.8 × 10 ⁻¹² exp(-1340/T)	240–300	± 200
844	HO + CH ₂ FCI → H ₂ O + CHFCl	4.4 × 10 ⁻¹⁴	± 0.10	2.0 × 10 ⁻¹² exp(-1135/T)	240–300	± 200
844	HO + CH ₂ Cl ₂ → H ₂ O + CHCl ₂	1.2 × 10 ⁻¹³	± 0.20	2.7 × 10 ⁻¹² exp(-920/T)	240–300	± 300
846	HO + CHF ₂ Cl → H ₂ O + CF ₂ Cl	4.6 × 10 ⁻¹⁵	± 0.10	7.8 × 10 ⁻¹³ exp(-1530/T)	240–300	± 200
847	HO + CHFCl ₂ → H ₂ O + CHFCl ₂	3.0 × 10 ⁻¹⁴	± 0.10	8.8 × 10 ⁻¹³ exp(-1010/T)	240–300	± 200
847	HO + CHCl ₃ → H ₂ O + CCl ₃	1.0 × 10 ⁻¹³	± 0.10	9.3 × 10 ⁻¹³ exp(-660/T)	240–300	± 100
848	HO + CF ₃ Cl ₂ → HOCl + CF ₂ Cl	< 7 × 10 ⁻¹⁸		< 1 × 10 ⁻¹² exp(-3540/T)	250–478	
848	HO + CFCl ₃ → HOCl + CFCl ₂	< 5 × 10 ⁻¹⁸		< 1 × 10 ⁻¹² exp(-3650/T)	250–480	
849	HO + CCl ₄ → HOCl + CCl ₃	< 5 × 10 ⁻¹⁶		< 1 × 10 ⁻¹² exp(-2260/T)	250–300	
849	HO + C ₂ HCl ₃ → products	2.2 × 10 ⁻¹²	± 0.10	5.0 × 10 ⁻¹³ exp(445/T)	230–420	± 200
849	HO + C ₂ Cl ₄ → products	1.7 × 10 ⁻¹³	± 0.10	9.4 × 10 ⁻¹² exp(-1200/T)	300–420	± 200
850	HO + CH ₃ CF ₂ Cl → H ₂ O + CH ₂ CF ₂ Cl	3.0 × 10 ⁻¹⁵	± 0.10	9.2 × 10 ⁻¹³ exp(-1705/T)	240–300	± 200
851	HO + CH ₃ CFCl ₂ → H ₂ O + CH ₂ CFCl ₂	5.9 × 10 ⁻¹⁵	± 0.15	7.0 × 10 ⁻¹³ exp(-1425/T)	240–300	± 200
852	HO + CH ₃ CCl ₃ → H ₂ O + CH ₂ CCl ₃	9.5 × 10 ⁻¹⁵	± 0.10	1.2 × 10 ⁻¹² exp(-1440/T)	240–300	± 200
853	HO + CH ₂ ClCF ₃ → H ₂ O + CHClCF ₃	1.3 × 10 ⁻¹⁴	± 0.2	5.2 × 10 ⁻¹³ exp(-1100/T)	260–380	± 250
853	HO + CH ₂ ClCF ₂ Cl → H ₂ O + CHClCF ₂ Cl	1.6 × 10 ⁻¹⁴	± 0.3	3.2 × 10 ⁻¹² exp(-1580/T)	250–350	± 500
854	HO + CHFClCF ₃ → H ₂ O + CFClCF ₃	9.5 × 10 ⁻¹⁵	± 0.20	5.4 × 10 ⁻¹³ exp(-1205/T)	240–300	± 300
855	HO + CHCl ₂ CF ₃ → H ₂ O + CCl ₂ CF ₃	3.6 × 10 ⁻¹⁴	± 0.15	5.5 × 10 ⁻¹³ exp(-815/T)	240–300	± 200
856	HO + CHFClCF ₂ Cl → H ₂ O + CFClCF ₂ Cl	1.2 × 10 ⁻¹⁴	± 0.3	8.4 × 10 ⁻¹³ exp(-1255/T)	298–460	± 400
856	HO + CHCl ₂ CF ₂ Cl → H ₂ O + CCl ₂ CF ₂ Cl	5.1 × 10 ⁻¹⁴	± 0.3	1.2 × 10 ⁻¹² exp(-940/T)	298–460	± 400
857	HO + CHFClCFCl ₂ → H ₂ O + CFClCFCl ₂	1.7 × 10 ⁻¹³	± 0.3	4.1 × 10 ⁻¹² exp(-945/T)	270–340	± 400
857	HO + CHCl ₂ CF ₂ CF ₃ → H ₂ O + CCl ₂ CF ₂ CF ₃	2.5 × 10 ⁻¹⁴	± 0.15	1.1 × 10 ⁻¹² exp(-1130/T)	270–400	± 300
858	HO + CHFClCF ₂ CF ₂ Cl → H ₂ O + CFClCF ₂ CF ₂ Cl	8.9 × 10 ⁻¹⁵	± 0.10	5.5 × 10 ⁻¹³ exp(-1230/T)	290–400	± 300
858	HO + CH ₃ CF ₂ CFCl ₂ → H ₂ O + CH ₂ CF ₂ CFCl ₂	2.4 × 10 ⁻¹⁵	± 0.3	7.0 × 10 ⁻¹³ exp(-1690/T)	290–370	± 300
858	HO + HC(O)Cl → H ₂ O + ClCO	< 5 × 10 ⁻¹³				
858	HO + COCl ₂ → products	< 5 × 10 ⁻¹⁵				

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/$ K
859	$\text{HO} + \text{CH}_3\text{ClCHO} \rightarrow \text{products}$	3.1×10^{-12}	± 0.20			
860	$\text{HO} + \text{CHFCICHCHO} \rightarrow \text{products}$	2.1×10^{-12}	± 0.20			
860	$\text{HO} + \text{CHCl}_2\text{CHO} \rightarrow \text{products}$	2.4×10^{-12}	± 0.20			
861	$\text{HO} + \text{CF}_2\text{ClCHO} \rightarrow \text{H}_2\text{O} + \text{CF}_2\text{ClCO}$	8.2×10^{-13}	± 0.25			
861	$\text{HO} + \text{CFCl}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CFCl}_2\text{CO}$	1.2×10^{-12}	± 0.20			
862	$\text{HO} + \text{CCl}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CCl}_3\text{CO}$	1.1×10^{-12}	± 0.15			
863	$\text{HO} + \text{CH}_3\text{COC}_2\text{H}_5 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{COC}_2\text{H}_5$	9×10^{-15}	± 1.0			
863	$\text{HO} + \text{CH}_2\text{FCH}_2\text{CF}_3 \rightarrow \text{products}$	2.1×10^{-14}	± 0.5			
864	$\text{HO} + \text{CHF}_2\text{OCF}_2\text{CH}_2\text{F} \rightarrow \text{products}$	1.6×10^{-14}	± 0.5		300–430	± 500
865	$\text{HO}_2 + \text{CF}_3\text{CCl}_2\text{O}_2 \rightarrow \text{O}_2 + \text{CF}_3\text{CCl}_2\text{O}_2\text{H}$	1.9×10^{-12}	± 0.3			
865	$\text{HO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow \text{O}_2 + \text{CH}_2\text{ClO}_2\text{H}$	5.0×10^{-12}	± 0.3	$6.1 \times 10^{-13} \exp(-1080/T)$	250–600	± 300
866	$\text{NO}_3 + \text{HCl} \rightarrow \text{HNO}_3 + \text{Cl}$	$< 5 \times 10^{-17}$	± 0.3	$3.2 \times 10^{-13} \exp(820/T)$		
866	$\text{NO}_3 + \text{C}_2\text{HCl}_3 \rightarrow \text{products}$	2.9×10^{-16}				
866	$\text{NO}_3 + \text{C}_2\text{Cl}_4 \rightarrow \text{products}$	$< 1 \times 10^{-16}$				
868	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$ $\rightarrow \text{HCl} + \text{O}_3$	5.0×10^{-12}	± 0.15	$4.6 \times 10^{-13} \exp(710/T)$	200–300	± 300
868	$\text{ClO} + \text{O}_3 \rightarrow \text{ClOO} + \text{O}_2$ $\rightarrow \text{OCIO} + \text{O}_2$	$< 1.5 \times 10^{-17}$				
868	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	1.7×10^{-11}	± 0.1	$6.2 \times 10^{-12} \exp(294/T)$	202–415	± 100
869	$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$1.6 \times 10^{-31} [\text{N}_2]$ 2×10^{-11} $F_c = 0.5$	± 0.1 ± 0.3	$1.6 \times 10^{-31} (T/300)^{-3.4} [\text{N}_2]$ $F_c = \exp(-T/430)$	200–300 200–300 200–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
870	$\text{ClO} + \text{NO}_3 \rightarrow \text{ClOO} + \text{NO}_2$ $\rightarrow \text{OCIO} + \text{NO}_2$	4.7×10^{-13}	± 0.2	4.7×10^{-13}	210–350	± 400
871	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$ $\rightarrow \text{Cl} + \text{ClOO}$ $\rightarrow \text{Cl} + \text{OCIO}$	4.8×10^{-15} 8.0×10^{-15} 3.5×10^{-15}	± 0.2 ± 0.2 ± 0.2	$1.0 \times 10^{-12} \exp(-1590/T)$ $3.0 \times 10^{-11} \exp(-2450/T)$ $3.5 \times 10^{-13} \exp(-1370/T)$	260–390 260–390 260–390	± 500 ± 500 ± 500
872	$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$	$1.7 \times 10^{-32} [\text{N}_2]$ 5.4×10^{-12} $F_c = 0.6$	± 0.1 ± 0.3	$1.7 \times 10^{-32} (T/300)^{-4} [\text{N}_2]$ 5.4×10^{-12}	200–300 200–300	$\Delta n = \pm 1.5$ $\Delta \log k = \pm 0.3$
874	$\text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M}$	$2.2 \times 10^{-18} [\text{N}_2]$	± 0.3	$1 \times 10^{-6} \exp(-8000/T) [\text{N}_2]$	260–310	± 900
875	$\text{ClO} + \text{OCIO} + \text{M} \rightarrow \text{Cl}_2\text{O}_3 + \text{M}$	6.7×10^2 $6.2 \times 10^{-32} [\text{N}_2]$ 2.4×10^{-11} $F_c = 0.6$	± 0.3 ± 0.3 ± 0.3	$4.8 \times 10^{15} \exp(-8820/T)$ $6.2 \times 10^{-32} (T/300)^{-4.7} [\text{N}_2]$ 2.4×10^{-11} $F_c = 0.6$	260–310 200–300 200–300 200–300	± 500 $\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
876	$\text{Cl}_2\text{O}_3 + \text{M} \rightarrow \text{ClO} + \text{OCIO} + \text{M}$	$2.8 \times 10^{-18} [\text{N}_2]$	± 0.5 (226 K)		200–300	
876	$\text{ClO} + \text{CH}_3\text{O}_2 \rightarrow \text{ClOO} + \text{CH}_3\text{O}$ $\rightarrow \text{CH}_3\text{OCl} + \text{O}_2$ $\rightarrow \text{OCIO} + \text{CH}_3\text{O}$	1.6×10^{-12} 6.3×10^{-13} $< 1 \times 10^{-15}$	± 0.3 ± 0.3	$4.9 \times 10^{-12} \exp(-330/T)$ $2.6 \times 10^{-13} \exp(260/T)$	225–355 225–355	± 200 ± 250
877	$\text{ClO} + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$	9×10^{-15}	± 0.5		262–298	± 1000
877	$\text{OCIO} + \text{O}_3 \rightarrow \text{ClO}_3 + \text{O}_2$	3.0×10^{-19}	± 0.4			
878	$\text{OCIO} + \text{NO} \rightarrow \text{NO}_2 + \text{ClO}$	3.4×10^{-13}	± 0.3			
878	$\text{OCIO} + \text{NO}_3 + \text{M} \rightarrow \text{O}_2\text{ClONO}_2 + \text{M}$	$1 \times 10^{-31} [\text{He}]$				
879	$\text{Cl}_2\text{O}_2 + \text{O}_3 \rightarrow \text{ClO} + \text{ClOO} + \text{O}_2$	$< 1 \times 10^{-19}$		$2.1 \times 10^{-12} \exp(-4700/T)$ ± 0.4		

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
879	CF ₂ Cl + O ₂ + M → CF ₂ ClO ₂ + M	1.4 × 10 ⁻²⁹ [N ₂] 9 × 10 ⁻¹² $F_c = 0.6$	± 0.5 ± 0.5	1.4 × 10 ⁻²⁹ (T/300) ⁻⁵ [N ₂] 9 × 10 ⁻¹²	200–300 200–300	$\Delta n = \pm 2$ $\Delta \log k = \pm 0.5$
880	CFCl ₂ + O ₂ + M → CFCl ₂ O ₂ + M	5.5 × 10 ⁻³⁰ [N ₂] 9 × 10 ⁻¹² $F_c = 0.6$	± 0.3 ± 0.5	5.5 × 10 ⁻³⁰ (T/300) ⁻⁶ [N ₂] 9 × 10 ⁻¹²	200–300 200–300	$\Delta n = \pm 2$ $\Delta n = \pm 1$
881	CCl ₃ + O ₂ + M → CCl ₃ O ₂ + M	9 × 10 ⁻³¹ [N ₂] 3 × 10 ⁻¹² $F_c = 0.6$	± 0.3 ± 0.4	9 × 10 ⁻³¹ (T/300) ⁻⁶ [N ₂] 3 × 10 ⁻¹²	200–300 200–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.4$
777	CHFCIO + O ₂ → COFCl + HO ₂	See data sheet				
777	CHFCIO + M → HCOF + Cl + M	See data sheet				
777	CF ₂ ClO + O ₂ → products	7 × 10 ⁻⁵				
*	CF ₂ ClO + M → COF ₂ + Cl + M	See data sheet				
777	CFCl ₂ O + O ₂ → products	7 × 10 ⁻⁵				
*	CFCl ₂ O + M → COFCl + Cl + M	8 × 10 ⁻⁶				
*	CCl ₃ O → COCl ₂ + Cl	See data sheet				
777	CF ₂ ClCH ₂ O + O ₂ → CF ₂ ClCHO + HO ₂	See data sheet				
777	CF ₂ ClCH ₂ O + M → CF ₂ Cl + HCHO + M	See data sheet				
777	CFCl ₂ CH ₂ O + O ₂ → CFCl ₂ CHO + HO ₂	See data sheet				
777	CFCl ₂ CH ₂ O + M → CFCl ₂ + HCHO + M	See data sheet				
777	CF ₃ CFClO + O ₂ → products	See data sheet				
777	CF ₃ CFClO + M → CF ₃ COF + Cl + M	See data sheet				
777	CF ₃ CCl ₂ O + O ₂ → products	See data sheet				
777	CF ₃ CCl ₂ O + M → CF ₃ COCl + Cl + M	See data sheet				
777	CF ₃ CF ₂ CCl ₂ O + O ₂ → products	See data sheet				
777	CF ₃ CF ₂ CCl ₂ O + M → CF ₃ CF ₂ COCl + Cl + M	See data sheet				
777	CF ₂ ClCF ₂ CFClO + O ₂ → products	See data sheet				
777	CF ₂ ClCF ₂ CFClO + M → CF ₂ ClCF ₂ COF + Cl + M	See data sheet				
777	CH ₂ ClO + O ₂ → HCOCl + HO ₂	See data sheet				
777	CH ₂ ClO + M → HCO + HCl + M	See data sheet				
777	CH ₃ CHClO + O ₂ → CH ₃ COCl + HO ₂	See data sheet				
777	CH ₃ CHClO + M → CH ₃ CO + HCl + M	See data sheet				
777	HOCH ₂ CHClO + O ₂ → HOCH ₂ COCl + HO ₂	See data sheet				
777	HOCH ₂ CHClO + M → CH ₂ OH + HCOCl + M	See data sheet				
777	HOCHClCH ₂ O + O ₂ → HOCHClCHO + HO ₂	See data sheet				
777	HOCHClCH ₂ O + M → CHClOH + HCHO + M	See data sheet				
777	CH ₃ CCl ₂ O + O ₂ → products	See data sheet				
777	CH ₃ CCl ₂ O + M → CH ₃ COCl + Cl + M	See data sheet				
777	CCl ₃ CH ₂ O + O ₂ → CCl ₃ CHO + HO ₂	See data sheet				
777	CCl ₃ CH ₂ O + M → CCl ₃ + HCHO + M	See data sheet				
777	CCl ₃ CCl ₂ O + O ₂ → products	See data sheet				
777	CCl ₃ CCl ₂ O + M → CCl ₃ COCl + Cl + M	See data sheet				
781	CH ₂ ClO ₂ + NO → CH ₂ ClO + NO ₂	1.9 × 10 ⁻¹¹	± 0.3			
781	CF ₂ ClO ₂ + NO → CF ₂ ClO + NO ₂	1.5 × 10 ⁻¹¹	± 0.2	1.5 × 10 ⁻¹¹ (T/298) ^{-1.5}	230–430	$\Delta \log k = \pm 0.2$

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
781	CFCl ₂ O ₂ + NO → CFCl ₂ O + NO ₂	1.5×10^{-11}	±0.2	$1.5 \times 10^{-11} (T/298)^{-1.3}$	230–430	$\Delta \log k = \pm 0.2$
781	CCl ₃ O ₂ + NO → CCl ₃ O + NO ₂	1.8×10^{-11}	±0.2	$1.8 \times 10^{-11} (T/298)^{-1.0}$	230–430	$\Delta \log k = \pm 0.2$
781	CF ₂ ClCH ₂ O ₂ + NO → CF ₂ ClCH ₂ O + NO ₂	1.2×10^{-11}	±0.3			
781	CFCl ₂ CH ₂ O ₂ + NO → CFCl ₂ CH ₂ O + NO ₂	1.3×10^{-11}	±0.3			
781	CF ₃ CCl ₂ O ₂ + NO → CF ₃ CCl ₂ O + NO ₂	1.8×10^{-11}	±0.3			
882	CF ₂ ClO ₂ + NO ₂ + M → CF ₂ ClONO ₂ + M	$1.4 \times 10^{-28} [N_2]$ 7.5×10^{-12}	±0.5 ±0.3	$1.4 \times 10^{-28} (T/300)^{-6.4} [N_2]$ $F_c = 0.26$	200–300 200–300	$\Delta n = \pm 2$ $\Delta \log k = \pm 0.3$
882	CF ₂ ClO ₂ NO ₂ + M → CF ₂ ClO + NO ₂ + M	$F_c = 0.26$ $9.0 \times 10^{-19} [N_2]$	±0.3	(k_0/s^{-1})	220–300	
883	CFCl ₂ O ₂ + NO ₂ + M → CFCl ₂ O ₂ NO ₂ + M	5.4×10^{-2} $F_c = 0.26$	±0.3	(k_0/s^{-1}) (k_∞/s^{-1})	260–300 260–300	±500 ±500
884	CFCl ₂ O ₂ NO ₂ + M → CFCl ₂ O ₂ + NO ₂ + M	$1.7 \times 10^{-28} [N_2]$ 7.5×10^{-12}	±0.3 ±0.3	(k_0) (k_∞)	230–300 250–300	$\Delta n = \pm 2$ $\Delta \log k = \pm 0.3$
884	CFCl ₂ O ₂ NO ₂ + M → CFCl ₂ O ₂ + NO ₂ + M	$F_c = 0.23$ $1.5 \times 10^{-18} [N_2]$	±0.3	(k_0/s^{-1})	250–300	±500
884	CCl ₃ O ₂ + NO ₂ + M → CCl ₃ O ₂ NO ₂ + M	9.6×10^{-2} $F_c = 0.23$	±0.3	(k_0/s^{-1}) (k_∞/s^{-1})	250–300 250–300	±500 ±500
885	CCl ₃ O ₂ NO ₂ + M → CCl ₃ O ₂ + NO ₂ + M	$3.2 \times 10^{-28} [N_2]$ 7.5×10^{-12}	±0.5 ±0.3	(k_0) (k_∞)	230–300 250–300	$\Delta n = \pm 3$ $\Delta \log k = \pm 0.3$
886	C ₂ H ₅ O ₂ + CF ₃ CCl ₂ O ₂ → CH ₃ CHO + CF ₃ CCl ₂ OH + O ₂ → C ₂ H ₅ O + CF ₃ CCl ₂ O + O ₂	3.6×10^{-12} 9×10^{-13}	±0.3 ±0.5			
886	CF ₂ ClCH ₂ O ₂ + CF ₂ ClCH ₂ O ₂ → CF ₂ ClCH ₂ OH + CF ₂ ClCHO + O ₂ → 2CF ₂ ClCH ₂ O + O ₂	$\leq 4 \times 10^{-12}$				
887	CFCl ₂ CH ₂ O ₂ + CFCl ₂ CH ₂ O ₂ → CFCl ₂ CH ₂ OH + CFCl ₂ CHO + O ₂ → 2CFCl ₂ CHO + O ₂	$\leq 4 \times 10^{-12}$				
887	CF ₃ CCl ₂ O ₂ + CF ₃ CCl ₂ O ₂ → CF ₃ CCl ₂ OCCl ₂ CF ₃ + O ₂ → 2CF ₃ CCl ₂ O + O ₂	$\leq 3 \times 10^{-12}$				
888	CH ₂ CHO ₂ + CH ₂ CHO ₂ → 2CH ₂ CHO + O ₂	3.7×10^{-12}	±0.2	$2.0 \times 10^{-13} \exp(870/T)$	250–600	±200
889	CCl ₃ O ₂ + CCl ₃ O ₂ → CCl ₃ OCCl ₃ + O ₂ → 2CCl ₃ O + O ₂	1.6×10^{-12}	±0.3	$8.9 \times 10^{-14} \exp(860/T)$	250–430	±300
890	CH ₃ CHClO ₂ + CH ₃ CHClO ₂ → CH ₃ CHClOH + CH ₃ COCl + O ₂ → 2CH ₃ CHClO + O ₂	5×10^{-12}	±0.3			
891	CH ₂ ClCH ₂ O ₂ + CH ₂ ClCH ₂ O ₂ → CH ₂ ClCH ₂ OH + CH ₂ ClCHO + O ₂ → 2CH ₂ ClCH ₂ O + O ₂	$\leq 4.8 \times 10^{-12}$				
892	O ₃ + C ₂ HCl ₃ → products	$< 5 \times 10^{-20}$				
892	O ₃ + C ₂ Cl ₄ → products	$< 10^{-21}$		$\leq 1.6 \times 10^{-13} \exp(1020/T)$	220–380	

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
892	HCl + $h\nu$ → products	See data sheet				
893	HOCl + $h\nu$ → products	See data sheet				
894	OCIO + $h\nu$ → products	See data sheet				
895	Cl ₂ O + $h\nu$ → products	See data sheet				
895	Cl ₂ O ₂ + $h\nu$ → products	See data sheet				
896	Cl ₂ O ₃ + $h\nu$ → products	See data sheet				
897	CINO + $h\nu$ → products	See data sheet				
898	CIONO + $h\nu$ → products	See data sheet				
898	CINO ₂ + $h\nu$ → products	See data sheet				
899	CIONO ₂ + $h\nu$ → products	See data sheet				
900	Cl ₂ + $h\nu$ → products	See data sheet				
901	CH ₃ Cl + $h\nu$ → products	See data sheet				
901	CHF ₂ Cl + $h\nu$ → products	See data sheet				
902	CF ₂ Cl ₂ + $h\nu$ → products	See data sheet				
902	CFCl ₃ + $h\nu$ → products	See data sheet				
903	CCl ₄ + $h\nu$ → products	See data sheet				
904	CH ₃ CF ₂ Cl + $h\nu$ → products	See data sheet				
905	CH ₃ CFCl ₂ + $h\nu$ → products	See data sheet				
905	CH ₃ CCl ₃ + $h\nu$ → products	See data sheet				
906	CF ₃ CHFCI + $h\nu$ → products	See data sheet				
907	CF ₃ CHCl ₂ + $h\nu$ → products	See data sheet				
907	CF ₂ ClCFCl ₂ + $h\nu$ → products	See data sheet				
908	CF ₂ ClCF ₂ Cl + $h\nu$ → products	See data sheet				
908	CF ₃ CF ₂ Cl + $h\nu$ → products	See data sheet				
909	CF ₃ CF ₂ CHCl ₂ + $h\nu$ → products	See data sheet				
909	CF ₂ ClCF ₂ CHFCI + $h\nu$ → products	See data sheet				
910	HCOCI + $h\nu$ → products	See data sheet				
910	COFCl + $h\nu$ → products	See data sheet				
911	COCl ₂ + $h\nu$ → products	See data sheet				
912	CF ₂ ClCHO + $h\nu$ → products	See data sheet				
913	CFCl ₂ CHO + $h\nu$ → products	See data sheet				
914	CCl ₃ CHO + $h\nu$ → products	See data sheet				
916	CF ₃ COCI + $h\nu$ → products	See data sheet				
<i>BrO_x Reactions</i>						
918	O + HOBr → HO + BrO	2.5×10^{-11}	±0.5			
918	O + BrO → O ₂ + Br	4.1×10^{-11}	±0.2	$1.9 \times 10^{-11} \exp(230/T)$	230–330	±150
919	Br + HO ₂ → HBr + O ₂	2.0×10^{-12}	±0.3	$1.4 \times 10^{-11} \exp(-590/T)$	260–390	±200
919	Br + H ₂ O ₂ → HBr + HO ₂ → HOBr + HO	$< 5 \times 10^{-16}$				
919	Br + O ₃ → BrO + O ₂	1.2×10^{-12}	±0.08	$1.7 \times 10^{-11} \exp(-800/T)$	195–392	±200
920	Br + NO ₂ + M → BrNO ₂ + M	$4.2 \times 10^{-31} [N_2]$	±0.3	$4.2 \times 10^{-31} (T/300)^{-2.4} [N_2]$	200–300	$\Delta n = \pm 1$
		2.7×10^{-11}	±0.4	2.7×10^{-11}	200–300	$\Delta \log k = \pm 0.4$
		$F_c = 0.55$				

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
920	Br + OClO → BrO + ClO	3.4×10^{-13}	±0.3	$2.6 \times 10^{-11} \exp(-1300/T)$	200–450	±300
921	Br + Cl ₂ O → BrCl + ClO	4.3×10^{-12}	±0.1	$2.1 \times 10^{-11} \exp(-470/T)$	220–400	±200
921	Br + Cl ₂ O ₂ → BrCl + ClOO	3.0×10^{-12}	±0.3			
922	Br + HCHO → HBr + HCO	1.1×10^{-12}	±0.15	$1.7 \times 10^{-11} \exp(-800/T)$	223–480	±250
922	Br + CH ₃ CHO → HBr + CH ₃ CO	3.9×10^{-12}	±0.2	$1.3 \times 10^{-11} \exp(-360/T)$	250–400	±200
923	HO + H ₂ Br → H ₂ O + Br	1.1×10^{-11}	±0.10	$1.1 \times 10^{-11} (T/298)^{-0.8}$	200–400	$\Delta n = +0.8$ $\Delta n = -0.2$
923	HO + Br ₂ → HOBr + Br	4.5×10^{-11}	±0.15	$1.2 \times 10^{-11} \exp(400/T)$	260–360	±400
924	HO + CH ₃ Br → H ₂ O + CH ₃ Br	2.9×10^{-14}	±0.08	$1.7 \times 10^{-12} \exp(-1215/T)$	240–300	±150
925	HO + CH ₂ Br ₂ → H ₂ O + CHBr ₂	1.1×10^{-13}	±0.20	$1.5 \times 10^{-12} \exp(-775/T)$	240–300	±300
926	HO + CHF ₂ Br → H ₂ O + CF ₂ Br	9.8×10^{-15}	±0.10	$8.1 \times 10^{-13} \exp(-1315/T)$	240–300	±150
927	HO + CF ₃ Br → products	$< 1 \times 10^{-16}$				
927	HO + CF ₂ ClBr → products	$< 1 \times 10^{-16}$				
927	HO + CF ₂ Br ₂ → products	$< 5 \times 10^{-16}$				
928	HO + CF ₃ CH ₂ Br → H ₂ O + CF ₃ CHBr	1.6×10^{-14}	±0.20	$1.4 \times 10^{-12} \exp(-1335/T)$	280–460	±300
928	HO + CF ₃ CHFBr → H ₂ O + CF ₃ CFBr	1.7×10^{-14}	±0.2	$8.1 \times 10^{-13} \exp(-1155/T)$	279–460	±300
929	HO + CF ₃ CHClBr → H ₂ O + CF ₃ CClBr	4.6×10^{-14}	±0.20	$1.2 \times 10^{-12} \exp(-970/T)$	298–460	±300
929	HO + CF ₂ BrCF ₂ Br → products	$< 1.3 \times 10^{-16}$				
930	Br + NO ₃ → BrO + NO ₂	1.6×10^{-11}	±0.3			
930	BrO + NO ₃ → BrOO + NO ₂	1.0×10^{-12}	±0.5			
931	NO ₃ + HBr → HNO ₃ + Br	$< 1 \times 10^{-16}$				
932	BrO + HO ₂ → HOBr + O ₂	3.3×10^{-11}	±0.2	$6.2 \times 10^{-12} \exp(500/T)$	200–300	±500
	→ HBr + O ₃					
932	BrO + O ₃ → Br + 2O ₂	$< 5 \times 10^{-17}$				
933	BrO + NO → Br + NO ₂	2.1×10^{-11}	±0.1	$8.7 \times 10^{-12} \exp(260/T)$	224–425	±100
934	BrO + NO ₂ + M → BrONO ₂ + M	$4.7 \times 10^{-31} [\text{N}_2]$	±0.1	$4.7 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2]$	200–300	$\Delta n = \pm 1$
		1.7×10^{-11}	±0.1	$1.7 \times 10^{-11} (T/300)^{-0.6}$	200–300	$\Delta n = \pm 1$
935	BrO + ClO → Br + OClO	$F_c = 0.40$		$F_c = \exp(-T/327)$	200–300	
	→ Br + ClOO	6.8×10^{-12}	±0.1	$1.6 \times 10^{-12} \exp(430/T)$	220–400	±200
	→ BrCl + O ₂	6.1×10^{-12}	±0.1	$2.9 \times 10^{-12} \exp(220/T)$	220–400	±200
936	BrO + BrO → 2Br + O ₂	1.0×10^{-12}	±0.1	$5.8 \times 10^{-13} \exp(170/T)$	220–400	±200
	→ Br ₂ + O ₂	2.1×10^{-12}	±0.1	$4.0 \times 10^{-12} \exp(-190/T)$	220–400	±150
781	CH ₂ BrO ₂ + NO → CH ₂ BrO + NO ₂	3.8×10^{-13}	±0.1	$4.2 \times 10^{-14} \exp(660/T)$	220–400	±300
937	CH ₂ BrO ₂ + CH ₂ BrO ₃	1.1×10^{-11}	±0.3			
	→ CH ₂ BrOOCH ₂ Br + O ₂					
	→ 2CH ₂ BrO + O ₂					
938	BrCH ₂ CH ₂ O ₂ + BrCH ₂ CH ₂ O ₂	$\leq 3.3 \times 10^{-11}$				
	→ BrCH ₂ CH ₂ OH + BrCH ₂ CHO + O ₂	1.6×10^{-12}	±0.3			
	→ 2BrCH ₂ CH ₂ O + O ₂	2.3×10^{-12}	±0.3			
939	BrO + CH ₃ SCH ₃ → products	$< 2.7 \times 10^{-13}$				
939	HOBr + hν → products	See data sheet				
940	BrO + hν → products	See data sheet				
941	BrONO ₂ + hν → products	See data sheet				
942	CH ₃ Br + hν → products	See data sheet				
943	CF ₃ Br + hν → products	See data sheet				

TABLE 2. (a) Gas Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page Number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/$ K
943	CF ₂ ClBr + $h\nu$ → products	See data sheet				
944	CF ₂ Br ₂ + $h\nu$ → products	See data sheet				
945	CHBr ₃ + $h\nu$ → products	See data sheet				
946	CF ₃ BrCF ₂ Br + $h\nu$ → products	See data sheet				
<i>IO Reactions</i>						
948	O + I ₂ → IO + I	1.4×10^{-10}	±0.3	1.4×10^{-10}	200–400	±250
948	O + IO → O ₂ + I	3×10^{-11}	±0.5			
948	I + HO ₂ → HI + O ₂	3.8×10^{-13}	±0.3	$1.5 \times 10^{-11} \exp(-1090/T)$	250–350	±500
949	I + O ₃ → IO + O ₂	1.0×10^{-12}	±0.2	$2.0 \times 10^{-11} \exp(-890/T)$	200–350	±300
949	I + NO + M → INO + M	$1.8 \times 10^{-32} [\text{N}_2]$ (k_0)	±0.1	$1.8 \times 10^{-32} (T/300)^{-1.0} [\text{N}_2]$	200–400	$\Delta n = \pm 0.5$
		1.7×10^{-11} (k_∞)	±0.3	1.7×10^{-11}	200–400	$\Delta n = \pm 0.5$
949	I + NO ₂ + M → INO ₂ + M	$F_c = 0.75$ $3.0 \times 10^{-31} [\text{N}_2]$ (k_0)	±0.2	$F_c = [\exp(-7710/40) + \exp(-4160/T)]$ $3.0 \times 10^{-31} (T/300)^{-1} [\text{N}_2]$	200–400	$\Delta n = \pm 1$
		6.6×10^{-11} (k_∞)	±0.3	6.6×10^{-11}	200–400	$\Delta \log k = \pm 0.3$
		$F_c = 0.63$		$F_c = [\exp(-77650) + \exp(-2600/T)]$	200–400	
950	I + NO ₃ → IO + NO ₂	No recommendation (see data sheet)				
951	I ₂ + NO ₃ → I + IONO ₂	1.5×10^{-12}	±0.3			
951	HO + HI → H ₂ O + I	3.0×10^{-11}	±0.3			
951	HO + I ₂ → HOI + I	1.8×10^{-10}	±0.3			
952	HO + CH ₃ I → H ₂ O + CH ₃ I	7.2×10^{-14}	±0.5		270–430	±500
952	HO + CF ₃ I → products	$< 4 \times 10^{-14}$		$3.1 \times 10^{-12} \exp(-1120/T)$		
953	NO ₃ + HI → HNO ₃ + I	No recommendation (see data sheet)				
953	IO + HO ₂ → HOI + O ₂	1.0×10^{-10}	±0.3			
954	IO + IO → products	5.2×10^{-11}	±0.3	$1.7 \times 10^{-12} \exp(1020/T)$	250–373	±500
954	IO + NO → I + NO ₂	2.2×10^{-11}	±0.3	$7.3 \times 10^{-12} \exp(330/T)$	200–400	±150
955	IO + NO ₂ + M → IONO ₂ + M	$7.7 \times 10^{-31} [\text{N}_2]$ (k_0)	±0.3	$7.7 \times 10^{-31} (T/300)^{-5} [\text{N}_2]$	250–350	$\Delta n = \pm 2$
		1.6×10^{-11} (k_∞)	±0.3	1.6×10^{-11}	250–350	$\Delta \log k = \pm 0.3$
		$F_c = 0.4$				
956	IO + CH ₃ SCH ₃ → products	1.2×10^{-14}	±0.5			
957	INO + INO → I ₂ + 2NO	1.3×10^{-14}	±0.4		300–450	±600
957	INO ₂ + INO ₂ → I ₂ + 2NO ₂	4.7×10^{-15}	±0.5	$8.4 \times 10^{-11} \exp(-2620/T)$	298–400	±1000
957	CH ₂ IO ₂ + CH ₂ IO ₂ → CH ₃ IOH + HCOI + O ₂ → 2CH ₂ IO + O ₂	No recommendation (see data sheet)		$2.9 \times 10^{-11} \exp(-2600/T)$		
958	HOI + $h\nu$ → products	See data sheet				
958	IO + $h\nu$ → products	See data sheet				
959	INO + $h\nu$ → products	See data sheet				
960	INO ₂ + $h\nu$ → products	See data sheet				
960	IONO ₂ + $h\nu$ → products	See data sheet				
961	CH ₃ I + $h\nu$ → products	See data sheet				
962	CF ₃ I + $h\nu$ → products	See data sheet				

*See data sheets in IUPAC (1992) [J. Phys. Chem. Ref. Data 21, 1125 (1992)].

TABLE 2. (b) Heterogeneous Reactions—Summary of Reactions.

Page Number	Reaction	
<i>Uptake Kinetics with Chemical Reaction</i>		
964	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ (including uptake studies)	See data sheets
968	$\text{N}_2\text{O}_5 + \text{HCl} \rightarrow \text{HNO}_3 + \text{NO}_2\text{Cl}$	See data sheets
969	$\text{N}_2\text{O}_5 + \text{HBr} \rightarrow \text{BrONO} + \text{HNO}_3$	See data sheets
970	$\text{N}_2\text{O}_5 + \text{NaCl} \rightarrow \text{ClONO}_2 + \text{NaNO}_3$	See data sheets
971	$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$ (including uptake studies)	See data sheets
975	$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	See data sheets
979	$\text{ClONO}_2 + \text{HBr} \rightarrow \text{BrCl} + \text{HNO}_3$	See data sheets
979	$\text{ClONO}_2 + \text{HF} \rightarrow \text{products}$	See data sheets
980	$\text{ClONO}_2 + \text{NaCl} \rightarrow \text{Cl}_2 + \text{NaNO}_3$	See data sheets
980	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	See data sheets
982	$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$	See data sheets
982	$\text{BrONO}_2 + \text{HCl} \rightarrow \text{BrCl} + \text{HNO}_3$	See data sheets
983	$\text{HBr} + \text{Cl}_2 \rightarrow \text{HCl} + \text{BrCl}$	See data sheets
983	$\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	See data sheets
983	$\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$	See data sheets
984	$\text{O}_3 + \text{Substrate (C}_{\text{am}}) \rightarrow \text{products (O}_2, \text{CO, CO}_2, \{\text{C}_{\text{am}}\text{O}\})$	See data sheets
984	$\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$	See data sheets
985	$\text{COF}_2 + \text{H}_2\text{O} \rightarrow 2\text{HF} + \text{CO}_2$	See data sheets
985	$\text{COCl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{CO}_2$	See data sheets
986	$\text{CCl}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CCl}_3\text{COOH} + \text{HCl}$	See data sheets
986	$\text{CF}_3\text{COF} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{COOH} + \text{HF}$	See data sheets
987	$\text{CF}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CF}_3\text{COOH} + \text{HCl}$	See data sheets
987	$\text{NO}_2/\text{N}_2\text{O}_4 + \text{Substrate (amorphous Carbon, NaCl)} \rightarrow \text{products}$	See data sheets
<i>Uptake Kinetics without Chemical Reaction</i>		
988	$\text{HO}_2 + \text{Substrate (SiO}_2, \text{H}_2\text{O aerosol)}$	See data sheets
989	$\text{OH} + \text{Substrate (H}_2\text{O, SiO}_2, \text{H}_2\text{SO}_4)$	See data sheets
990	$\text{H}_2\text{O} + \text{Substrate (water ice, NAT, NaCl)}$	See data sheets
991	$\text{HCl} + \text{Substrate (water ice, NAT, H}_2\text{SO}_4/\text{H}_2\text{O, NaCl)}$	See data sheets
993	$\text{HOCl} + \text{Substrate (water ice)}$	See data sheets
994	$\text{HBr} + \text{Substrate (water ice, NAT)}$	See data sheets
994	$\text{HOBr} + \text{Substrate (Pyrex, water ice, H}_2\text{SO}_4/\text{H}_2\text{O)}$	See data sheets
995	$\text{HNO}_3 + \text{Substrate (water ice, water droplets, H}_2\text{SO}_4/\text{H}_2\text{O, salt surfaces)}$	See data sheets
997	$\text{HONO} + \text{Substrate (water droplets and liquid jet)}$	See data sheets
998	$\text{NO} + \text{Substrate (water ice, 70% H}_2\text{SO}_4\text{-H}_2\text{O-ice)}$	See data sheets
999	$\text{NO}_2 + \text{Substrate (water ice and droplets, 70% H}_2\text{SO}_4\text{-H}_2\text{O-ice)}$	See data sheets
999	$\text{CH}_3\text{CO(O)NO}_2 \text{ (PAN)} + \text{Substrate (water jet)}$	See data sheets
1000	$\text{NH}_3 + \text{Substrate (liquid water jet, water droplets)}$	See data sheets
1000	$\text{O}_3 + \text{Substrate (water ice, liquid, NAT, Pyrex)}$	See data sheets
1001	$\text{Cl}_2 + \text{Substrate (water ice)}$	See data sheets
1001	$\text{ClO} + \text{Substrate (water ice, H}_2\text{SO}_4\text{-H}_2\text{O, NAT, Pyrex)}$	See data sheets
1002	$\text{Cl} + \text{Substrate (SiO}_2, \text{H}_2\text{SO}_4\text{-H}_2\text{O, Teflon)}$	See data sheets
1003	$\text{Br} + \text{Substrate (Teflon)}$	See data sheets
1003	$\text{SO}_2 + \text{Substrate (water droplets and jet)}$	See data sheets
1004	$\text{H}_2\text{O}_2 + \text{Substrate (water droplets)}$	See data sheets
1005	$\text{CH}_3\text{COCH}_3 + \text{Substrate (water droplets)}$	See data sheets
1005	$\text{H}_2\text{CO} + \text{Substrate (water droplets, H}_2\text{SO}_4/\text{H}_2\text{O solution)}$	See data sheets
1006	$\text{CH}_3\text{CHO} + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{CHBr}_3 + \text{Substrate (water ice, H}_2\text{SO}_4)$	See data sheets
1006	$\text{CH}_3\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{C}_2\text{H}_5\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$1\text{-C}_3\text{H}_7\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$2\text{-C}_3\text{H}_7\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{CH}_3\text{C(CH}_3\text{)(OH)CH}_3 + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{ClCH}_2\text{CH}_2\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{BrCH}_2\text{CH}_2\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{ICH}_2\text{CH}_2\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1006	$\text{HOCH}_2\text{CH}_2\text{OH} + \text{Substrate (water droplets)}$	See data sheets
1007	$\text{HCOOH} + \text{Substrate (water droplets)}$	See data sheets
1007	$\text{CH}_3\text{COOH} + \text{Substrate (water droplets)}$	See data sheets
1008	$\text{CCl}_3\text{COOH} + \text{Substrate (water droplets)}$	See data sheets
1008	$\text{CCl}_2\text{HCOOH} + \text{Substrate (water droplets)}$	See data sheets
1008	$\text{CClH}_2\text{COOH} + \text{Substrate (water droplets)}$	See data sheets
1008	$\text{CF}_2\text{ClCOOH} + \text{Substrate (water droplets)}$	See data sheets
1008	$\text{CF}_3\text{COOH} + \text{Substrate (water droplets)}$	See data sheets

3. Guide to the Data Sheets

3.1. Gas-Phase Reactions

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions. We also include a few composite data sheets consisting of a group of analogous reactions usually studied by a common technique.

3.1.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in Appendix 1.

The available kinetic data on the reactions are summarized under three headings: (i) absolute rate coefficients, (ii) relative rate coefficients, and (iii) reviews and evaluations. Under headings (i) and (ii), we list new data which have been published since the last IUPAC evaluation.⁵ Under heading (iii) are listed the preferred rate data from the most recently published NASA evaluation available at the date of submission of this evaluation and our own IUPAC evaluations, together with data from any new review or evaluation source. Under all three of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated range of temperatures. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A \exp(-B/T)$, where $B = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^{-n}$ or $CT^n \exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of the Introduction.

Single temperature data are presented as such and whenever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used mainly in the comments section:

EPR - electron paramagnetic resonance
 FTIR - Fourier transform infrared
 GC - gas chromatography/gas chromatographic
 HPLC - high performance liquid chromatography
 IR - infrared
 LIF - laser induced fluorescence

LMR - laser magnetic resonance
 MS - mass spectrometry/mass spectrometric
 UV - ultraviolet

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated range of temperatures.

This is followed by a statement of the error limits in log k at 298 K and the error limits either in (E/R) or in n , for the mean temperature in the range. Some comments on the assignment of errors are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.1.2. Conventions Concerning Rate Coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.,

Note that the stoichiometric coefficient for A, i.e., 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[\text{A}]^2$) and as a power on the right-hand side.

3.1.3. Treatment of Combination and Dissociation Reactions

The rates of combination and the reverse dissociation reactions

depend on the temperature T , and the nature and concentration of the third body [M]. The rate coefficients of these reactions have to be expressed in a form which is more complicated than those for simple bimolecular reactions. The combination reactions are described by a pseudo second-order rate law

$$\frac{d[\text{AB}]}{dt} = k[\text{A}][\text{B}]$$

in which the second-order rate coefficient depends on [M]. The low-pressure third-order limit is characterized by k_0 ,

$$k_0 = \lim_{[M] \rightarrow 0} k([M])$$

which is proportional to $[M]$. The high-pressure second-order limit is characterized by k_∞ ,

$$k_\infty = \lim_{[M] \rightarrow \infty} k([M])$$

which is independent of $[M]$. For a combination reaction in the low-pressure range, the summary table gives a second-order rate coefficient expressed as the product of a third-order rate coefficient and the third body concentration which is expressed in molecule cm^{-3} . The transition between the third-order and the second-order range is represented by a reduced falloff expression of k_0/k_∞ as a function of

$$k_0/k_\infty = [M]/[M]_c,$$

where the "center of the falloff curve" $[M]_c$ indicates the third-body concentration for which the extrapolated k_0 would be equal to k_∞ . The dependence of k on $[M]$ in general is complicated and has to be analyzed by unimolecular rate theory. For moderately complex molecules at not too high temperatures, however, a simple approximate relationship holds:

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \frac{1}{1 + k_0/k_\infty} F = k_\infty \frac{k_0/k_\infty}{1 + k_0/k_\infty} F,$$

where the first factors at the right-hand side represent the Lindemann-Hinshelwood expression, and the additional broadening factor F , at not too high temperature, is approximately given by⁶⁻⁸

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)]^2}.$$

With increasing temperature, a better representation is obtained⁶⁻⁸ by replacing $[\log(k_0/k_\infty)]^2$ by $[\log(k_0/k_\infty)/N]^2$ with $N = \{0.75 - 1.27 \log F_c\}$. In this way the three quantities k_0 , k_∞ , and F_c characterize the falloff curve for the present application.

Alternatively, the three quantities k_∞ , $[M]_c$, and F_c (or k_0 , $[M]_c$, and F_c) can be used. The temperature dependence of F_c , which is sometimes significant, can be estimated by the procedure of Troe.⁷⁻⁹ The results can usually be represented⁹ approximately by an equation

$$F_c = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^*) + \exp(-T^*/T).$$

Whereas the two first terms are of importance for atmospheric conditions, the last term in most cases becomes relevant only at much higher temperatures. In Ref. 2, for simplicity $a=1$ and $T^{**}=4T^*$ was adopted. Often $F_c = \exp(-T/T^*)$ is sufficient for low temperature conditions. With molecules of increasing complexity, additional broadening of the falloff curves may have to be taken into account.⁷⁻⁹ For simplicity these effects are neglected in the present evalua-

tion. An even simpler policy was chosen in Ref. 6 where a temperature independent standard value of $F_c=0.6$ was adopted.

Changes in F_c would require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this will be irrelevant in most cases, if the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected value of F_c is too large, the values of k_0 and k_∞ , obtained by fitting the falloff expression to the experimental data, are underestimated.

Theoretical predictions of F_c have been derived from rigid RRKM-type models including weak collision effects.⁷⁻⁹

The dependence of k_0 and k_∞ on the temperature T is represented in the form:

$$k \propto T^{-n}$$

(except for the cases with an established energy barrier in the potential). We have used this form of temperature dependence because it often gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. The dependence of k_0 on the nature of the third-body M generally is represented by the relative efficiencies of M_1 and M_2 .

$$k_0(M_1)/[M_1]:k_0(M_2)/[M_2]$$

The few thermal dissociation reactions of interest in the present application are treated by analogy with combination reactions, with pseudo-first-order rate coefficients $k([M])$. The limiting low- and high-pressure rate coefficients expressed in units of s^{-1} are denoted in the tables by the symbols (k_0/s^{-1}) and (k_∞/s^{-1}) . F_c is the same in combination and dissociation reactions.

3.1.4. Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in Appendix 1. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true "threshold values."

This is followed by tables summarizing the available experimental data on (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1, 5, or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer-Wieland type expressions.¹⁰

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

In this evaluation we have provided data sheets for all of the photochemical reactions listed in the Summary Table and not just those for which new data have become available since our last evaluation.

3.1.5. Conventions Concerning Absorption Cross-Sections

These are presented in the data sheets as "absorption cross-sections per molecule, base e." They are defined according to the equations

$$I/I_0 = \exp(-\sigma[N]l),$$

$$\sigma = \{1/([N]l)\} \ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), $[N]$ is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition; it is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Napierian (base e) absorption coefficient of a gas at a pressure of one standard atmosphere and temperature of 273 K (expressed in cm^{-1}), multiply the value of σ in cm^2 by 2.69×10^{19} .

3.1.6. Assignment of Errors

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F , where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298) + 0.4343 \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

(note that the exponent in this equation is an absolute value).

The assignment of these absolute error limits in k and E/R is a subjective assessment of the evaluators. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e., the reproducibility, is usually good. Thus, for single

studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of $\pm 10\%$ or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic errors which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of errors made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations made and the number of different techniques used. On the whole, our assessment of error limits errs towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum error limits of a factor of 2 are appropriate.

In contrast with the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparent reliable data. Thus, we do not feel justified at present in assigning error limits to the parameters reported for the photochemical reactions.

3.2. Heterogeneous Reactions

The data sheets contain six columns listing (i) the type of uptake coefficient which has been measured, (ii) the value of the reported uptake coefficient with the observed error limits, (iii) the nature of the condensed phase with specific experimental conditions where appropriate, (iv) the temperature of the experiments, (v) the literature reference, and (vi) the reference to the **Comments** on the experimental techniques.

The Comments are written to enable the reader to obtain an impression of the experimental variables of the complex kinetic systems in question. These brief experimental descriptions are also intended to facilitate the comparison of results obtained using different kinetic techniques.

Where possible under the heading **Preferred Values** is given a summary of the conclusions we have reached regarding the values of the uptake coefficients for any given reaction.

In reviewing the literature on heterogeneous reactions relevant to atmospheric chemistry, we have disregarded some early work which is not in line with more recent findings as well as early work involving the same techniques on reactions for which no recent data are available.

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4. Gas-Phase Reactions—Data Sheets

4.1. Oxygen Species

$$\Delta H^\circ = -106.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 5.6 \times 10^{-34} (T/300)^{-2.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 100–300 K.

$k_0 = 6.0 \times 10^{-34} (T/300)^{-2.8} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 100–300 K.

Reliability

$$\Delta \log k_0 = \pm 0.05 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The results from Ref. 1, obtained over extended temperature ranges, confirm the large negative values of n and also confirm earlier absolute values of k_0 at 298 K. The value of n is probably similar for N_2 and O_2 , as for the reaction $\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$ also studied at low temperatures

(see this evaluation), and governed by a radical-complex mechanism. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

Comments on High-pressure Rate Coefficients and Falloff Range

The experiments from Ref. 1 under low temperature and high pressure conditions indicate anomalous falloff behavior different from the formalism described in the Introduction. These effects are not relevant for atmospheric conditions such that they are not included in this evaluation.

References

¹H. Hippler, R. Rahn, and J. Troe, *J. Chem. Phys.* **93**, 6560 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -391.9 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 8.0 \times 10^{-12} \exp(-2060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$$\Delta \log k = \pm 0.08 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The study of Wine *et al.*¹ yields values of k in close agreement with those from other studies over the whole temperature range covered. Our recommendations are based on the least-squares expression obtained by Wine *et al.*¹ from a fit

of their own data plus those of McCrumb and Kaufman,² Davis *et al.*,³ West *et al.*⁴ and Arnold and Comes.⁵ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

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⁵I. Arnold and F. J. Comes, *Chem. Phys.* **42**, 231 (1979).

⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -32.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -95.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

No new data have been published since our last evaluation.

Preferred Values

$$k = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.2 \times 10^{-11} \exp(67/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}350 \text{ K.}$$

$$k_1/k = 0.8 \text{ at } 298 \text{ K.}$$

$$k_2/k \leq 0.05 \text{ at } 298 \text{ K.}$$

Lambert-Beer law used for the $\text{O}(^1\text{D})$ absorption results was too small. The preferred 298 K rate coefficient is the average of the results from Amimoto *et al.*,² Brock and Watson,³ Lee and Slanger,⁴ and Streit *et al.*⁵ The branching ratios of Lee and Slanger⁴ and Gauthier and Snelling⁶ are recommended. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁷

Reliability

$$\Delta \log k = \pm 0.05 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

$$\Delta \log(k_1/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.¹ The earlier controversy between measurements using $\text{O}(^1\text{D})$ emission at 630 nm and absorption at 115 nm now appears to be resolved, since $\text{O}(^3\text{P})$ atom detection by absorption at 130 nm and fluorescence support the $\text{O}(^1\text{D})$ emission results. Apparently the γ -value in the

References

¹CODATA, Supplement I, 1982 (see references in Introduction).

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⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -83.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -393.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(4) = -424.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(5) = -581.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 100\text{--}400 \text{ K.}$$

$$k_1/k = k_5/k = 0.5 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.05 \text{ over the temperature range } 100\text{--}400 \text{ K.}$$

$$\Delta \log k_1/k = \Delta \log k_5/k = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1984.¹ The measurement of the rate coefficient k at 298 K by Greenblatt and Wiesenfeld² is in excellent agreement with our earlier recommendation.³ The determination of k_1/k_5 by Cobos *et al.*⁴ is rather indirect, but provides further evidence that $k_1 \approx k_5$. Our previous recommendations^{1,3,5} are unchanged.

References

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- ²G. D. Greenblatt and J. R. Wiesenfeld, *J. Chem. Phys.* **78**, 4924 (1983).
- ³CODATA, Supplement I, 1982 (see references in Introduction).
- ⁴C. Cobos, E. Castellano, and H. J. Schumacher, *J. Photochem.* **21**, 291 (1983).
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Comments

These comments are reproduced from our previous evaluation, IUPAC, 1992.¹ Arnold and Comes^{2,3} have studied this reaction of vibrationally excited oxygen molecules in the ground electronic state with ozone and they report a rate coefficient of $2.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The vibrationally excited oxygen molecules were produced in the reaction of $\text{O}(^1\text{D})$ atoms with O_3 following the UV photolysis of ozone. This is the only reported study of this rate

coefficient, and we make no recommendation. For further discussion the reader is referred to the review by Steinfeld *et al.*⁴

References

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M	ν	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>					
$(4.7 \pm 0.3) \times 10^{-15}$	O_2	19	295	Price <i>et al.</i> , 1993 ¹	(a)
$(3.2 \pm 0.3) \times 10^{-15}$		20			
$(5.8 \pm 1.2) \times 10^{-15}$		21			
$(5.4 \pm 0.8) \times 10^{-14}$		22			
$(1.2 \pm 0.4) \times 10^{-14}$		23			
$(0.84 \pm 0.04) \times 10^{-14}$	O_2	24	460		
$(1.8 \pm 0.05) \times 10^{-14}$		25			
$(4.7 \pm 0.2) \times 10^{-14}$		26			
$(2.3 \pm 0.1) \times 10^{-14}$		19			
$(3.1 \pm 0.08) \times 10^{-14}$		20			
$(2.2 \pm 0.9) \times 10^{-14}$		21			
$(3.7 \pm 0.3) \times 10^{-14}$		22			
$(4.1 \pm 0.6) \times 10^{-14}$		23			
$(6.9 \pm 0.5) \times 10^{-14}$		24			
$(11.7 \pm 0.2) \times 10^{-14}$		25			
$(16.4 \pm 2) \times 10^{-14}$	O_2	26	300	Park and Slinger, 1994 ²	(b)
$> 8.3 \times 10^{-14}$		27			
$> 1.2 \times 10^{-11}$		28			
6.5×10^{-14}	O_2	8			
$> 1.3 \times 10^{-13}$	He	22			
$(1.53 \pm 0.25) \times 10^{-11}$	O_3	22			
2×10^{-13}	CO_2	14			
9×10^{-14}		22			

Comments

- (a) Vibrationally highly excited electronic ground state O_2 molecules were generated by stimulated emission pumping, and detected by LIF.
- (b) Vibrationally highly excited electronic ground state

O_2 molecules were formed by ozone photodissociation at 248 nm (Hartley band). The excited molecules were detected by LIF. Rate coefficients were evaluated using a cascade model, in which relaxation through single-quantum V-V and V-T steps was assumed.

Preferred Values

See table.

Reliability

$$\Delta \log k = \pm 0.5.$$

Comments on Preferred Values

The results given from Ref. 1 and more results presented in graphical form from Ref. 2 appear consistent with each other.

References

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²H. Park and T. G. Slanger, J. Chem. Phys. **100**, 287 (1994).

$$\Delta H^\circ = -94.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate Coefficient Data

No new data have been published since our last evaluation.

Preferred Values

$$\begin{aligned} k &= 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M}=\text{O}_2 \text{ at } 298 \text{ K.} \\ k &= 3.0 \times 10^{-18} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M} \\ &= \text{O}_2 \text{ over the temperature range } 100\text{--}450 \text{ K.} \\ k &\leq 1.4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M}=\text{N}_2 \text{ at } 298 \text{ K.} \\ k &= 5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M}=\text{H}_2\text{O} \text{ at } 298 \text{ K.} \\ k &\leq 2 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{M}=\text{CO}_2 \text{ at } 298 \text{ K.} \end{aligned}$$

Reliability

$$\begin{aligned} \Delta \log k &= \pm 0.2 \text{ for } \text{M}=\text{O}_2 \text{ at } 298 \text{ K.} \\ \Delta(E/R) &= \pm 200 \text{ K for } \text{M}=\text{O}_2. \\ \Delta \log k &= \pm 0.3 \text{ for } \text{M}=\text{H}_2\text{O} \text{ at } 298 \text{ K.} \end{aligned}$$

Comments on Preferred Values

The preferred value of $k(\text{M}=\text{O}_2)$ is based on the results of Raja *et al.*,¹ Billington and Borrell,² Borrell *et al.*³ and Leiss

*et al.*⁴ The temperature dependence of Billington and Borrell² is adopted in this evaluation. The previous CODATA recommendations⁵ for $\text{M}=\text{N}_2$, H_2O and CO_2 are unchanged. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

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⁵CODATA, Supplement II, 1984 (see references in Introduction).
⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 12.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

No new data have been published since our last evaluation.

Preferred Values

$$\begin{aligned} k &= 3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.} \\ k &= 5.2 \times 10^{-11} \exp(-2840/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the} \\ &\text{temperature range } 280\text{--}360 \text{ K.} \end{aligned}$$

Reliability

$$\begin{aligned} \Delta \log k &= \pm 0.10 \text{ at } 298 \text{ K.} \\ \Delta(E/R) &= \pm 500 \text{ K.} \end{aligned}$$

Comments on Preferred Values

Whereas there is good agreement on the room temperature value, the temperature coefficient appears less certain. In view of the consistency of the results from Ref. 1, which were obtained by two completely different techniques, we favor their temperature coefficient over that from Ref. 2. The preferred values of our previous evaluation are unchanged.³

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$$\Delta H^\circ(1) = -156.9 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -62.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	M	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>				
5.6×10^{-17}	O ₂	302	Knickelbein <i>et al.</i> , 1987 ¹	(a)
$< 1.0 \times 10^{-16}$	O ₂	298	Shi and Barker, 1990 ²	(b)
$(2.2 \pm 0.2) \times 10^{-15}$	N ₂	298	Wildt <i>et al.</i> , 1988 ³	(c)
$(2.32 \pm 0.14) \times 10^{-15}$	N ₂	298	Shi and Barker, 1990 ²	(b)
$(6.0 \pm 0.3) \times 10^{-12}$	H ₂ O	298	Shi and Barker, 1990 ²	(b)
$(2.4 \pm 0.4) \times 10^{-13}$	CO ₂	298	Wildt <i>et al.</i> , 1988 ³	(c)
$(4.0 \pm 0.1) \times 10^{-13}$	CO ₂	298	Shi and Barker, 1990 ²	(b)
<i>Reviews and Evaluations</i>				
4.0×10^{-17}	O ₂	298	IUPAC, 1989 ⁴	(d)
2.0×10^{-15}	N ₂	200–350		(e)
8.0×10^{-14}	O(³ P)	298		(f)
4.0×10^{-12}	H ₂ O	298		(g)
4.1×10^{-13}	CO ₂	245–360		(h)
3.9×10^{-17}	O ₂	298	NASA, 1994 ⁵	(i)
2.1×10^{-15}	N ₂	200–300		(j)
8×10^{-14}	O(³ P)	298		(k)
5.4×10^{-12}	H ₂ O	298		(l)
4.2×10^{-13}	CO ₂	200–300		(m)

Comments

- (a) O₂(¹Σ_g⁺) was generated by excitation of O₂ with a tunable alexandrite laser at 760 nm, and detected by measuring the fluorescence emission at 860 nm.
 (b) O₂(¹Σ_g⁺) was generated by the reaction O(¹D) + O₂ → O + O₂(¹Σ_g⁺), with O(¹D) atoms being formed by photolysis of O₃/O₂ mixtures at 308 nm. Rate coefficients were measured by detecting the decay of O₂(¹Σ_g⁺) at 762 nm.
 (c) O₂(¹Σ_g⁺) was formed by direct laser excitation of O₂ at 600–800 nm, and detected by fluorescence at 600–900 nm and 1270 nm.
 (d) Based on the data of Thomas and Thrush,⁶ Martin *et al.*,⁷ Lawton *et al.*,⁸ and Chatha *et al.*⁹
 (e) Based on the data of Kohse-Höinghaus and Stuhl,¹⁰ Martin *et al.*,⁷ Chatha *et al.*,⁹ and Choo and Leu.¹¹
 (f) Value of Slanger and Black.¹²
 (g) Value of Thomas and Thrush.⁶
 (h) Based on the results of Choo and Leu,¹¹ Filseth

et al.,¹³ Noxon,¹⁴ Davidson *et al.*,¹⁵ Avilés *et al.*,¹⁶ Muller and Houston,¹⁷ Borrell *et al.*,¹⁸ and Boodaghians *et al.*¹⁹

- (i) Based on the data of Martin *et al.*,⁷ Lawton *et al.*,⁸ and Lawton and Phelps.²⁰
 (j) Based on the data of Izod and Wayne,²¹ Stuhl and Welge,²² Filseth *et al.*,¹³ Martin *et al.*,⁷ Kohse-Höinghaus and Stuhl,¹⁰ Choo and Leu,¹¹ Wildt *et al.*,³ and Shi and Barker.²
 (k) Based on the data of Slanger and Black.¹²
 (l) Based on the data of Stuhl and Niki,²³ Filseth *et al.*,¹³ Wildt *et al.*,³ and Shi and Barker.²
 (m) Based on the data of Filseth *et al.*,¹³ Davidson *et al.*,¹⁵ Avilés *et al.*,¹⁶ Muller and Houston,¹⁷ Choo and Leu,¹¹ Wildt *et al.*,³ and Shi and Barker.²

Preferred Values

$k = 4.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for M=O₂ at 298 K.

$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for M=N₂ over the temperature range 200–350 K.

$k=8.0\times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ for M=O(³P) at 298 K.
 $k=4.0\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ for M=H₂O at 298 K.
 $k=4.1\times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ for M=CO₂ over the temperature range 245–360 K.

Reliability

$\Delta \log k = \pm 0.3$ for M=O₂, O(³P), H₂O at 298 K.
 $\Delta \log k = \pm 0.10$ for M=N₂, CO₂ at 298 K.
 $\Delta(E/R) = \pm 200$ K for M=N₂, CO₂.

Comments on Preferred Values

The results of the recent studies of Knickelbein *et al.*,¹ Shi and Barker,² and Wildt *et al.*³ are in generally good agreement with those of our earlier evaluation.⁴ Thus, no changes are recommended. However, it has to be noted that Wildt *et al.*³ and Knickelbein *et al.*¹ report yields of O₂(¹Δ_g) formation, k_2/k , which are greater than 0.9 and close to unity, respectively.

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²²F. Stuhl and K. H. Welge, *Can. J. Chem.* **47**, 1870 (1969).
²³F. Stuhl and H. Niki, *Chem. Phys. Lett.* **7**, 473 (1970).

$$\Delta H^\circ(1) = -50.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -62.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -156.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.96 \pm 0.09) \times 10^{-11}$	300	Shi and Barker, 1990 ¹	(a)
$(2.06 \pm 0.22) \times 10^{-11}$	300	Turnipseed <i>et al.</i> , 1991 ²	(b)
<i>Reviews and Evaluations</i>			
2.2×10^{-11}	295–360	IUPAC, 1989 ³	(c)
$k_1 = 1.5 \times 10^{-11}$	298		
2.2×10^{-11}	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) O₂(¹Σ_g⁺) was generated by the reaction O(¹D) + O₂ → O + O₂(¹Σ_g⁺), with O(¹D) being formed by photolysis of O₃/O₂ mixtures at 308 nm. Rate coefficients were measured by detecting the decay of O₂(¹Σ_g⁺) at 762 nm.
 (b) Laser flash photolysis study of O₃ at 193 and 222 nm. Measurements of quantum yields for the formation of O(¹D) and O(³P) were by time-resolved resonance

fluorescence. Rate coefficients for the global reaction of O₂(¹Σ_g⁺) with O₃ were derived by modeling.

- (c) Based on the rate coefficients reported in Refs. 5–10.
 (d) Based on the data of Refs. 1, 2, and 5–10.

Preferred Values

$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 295–360 K.

$k_1 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta \log k_1 = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The two more recent studies^{1,2} are in very good agreement with the previous evaluations^{3,11,12} at room temperature. The preferred values from our earlier evaluations remain unchanged.^{3,11,12} Channel 1 accounts for $70 \pm 20\%$ of the total reaction.^{7,8}

References

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O₂ + $h\nu$ → products

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{O}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P})$	494	242
$\rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{D})$	683	175
$\rightarrow \text{O}(^1\text{D}) + \text{O}(^1\text{D})$	873	137
$\rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{S})$	898	132

Absorption cross-section data

Wavelength range/nm	Reference	Comment
180–195	Yoshino <i>et al.</i> , 1992 ¹	(a)

Comments

(a) Absorption cross-sections of the Schumann-Runge bands (1,0)-(12,0) in the window region between the rotational lines were measured over the pressure range 1.8–1000 mbar O₂, allowing the pressure-dependent absorption to be separated from the main cross-sections. The resulting Herzberg continuum sections below 200 nm are significantly smaller than any previous measurements.

Preferred Values

Absorption cross-section of O₂ in the 205–240 nm region of the Herzberg continuum

λ/nm	$10^{24}\sigma/\text{cm}^2$	λ/nm	$10^{24}\sigma/\text{cm}^2$
205	7.35	223	3.89
207	7.05	225	3.45
209	6.68	227	2.98
211	6.24	229	2.63
213	5.89	231	2.25
215	5.59	233	1.94
217	5.13	235	1.63
219	4.64	237	1.34
221	4.26	239	1.10
		240	1.01

Comments on Preferred Values

The recommended absorption cross-section values for the Herzberg continuum are taken from the study of Yoshino *et al.*,² where values are tabulated for every nm from 205–240 nm. These values were derived from an analysis and combination of the data of Cheung *et al.*³ and Jenouvrier *et al.*⁴ They are in agreement with the results of Johnston *et al.*⁵ They are consistent with the lower absorption cross-section values inferred from balloon-borne measurements of solar irradiance attenuation in the stratosphere by Frederick and Mentall,⁶ Herman and Mentall,⁷ and Anderson and Hall.⁸ Herzberg continuum cross-section values under the S-R bands (<200 nm) have recently been determined more accurately by Yoshino *et al.*¹ and are significantly smaller than any previous values.

In the Schumann-Runge wavelength region (175–200 nm), a detailed analysis of the penetration of solar radiation requires absorption cross-section measurements with very high spectral resolution. Absorption cross-section values for the (0, 0)-(12, 0) S-R bands measured by the Harvard-Smithsonian group^{1,9–17} are the first set of values which are independent of instrumental width. Band oscillator strengths for these bands have been determined by direct numerical integration of these absolute cross-section values. Minschwaner *et al.*^{18,19} have fitted O₂ cross-sections for the frequency range 49000–57000 cm⁻¹ (175–204 nm) with temperature dependent polynomial expressions for 130–500 K using the latest laboratory spectroscopic data. This model provides an efficient and accurate means of determining S-R band absorption cross-sections at 0.5 cm⁻¹ resolution. These high resolution calculated values differ from the WMO²⁰ recommendations by up to 10–20% at some wavelengths. Mean-band parameterizations of O₂ absorption in the S-R bands for calculating UV transmission and photolysis rates have been presented by Murtagh²¹ and by Nicolet and Kennes.²²

The effect on ozone formation in the 214 nm photolysis of oxygen due to O₂-O₂ collision pairs at high O₂ pressure and the effect of high N₂ pressure have been studied by Horowitz *et al.*²³ Greenblatt *et al.*²⁴ studied the absorption spectrum of O₂ and O₂-O₂ collision pairs over the wavelength range 330

–1140 nm for O₂ pressures from 1 to 55 bar at 298 K. Band centers, band widths, and absorption cross-sections were reported for the absorption features in this wavelength region.

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O₃ + *hν* → products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
O ₃ + <i>hν</i> → O(³ P) + O ₂ (³ Σ _g) (1)	101	1180
→ O(³ P) + O ₂ (¹ Δ _g) (2)	196	611
→ O(³ P) + O ₂ (¹ Σ _g ⁺) (3)	258	463
→ O(¹ D) + O ₂ (³ Σ _g) (4)	291	411
→ O(¹ D) + O ₂ (¹ Δ _g) (5)	386	310
→ O(¹ D) + O ₂ (¹ Σ _g ⁺) (6)	448	267

Absorption cross-section data

Wavelength range/nm	Reference	Comment
195–345	Daumont <i>et al.</i> , 1992 ¹	(a)
195–345	Brion <i>et al.</i> , 1993 ²	(b)
185–254	Yoshino <i>et al.</i> , 1993 ³	(c)
410–760	Burkholder and Talukdar, 1994 ⁴	(d)

Quantum yield data

Measurement	λ /nm	Reference	Comment
ϕ [O(¹ D)]	222	Turnipseed <i>et al.</i> , 1991 ⁵	(e)
ϕ [O(¹ D)]	221–243.5	Cooper, Neill and Wiesenfeld, 1993 ⁶	(f)
ϕ [O ₂ (¹ Δ)]	270–329	Ball <i>et al.</i> , 1993 ^c	(g)
ϕ [O(¹ D)]	305–325	Michelsen <i>et al.</i> , 1991 ⁸	(h)

Comments

- (a) Measured at 295 K with a spectral resolution of 0.005 nm. Two independent methods were used to measure the ozone pressure.
- (b) Extension of study reported in Daumont *et al.*¹ to low temperatures, 220–295 K.
- (c) Measured at 195, 228, and 295 K. Relative cross-sections measured over the range 185–254 nm were normalized using absolute values measured at 12 fixed wavelengths in this region.
- (d) Relative values measured at 220–298 K were normalized using absolute values reported by Anderson and Mauersberger⁹ for five He-Ne laser wavelengths.
- (e) Laser photolysis with time-resolved resonance fluorescence detection of O(³P). At 222 nm ϕ [O(³P)]=0.13 ± 0.02 and ϕ [O(¹D)]=0.87 ± 0.04. Results were also reported for 193 nm.
- (f) Tunable dye laser photolysis with detection of O(¹D) by the weak 630 nm fluorescence from the spin-forbidden ¹D → ³P transition. Relative O(¹D) quantum yields were normalized to the value of 0.87 ± 0.04 at 222 nm reported by Turnipseed *et al.*⁵
- (g) Relative O₂(¹Δ) quantum yields in the tunable dye laser photolysis of ozone were determined by [2+1] resonance enhanced multiphoton ionization (REMPI). The quantum yield agrees with that recommended for O(¹D), except at the longer wavelengths where O₂(¹Δ) is still produced with a yield of ≥ 0.10.
- (h) Authors developed a model accounting for absorption by vibrationally and rotationally excited ozone and, using this model to examine published measurements of the quantum yield of O(¹D) production in the Huggins band, concluded that ϕ [O(¹D)] has a value of 0.2–0.3 for wavelengths between 312 and 320 nm at 298 K.

Preferred Values

Ozone absorption cross-sections at 273 K averaged over spectral internals

Int #	$\Delta\lambda$ /nm	$10^{20}\sigma/\text{cm}^2$	Int #	$\Delta\lambda$ /nm	$10^{20}\sigma/\text{cm}^2$
1	175.4–177.0	81.1	31	238.1–241.0	797
2	178.6	79.9	32	243.9	900
3	180.2	78.6	33	246.9	1000
4	181.8	76.3	34	250.1	1080
5	183.5	72.9	35	253.2	1130
6	185.2	68.8	36	256.4	1150
7	186.9	62.2	37	259.7	1120
8	188.7	57.6	38	263.2	1060
9	190.5	52.6	39	266.7	965
10	192.3	47.6	40	270.3	834
11	194.2	42.8	41	274.0	692
12	196.1	38.3	42	277.8	542
13	198.0	34.7	43	281.7	402
14	200.0	32.3	44	285.7	277
15	202.0	31.4	45	289.9	179
16	204.1	32.6	46	294.1	109
17	206.2	36.4	47	298.5	62.4
18	208.3	43.4	48	303.0	34.3
19	210.5	54.2	49	307.7	18.5
20	212.8	69.9	50	312.5	9.8
21	215.0	92	51	317.5	5.0
22	217.4	119	52	322.5	2.49
23	219.8	155	53	327.5	1.20
24	222.2	199	54	332.5	0.617
25	224.7	256	55	337.5	0.274
26	227.3	323	56	342.5	0.117
27	229.9	400	57	347.5	0.059
28	232.6	483	58	352.5	0.027
29	235.3	579	59	357.5	0.011
30	238.1	686	60	362.5	0.005

$$\sigma = (1147 \pm 20) \times 10^{-20} \text{ cm}^2 \text{ at } 253.7 \text{ nm}$$

Ozone absorption cross-sections in the visible spectral region

λ/nm	$10^{23} \sigma/\text{cm}^2$	λ/nm	$10^{23} \sigma/\text{cm}^2$
410	1.2	560	394
420	2.2	580	459
440	11.2	600	511
460	32.8	620	400
480	68.4	640	296
500	122	660	209
520	182	680	136
540	291	700	91

Quantum yields for $\text{O}(^1\text{D})$ production, ϕ_5 , from O_3 photolysis at 298 K

λ/nm	Quantum yield
290	$\phi_5=0.95$
295	0.95
300	0.95
305	0.95
306	0.93
307	0.89
308	0.81
309	0.68
310	0.53
311	0.38
312	0.25
313	0.14
314	0.08
315	0.05
316	0.03
317	0.02
318	0.01
319	0.00
320	0.00

Comments on Preferred Values

Absorption cross-sections. The recommended absorption cross-section values at 273 K for the wavelength range 175–362 nm are averaged values for the standard spectral intervals used in modeling calculations. These values have been adopted from the NASA 1994 review,¹⁰ which accepted the values tabulated in the WMO 1986 review,¹¹ except for the region 185–225 nm where the values were taken from the study of Molina and Molina.¹² The value recommended for the mercury line at 253.7 nm is based on results reported by Hearn,¹³ Molina and Molina¹² and Mauersberger *et al.*¹⁴ The

values for the wavelength range 400–700 nm are taken from Burkholder and Talukdar.⁴ The spectroscopy of ozone has been reviewed by Steinfeld, Adler-Golden and Gallagher.¹⁵

Quantum yields

The quantum yield values for 305–320 nm and 298 K have been calculated from the expression for $\phi_5(\lambda, T)$ given in the NASA 1994 review.¹⁰ That expression is based on the high resolution laser data of Arnold *et al.*,¹⁶ Brock and Watson¹⁷ and Trolier and Wiesenfeld.¹⁸ The temperature dependence is based on the xenon arc lamp-monochromator results reported in Moortgat and Kudzus.¹⁹ An extensive discussion of quantum yield data for this region and extending down to 220 nm is given in the NASA 1994 review,¹⁰ to which the reader is referred. There it is noted that for the wavelength region 220–280 nm the more recent studies yield ϕ_5 values around 0.85–0.90, and that for the region 290–305 nm the value $\phi_5=0.95$ is recommended.¹⁰

References

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4.2. Hydrogen Species

$$\Delta H^\circ(1) = -232.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -154.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -225.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 245–300 K.

$k_1 = 5.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 245–300 K.

$k_2 = 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 245–300 K.

$k_3 = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 245–300 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 245–300 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

$\Delta \log k_1 = \pm 0.5$ over the temperature range 245–300 K.

$\Delta \log k_2 = \pm 0.1$ over the temperature range 245–300 K.

$\Delta \log k_3 = \pm 0.5$ over the temperature range 245–300 K.

Comments on Preferred Values

The study of Keyser¹ is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with the values obtained by Sridharan *et al.*² who used a similar technique. The recommended values for k and the branching ratios are the means of the values from these two studies. In

both cases k_1/k was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

The yield of $\text{O}_2(^1\Sigma_g^+)$ has been measured by Hislop and Wayne,³ Keyser *et al.*,⁴ and Michelangeli *et al.*⁵ who report values of $(2.8 \pm 1.3) \times 10^{-4}$, $< 8 \times 10^{-3}$ and $< 2.1 \times 10^{-2}$, respectively. Keyser¹ observed no effect of temperature on the rate coefficient k over the small range studied. This suggests that the value of $k_2 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 349 K obtained by Pagsberg *et al.*⁶ is too low or there is a substantial negative temperature coefficient. We provisionally recommend $E/R = 0$ but only over the temperature range 245–300 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁷

References

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$$\Delta H^\circ = -203.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients**Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.2) \times 10^{-32} [\text{Ar}]$	298	Carleton, Kessler, and Marinelli, 1993 ¹	(a)
$2.9 \times 10^{-33} \exp[(825 \pm 130)/T][\text{N}_2]$	298–580		
$3.9 \times 10^{-32} \exp[(600 \pm 1050)/T][\text{H}_2\text{O}]$	575–750		
<i>Reviews and Evaluations</i>			
$6.2 \times 10^{-32} (T/300)^{-1.6} [\text{N}_2]$	200–600	IUPAC, 1992 ²	(b)
$5.7 \times 10^{-32} (T/300)^{-1.6} [\text{air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Flash photolysis study. H atoms were generated by the 193 nm photolysis of H₂O and H₂S in excess O₂, and probed by LIF (M=H₂O) or Lyman- α resonance absorption at 121.6 nm (M=Ar, N₂). Typical pressures were varied between 50–500 Torr.
- (b) Based on the study by Hsu *et al.*,⁴ which is in excellent agreement with previous data from Refs. 5–8.
- (c) The recommended value was an average of the measurements from Refs. 4–6.

Reliability

$$\Delta \log k_0 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.6.$$

Comments on Preferred Values

We have slightly modified our previous preferred values to account for the recent measurements from Carleton *et al.*¹ These new data and previous measurements from Refs. 4–8 are in good agreement.

Preferred Values

$$k_0 = 5.4 \times 10^{-32} (T/300)^{-1.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}600 \text{ K.}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.6.$$

Comments on Preferred Values

Measurements in M=Ar, N₂, and CH₄ all extrapolate to the same limiting high pressure value. The results are from a single study.⁷ The preferred values of k_∞ are identical to our previous evaluation, IUPAC, 1992.²

Intermediate Falloff Range

The measured broadening factor $F_c = 0.55 \pm 0.15$ at 298 K for M=N₂ from Ref. 7 is in agreement with a calculated value of $F_c = 0.66$. Representation of the measured F_c by $F_c = \exp(-T/T^*)$ gives $T^* = 498 \text{ K}$.

References

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$$\Delta H^\circ = -70.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.3 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}500 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The recommended temperature dependence is based on a least-squares fit of the data of Lewis and Watson¹ and Howard and Smith,² which are in close agreement. Other studies at ambient temperatures^{3–5} are also in excellent agreement with these results.^{1,2} The reaction has been the subject of a number of theoretical studies; see Troe⁶ and Miller.⁷ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁸

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$$\Delta H^\circ = -224.5 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.7 \times 10^{-11} \exp(224/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.08 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The recommended value at 298 K is the mean of values obtained in the studies of Nicovich and Wine,¹ Keyser,² Sridharan *et al.*,³ Ravishankara *et al.*,⁴ and Brune *et al.*,⁵ all of which are in excellent agreement. The temperature coefficient is the mean of the values obtained by Nicovich and Wine¹ and Keyser,² with the pre-exponential factor being based on this value of E/R and the recommended value of k at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

In the two most recent studies of the reaction mechanism, Keyser *et al.*⁷ have shown that the yield of $\text{O}_2(^1\Sigma_g^+)$ from the reaction is $< 1 \times 10^{-2}$ per HO_2 radical removed and Sridharan *et al.*⁸ have shown, in an ^{18}O labeling experiment, that the reaction proceeds via formation of an $\text{HO}_2\text{--}^{18}\text{O}$ intermediate which dissociates to HO and ^{18}OO by rupture of an O–O bond rather than via a four center intermediate yielding $\text{H}^{18}\text{O} + \text{OO}$.

References

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$$\Delta H^\circ = -59.0 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.4 \times 10^{-12} \exp(-2000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}390 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 1000 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the results of Wine *et al.*¹ and Davis *et al.*,² and are identical to our previous

evaluation, IUPAC, 1992.³ These two studies are in agreement with regard to the temperature dependence of the rate coefficient but the absolute values of k differ by a factor of 2 throughout the range. In both cases the preexponential factor obtained is low compared with other atom-molecule reactions. To obtain the preferred values the temperature coefficient is accepted and the pre-exponential factor adjusted to obtain agreement with the recommended value of k at 298 K, which is the mean of the values found in the two studies.

Roscoe⁴ has discussed earlier work on this reaction, which was invalidated by secondary reactions affecting the measurements.

References

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$$\Delta H^\circ(1) = -181.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–350 K.

Wiesenfeld,³ all of which are in excellent agreement, and are identical to our previous evaluation, IUPAC, 1992.⁴ Channel (1) appears to be the predominant pathway (>95%)⁵ for the reaction.

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The preferred values are the mean of the values of Wine and Ravishankara,¹ Davidson *et al.*,² and Force and

References

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$$\Delta H^\circ(1) = -118.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -197.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–350 K.

$$k_1 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 < 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_3 < 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

agreement. Our recommendations for k_2/k and k_3/k are based on the data of Zellner *et al.*⁶ and Glinski and Birks⁷ (k_2/k) and Zellner *et al.*⁶ and Wine and Ravishankara⁸ (k_3/k). The preferred values are identical to our previous evaluation, IUPAC, 1992.⁹

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Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

$$\Delta \log k_1 = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value for k is a mean of the values of Gericke and Comes,¹ Amimoto *et al.*,² Lee and Slanger,³ Wine and Ravishankara⁴ and Streit *et al.*,⁵ all of which are in good

$$\Delta H^\circ = -63.1 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 6.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.7 \times 10^{-12} \exp(-2100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

There are several studies in good agreement on both the temperature coefficient and absolute values of the rate coefficient. The preferred value of k at 298 K is the mean of the results of Greiner,¹ Stuhl and Niki,² Westenberg and deHaas,³ Smith and Zellner,⁴ Overend *et al.*,⁵ Atkinson *et al.*,⁶ Tully and Ravishankara,⁷ Zellner and Steinert,⁸ and Ravishankara *et al.*⁹ The preferred value of E/R is the mean of the values of Smith and Zellner,⁴ Atkinson *et al.*,⁶ and

Ravishankara *et al.*⁹ The preexponential factor in the rate expression is calculated to fit the preferred value of k at 298 K and that of E/R . The preferred values are identical to our previous evaluation, IUPAC, 1992.¹⁰

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- ¹⁰IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -71.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.9 \times 10^{-14} (T/298)^{2.6} \exp(945/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}500 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

There are a number of measurements^{1–10} of k at temperatures close to 298 K falling in the range $(1.4\text{--}2.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We take the mean of the more recent studies^{1–6} for our preferred value at 298 K. This value is confirmed by recent measurements¹¹ of the pressure dependence of the $\text{HO} + \text{HO} + \text{M}$ reaction system which allow the reactions $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ and $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O}_2$ to be separated. The temperature coefficient is taken from an ab initio modeling study¹² which well accommodates the experimental high temperature results.

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- ¹¹R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlegel, and J. Troe, *J. Chem. Phys.* **103**, 2949 (1995).
- ¹²L. B. Harding and A. F. Wagner, *22nd International Symposium on Combustion* (Combustion Institute, Pittsburgh, 1988), p. 983.

$$\Delta H^\circ = -214.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.9 \times 10^{-31} [\text{N}_2]$	298	Fulle <i>et al.</i> , 1996 ¹	(a)
<i>Reviews and Evaluations</i>			
$8.0 \times 10^{-31} (T/300)^{-0.8} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$6.9 \times 10^{-31} (T/300)^{-0.8} [\text{air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Laser flash photolysis system with saturated LIF detection of HO radicals. Measurements were made between 1 and 180 bar. Falloff extrapolation was carried out with $F_c=0.5$ at 298 K. Separation between the reactions $\text{HO} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$ and $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ was made from the pressure dependence.
- (b) Based on the measurements of Zellner *et al.*,⁴ Trainor and von Rosenberg,⁵ and preliminary results from Ref. 1. The temperature dependence was obtained from the theoretical analysis of Ref. 6.
- (c) Based on direct measurements from Zellner *et al.*⁴

Reliability

$$\Delta \log k_0 = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The previously noted³ discrepancies between the results from Refs. 4 and 5 disappear when the pressure dependence of the reaction is analyzed over the wide range applied in Ref. 1. By this representation the reactions $\text{HO} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$ and $\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$ can be separated conveniently. The preferred values then are the average of results from Refs. 1, 4, and 5, based on a falloff curve using $F_c=0.5$ at 298 K. The temperature dependence of k_0 is from the theoretical analysis of Ref. 6.

Preferred Values

$$k_0 = 6.9 \times 10^{-31} (T/300)^{-0.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
2.6×10^{-11}	298	Fulle <i>et al.</i> , 1996 ¹	(a)
<i>Reviews and Evaluations</i>			
3.0×10^{-11}	200–300	IUPAC, 1992 ²	(b)
1.5×10^{-11}	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 .
- (b) The new experiments from Ref. 1, together with the analysis⁶ of photolysis and thermal dissociation rates, provide a consistent picture of the falloff curve. A value of $F_c=0.5$ is recommended over the temperature range 200–300 K.
- (c) See comment (c) for k_0 .

Preferred Values

$$k_\infty = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.2 \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Comments on Preferred Values

The falloff curve from Ref. 1 now allows for a reliable extrapolation to k_∞ at 298 K. The temperature dependence of

k_{∞} is probably small,⁶ although more extensive experiments and a more detailed theoretical analysis are needed.

References

¹D. Fulle, H. F. Hamann, H. Hippler, and J. Troe, *J. Chem. Phys.* **105**, 1001 (1996).

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⁶L. Brouwer, C. J. Cobos, J. Troe, H. R. Düball, and F. F. Crim, *J. Chem. Phys.* **86**, 6171 (1987).

$$\Delta H^\circ = -295.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.8 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

There has been some controversy over the effects of pressure on the rate coefficient for this reaction. Early discharge-flow measurements at low pressures (1–10 Torr) consistently gave values of k approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The discharge-flow study of Keyser¹ appears to have resolved the problem. His results¹ suggest that the presence

of small quantities of H and O present in previous discharge-flow studies could have led to erroneously low values of k , and that there is no evidence for any variation in k with pressure. These findings¹ are accepted and we take the expression of Keyser¹ for k as our recommendation. There are a number of other studies in excellent agreement with the value recommended for k at 298 K, which is identical to our previous evaluation, IUPAC, 1992.²

In another discharge-flow study Keyser *et al.*,³ by monitoring the $\text{O}_2(b^1\Sigma_g^+) \rightarrow \text{X}(^3\Sigma_g^-)$ transition at 762 nm, have shown that the yield of $\text{O}_2(b^1\Sigma_g^+)$ from the reaction is small ($< 1 \times 10^{-3}$).

References

¹L. F. Keyser, *J. Phys. Chem.* **92**, 1193 (1988).

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$$\Delta H^\circ = -130.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.9 \times 10^{-12} \exp(-160/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}460 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

There are a number of studies in excellent agreement on the value of the rate coefficient.^{1–7} The recommended expression is that derived by Kurylo *et al.*,⁷ from a least-squares fit to the data in Refs. 2–7, and is identical to our previous evaluation, IUPAC, 1992.⁸

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³L. F. Keyser, *J. Phys. Chem.* **84**, 1659 (1980).

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⁸IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -167.4 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 6.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.9 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

There is good agreement among the various studies of k . The recommended value for E/R is the mean of the values of Anderson and Kaufman,¹ Ravishankara *et al.*,² and Smith *et al.*³ The recommended value of k at 298 K is the mean of

values from these studies plus those of Kurylo⁴ and Zahniser and Howard.⁵ The pre-exponential factor is derived from the recommended values of E/R and k at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

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$$\Delta H^\circ(1) = \Delta H^\circ(2) = -165.5 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k_1 = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 5.2 \times 10^{-32} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 4.5 \times 10^{-32} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 2.2 \times 10^{-13} \exp(600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}420 \text{ K.}$$

$$k_2 = 1.9 \times 10^{-33} [\text{N}_2] \exp(980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}420 \text{ K.}$$

In the presence of H_2O the expressions for k_1 and k_2 should be multiplied by the factor $\{1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \times \exp(2200/T)\}$.

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \pm 200 \text{ K.}$$

$$\Delta(E_2/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

Although no new data have been published since our last evaluation, the data have been reviewed by Wallington *et al.*¹ who recommend use of the preferred values given here which are also identical with the values derived by Kircher and Sander.²

At temperatures close to 298 K, the reaction proceeds by two channels, one bimolecular and the other termolecular. The preferred values for k_1 are based on the work of Cox and Burrows,³ Kircher and Sander,² Thrush and Tyndall,⁴ Takacs and Howard,⁵ Kurylo *et al.*,⁶ and Lightfoot *et al.*⁷ The work of Kurylo *et al.*⁶ and of Lightfoot *et al.*⁷ has confirmed quantitatively the effects of pressure previously observed by Kircher and Sander² and Simonaitis and Heicklen.⁸ The recommendations for k_2 are based on the work of these authors, the temperature coefficient of k_2 being taken from Lightfoot *et al.*⁷ and Kircher and Sander.² At higher temperatures, $T > 600 \text{ K}$, Hippler *et al.*⁹ and Lightfoot *et al.*⁷ observe a sharp change in the temperature coefficient. The values of k obtained by Crowley *et al.*¹⁰ in experiments primarily aimed at characterizing the UV absorption spectrum are in good agreement with the recommended expression for k .

There have been no recent experimental studies to check the marked effect of H_2O on the rate coefficient, but the work of Andersson *et al.*¹¹ shows that CH_3OH has a similar effect, suggesting that it is typical of strongly polar hydrogen bonding species. Mozurkewich and Benson¹² have considered the effect theoretically and conclude that the negative temperature dependence, the pressure dependence, and the observed isotope effects can most reasonably be explained in

terms of a cyclic hydrogen bonded, H_2OHO_2 , intermediate to alternative structures suggested by others.

Sahetchian *et al.*¹³ reported the formation of H_2 ($\sim 10\%$ at 500 K) in the system but this is contrary to earlier evidence of Baldwin *et al.*¹⁴ and the more recent and careful study of Stephens *et al.*¹⁵ who find less than 0.01 fractional contribution from the channel leading to $\text{H}_2 + 2\text{O}_2$.

Keyser *et al.*¹⁶ have measured a yield of $\text{O}_2(b^1\Sigma_g^+)$ of $< 3 \times 10^{-2}$ per HO_2 consumed.

References

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$$\Delta H^\circ = -118.0 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.4 \times 10^{-14} \exp(-600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}350 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = {}^{+500 \text{ K}}_{-100 \text{ K}}$$

Comments on Preferred Values

A number of studies¹⁻⁴ are in close agreement on the value of k at 298 K, but there is some divergence on the temperature coefficient of k . The studies of Sinha *et al.*³ and Wang *et al.*⁴ both agree that k exhibits non-Arrhenius behavior, apparently approaching a constant value of approximately $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T < 250 \text{ K}$. There are experimental difficulties in working at these temperatures and this finding^{3,4} is not incorporated in our recommendation without further confirmation. At higher temperature the results from these two studies^{3,4} diverge, giving values of k differing by nearly a factor of 2 at 400 K. We therefore limit the temperature range of our recommendation to $T < 350 \text{ K}$ until this discrepancy is resolved.

The preferred values for the range 250–350 K are based on the results of Zahniser and Howard¹ and Wang *et al.*⁴ For modeling at temperatures in the range 200–250 K a value of $k = 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ should be used. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

Isotopic exchange studies⁶ of the reaction between H^{18}O_2 and O_3 show that at room temperatures the reaction proceeds almost exclusively by H atom transfer rather than by transfer of an oxygen atom. Moreover there is little change in this finding with temperature over the range 226–355 K,⁶ indicating that any curvature on the Arrhenius plot cannot be due to competition between these two reaction paths.

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$\text{H}_2\text{O} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reactions	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + \text{O}(^3\text{P})$ (1)	491.0	243
$\rightarrow \text{H} + \text{HO}$ (2)	499.1	239
$\rightarrow \text{H}_2 + \text{O}(^1\text{D})$ (3)	680.7	176

No new data have been published since our last evaluation.

Preferred Values

λ/nm	$10^{20} \sigma/\text{cm}^2$	ϕ_2
175.5	263	1.0
177.5	185	1.0
180.0	78	1.0
182.5	23	1.0
185.0	5.5	1.0
186.0	3.1	1.0
187.5	1.6	1.0
189.3	0.70	1.0

Comments on Preferred Values

Water vapor has a continuous spectrum between 175 and 190 nm; the cross-section decreases rapidly towards longer wavelengths. The cross-section data from four studies¹⁻⁴ are in reasonable agreement. None of these studies report numerical data. The preferred values of the absorption cross section are taken from the review of Hudson,⁵ and were obtained by drawing a smooth curve through the data of

Schurgers and Welge,⁴ Watanabe and Zelickoff,¹ and Thompson *et al.*²

On the basis of the nature of the spectrum and the results of Chou *et al.*⁶ on the photolysis of HTO, it is assumed that over the wavelength region 175–190 nm, reaction (2) is the only primary process and that $\phi_2=1.0$.⁷

These recommendations are identical to our previous evaluation, IUPAC, 1992.⁸

References

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 $\text{H}_2\text{O}_2 + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reactions	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{H}_2\text{O}_2 + h\nu \rightarrow \text{HO} + \text{HO}$ (1)	215	557
$\rightarrow \text{H}_2\text{O} + \text{O}(^1\text{D})$ (2)	333	359
$\rightarrow \text{H} + \text{HO}_2$ (3)	369	324
$\rightarrow \text{HO} + \text{HO}(^2\Sigma)$ (4)	606	197

Quantum yield data

$$(\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4)$$

Measurement	Wavelength Range/nm	Reference	Comments
$\phi=1.0$	253.7	Volman, 1963 ¹	(a)
$\phi_1=1.04\pm0.18$	248	Vaghjiani and Ravishankara, 1990 ²	(b)
$\phi_2<0.002$	248		
$\phi_3<0.0002$	248		
$\phi_1=1.01\pm0.17$	222	Vaghjiani <i>et al.</i> , 1992 ³	(c)
$\phi_2<0.002$	222		
$\phi_3=0.024\pm0.012$	222		
$\phi_1=0.79\pm0.12$	248	Schiffman <i>et al.</i> , 1993 ⁴	(d)

Comments

- (a) Based on a measured overall quantum yield for H_2O_2 removal of $\phi(-\text{H}_2\text{O}_2)=1.7\pm0.4$ and the assumed mechanism, $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO}$, $\text{HO} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$, and $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. This interpretation has been criticized by Greiner.⁵
- (b) Photolysis of flowing mixtures of $\text{H}_2\text{O}_2\text{--H}_2\text{O--N}_2$ (or He) and of $\text{O}_3\text{--H}_2\text{O--N}_2$ (or He) at 298 K. H_2O_2 and O_3 were determined by UV absorption at 213.9 nm or 228.8 nm. Quantum yield of HO formation from $\text{H}_2\text{O}_2\text{--H}_2\text{O}$ mixture was measured relative to that from $\text{O}_3\text{--H}_2\text{O}$ mixture. These relative yields were placed on an absolute basis using the known quantum yield of HO radical production from the photolysis of $\text{O}_3\text{--H}_2\text{O}$ mixtures at 248 nm, taken as $\phi(\text{HO})=1.73\pm0.09$.^{2,6} O and H yields were determined by resonance fluorescence.
- (c) Pulsed laser photolysis of $\text{H}_2\text{O}_2\text{--N}_2$ or SF_6 mixtures at 222 nm and 248 nm. $[\text{HO}]$ monitored by LIF. The quantum yield of HO production at 248 nm was assumed to be 2.0 and the value at 222 nm was determined from this and the relative HO yields at the two wavelengths. H atom concentrations were monitored by resonance fluorescence. The quantum yield was determined by reference to CH_3SH photolysis at 193 nm. $\text{O}(^3\text{P})$ atom formation was investigated using resonance fluorescence but only a very small signal was detected, possibly due to secondary chemistry.
- (d) Pulsed laser photolysis of H_2O_2 mixtures. Energy, and hence number of photons, of laser pulse absorbed determined by calorimetry. HO concentrations were monitored by infrared absorption using a color center dye-laser (2.35–3.40 μm) and interferometer for wavelength measurement. Absolute HO radical concentrations were obtained using integrated absorption cross-sections measured in the same laboratory.⁷

Preferred Values

λ/nm	$10^{20} \sigma/\text{cm}^2$	ϕ_1	λ/nm	$10^{20} \sigma/\text{cm}^2$	ϕ_1
190	67.2		275	2.6	1.0
195	56.3		280	2.0	1.0
200	47.5		285	1.5	1.0
205	40.8		290	1.2	1.0
210	35.7		295	0.90	1.0
215	30.7		300	0.68	1.0
220	25.8	1.0	305	0.51	1.0
225	21.7	1.0	310	0.39	1.0
230	18.2	1.0	315	0.29	1.0
235	15.0	1.0	320	0.22	1.0
240	12.4	1.0	325	0.16	1.0
245	10.2	1.0	330	0.13	1.0
250	8.3	1.0	335	0.10	1.0
255	6.7	1.0	340	0.07	1.0
260	5.3	1.0	345	0.05	1.0
265	4.2	1.0	350	0.04	1.0
270	3.3	1.0			

Comments on Preferred Values

There have been no new measurements of the absorption cross-sections and our recommendations are unchanged from our previous evaluation, IUPAC, 1992.⁸ The preferred values are the means of those determined by Lin *et al.*,⁹ Molina and Molina,¹⁰ Nicovich and Wine,¹¹ and Vaghjiani and Ravishankara.¹² These agree with the earlier values of Holt *et al.*¹³ The absorption cross-sections have also been measured at other temperatures by Troe¹⁴ (220–290 nm at 600 K and 1100 K) and by Nicovich and Wine¹¹ (260–250 nm, 200–400 K). Both Nicovich and Wine¹¹ and Troe¹⁴ have expressed their results in an analytical form.

It has long been assumed that channel (1) is the only significant primary photochemical channel at $\lambda > 200$ nm. There are measurements by Vaghjiani and Ravishankara² and Vaghjiani *et al.*³ at 248 nm and 222 nm which support this at these wavelengths. However, measurements at 193 nm by Vaghjiani *et al.*³ show a decline in the HO radical quantum yield (1.51 relative to an assumed value of 2 at 248 nm) with a growth in the H atom quantum yield, a feature previously observed by Gerlach-Meyer *et al.*¹⁵ The results of Schiffman *et al.*⁴ also agree well with this relative change in HO radical production in going from 248 nm to 193 nm. However, Schiffman *et al.*⁴ obtain much lower absolute values for the quantum yield of HO radical production than obtained by Vaghjiani and Ravishankara.²

The evidence therefore indicates that there is a decline in the relative importance of channel (1) in going from 248 nm to 193 nm but the point of onset of this decline and its form are uncertain. Furthermore, the reason for the difference in the absolute values of the quantum yield between the studies of Schiffman *et al.*⁴ and Vaghjiani and Ravishankara² is unclear; further work is urgently required to clarify this.

Provisionally we continue to recommend the use of a quantum yield of 2 for HO radical production ($\phi_1=1.0$) at $\lambda > 220$ nm.

References

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4.3. Nitrogen Species

$$\Delta H^\circ = -306.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.7 \times 10^{-32} (T/300)^{-(1.41 \pm 0.02)} [\text{Ar}]$	300–1341	Yarwood <i>et al.</i> , 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.0 \times 10^{-31} (T/300)^{-1.6} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$9.0 \times 10^{-32} (T/300)^{-1.5} [\text{air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Two experimental techniques were employed. Over the temperature range 300–1000 K, flash photolysis of NO with light from a N₂ discharge lamp was carried out in a temperature-controlled quartz cell. O(³P) atoms were monitored by resonance fluorescence and the total pressure varied between 50 and 300 Torr. A flash photolysis-shock tube technique was employed between 915 and 1341 K at 30 Torr total pressure. O(³P) atoms were detected by atomic resonance absorption spectroscopy. Collisional efficiencies $\beta_c = 0.29, 0.26, 0.18$, and 0.16 were derived at 300, 400, 1000, and 2000 K, respectively. In the theoretical analysis, recombination into the X(²A₂), A(²B₂), and C(²A₂) states of NO₂ were taken into account.
- (b) Based on the experiments of Ref. 4.
- (c) Based on the experiments of Ref. 4 and their

reanalysis⁴ of the data from Ref. 5 and measurements from Ref. 1.

Preferred Values

$$k_0 = 1.0 \times 10^{-31} (T/300)^{-1.6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.10 \text{ at 298 K.}$$

$$\Delta n = \pm 0.3.$$

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.² The recent measurements by Yarwood *et al.*¹ at the lowest temperatures are consistent with those recommended in this evaluation.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 3.0 \times 10^{-11} (T/300)^{0.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–1500 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3.$$

$$\Delta n = \pm 0.3.$$

Comments on Preferred Values

The preferred values are based on the relative rate measurements of Ref. 6. A reconfirmation by an absolute rate measurement is required. A broadening factor $F_c = 0.85$ at 300 K was estimated, which would correspond to an esti-

mated temperature dependence of $F_c = \exp(-T/1850)$. These preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹G. Yarwood, J. W. Sutherland, M. A. Wickramaratchi, and R. B. Klemm, *J. Phys. Chem.* **95**, 8771 (1991).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
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- ⁵D. A. Whytock, J. V. Michael, and W. A. Payne, *Chem. Phys. Lett.* **42**, 466 (1976).
- ⁶H. Hippler, C. Schipper, and J. Troe, *Int. J. Chem. Kinet. Symp.* **1**, 27 (1975).

$$\Delta H^\circ = -192.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 6.5 \times 10^{-12} \exp(120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–350 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
 $\Delta(E/R) = \pm 120 \text{ K}$.

Comments on Preferred Values

The preferred value at 298 K is the average of the values reported by Ongstad and Birks,¹ Geers-Müller and Stuhl,² Davis *et al.*,³ Bemand *et al.*,⁴ and Slanger *et al.*⁵ The recom-

mended temperature dependence results from a least-squares fit to the data of Ongstad and Birks,⁶ Geers-Müller and Stuhl² and Davis *et al.*,³ and the preexponential factor has been adjusted to fit the preferred value of $k(298 \text{ K})$. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁷

References

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- ⁵T. G. Slanger, B. J. Wood, and G. Black, *Int. J. Chem. Kinet.* **5**, 615 (1973).
- ⁶A. P. Ongstad and J. W. Birks, *J. Chem. Phys.* **85**, 3359 (1986).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -208.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 9.0 \times 10^{-32} (T/300)^{-2.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from relative rate data.¹ Absolute rate measurements are required. Changes of the reference rate constant $k(\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO})$ from the originally used value of $9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (this evaluation) does not influence the preferred value.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

See comments on k_0 .

Intermediate Falloff Range

A broadening of the falloff curve with F_c (300 K) $= 0.8$ and an estimated temperature dependence $F_c = \exp(-T/1300)$ has to be taken into account. The preferred k_0 and k_∞ values depend on the F_c value chosen. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.²

References

- ¹CODATA, 1980 (see references in Introduction).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -289.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is that reported by Canosa-Mas *et al.*,¹ which is the only direct measurement of this rate coefficient. The earlier relative rate value of Graham and Johnston² is consistent with the preferred value, taking into account the

experimental uncertainties. The temperature dependence is probably near zero by analogy with the reaction of O(³P) atoms with NO₂. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.³

References

¹C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **85**, 697 (1989).

²R. A. Graham and H. S. Johnston, J. Phys. Chem. **82**, 254 (1978).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(2.6 \pm 0.3) \times 10^{-11}$	296	Shi and Barker, 1990 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.8 \times 10^{-11} \exp(107/T)$	200–350	IUPAC, 1992 ²	(b)
$1.8 \times 10^{-11} \exp(110/T)$	200–350	NASA, 1994 ³	(b)

Comments

- (a) The kinetics of deactivation of O₂(¹Σ_g⁺) were studied by time-resolved emission from O₂(¹Σ_g⁺) at 762 nm. O₂(¹Σ_g⁺) was produced by reaction of O(¹D) atoms with O₂ following laser flash photolysis of O₃. The effect of N₂ (and other quenchers) on the initial fluorescence intensity gives the O(¹D) atom deactivation rate coefficient relative to that for O₂. The rate coefficient for the reaction of O(¹D) atoms with O₂ (this evaluation) is used to determine *k*.
- (b) Based on the measurements of Amimoto *et al.*,⁴ Brock and Watson,⁵ Wine and Ravishankara,⁶ and Streit *et al.*⁷

Preferred Values

$$k = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.8 \times 10^{-11} \exp(107/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}350 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The relative rate data of Shi and Barker¹ are in excellent agreement with the earlier studies,^{4–7} and there is no change in the recommendation. The preferred value at room temperature is the average of the results of Amimoto *et al.*,⁴ Brock and Watson,⁵ Wine and Ravishankara,⁶ and Streit *et al.*,⁷ all of which are in close agreement. The temperature dependence of Streit *et al.*⁷ is accepted, and the preexponential factor has been adjusted to fit the preferred room temperature value. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

¹J. Shi and J. R. Barker, Int. J. Chem. Kinet. **22**, 1283 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴S. T. Amimoto, A. P. Force, R. G. Gulotty, Jr., and J. R. Wiesenfeld, J. Chem. Phys. **71**, 3640 (1979).

⁵J. C. Brock and R. T. Watson, results presented at the NATO Advanced Study Institute on Atmospheric Ozone, Portugal, 1979; see G. K. Moortgat's review in Report No. FAA-EE-80-2 (1980).

⁶P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. **77**, 103 (1981).

⁷G. E. Streit, C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, J. Chem. Phys. **65**, 4761 (1976).

$$\Delta H^\circ(1) = -521.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -340.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Branching Ratios			
$k_2/k=0.61\pm0.08$	296	Cantrell, Shetter, and Calvert, 1994 ¹	(a)
Reviews and Evaluations			
$k_1=4.4\times10^{-11}$	200–350	IUPAC, 1992 ²	(b)
$k_2=7.2\times10^{-11}$	200–350		
$k_3<1\times10^{-12}$	200–350		
$k_1=4.9\times10^{-11}$	200–300	NASA, 1994 ³	(b)
$k_2=6.7\times10^{-11}$	200–350		

Comments

- (a) Static photolysis of $\text{N}_2\text{O}-\text{O}_3$ mixtures at $\lambda>240$ nm with product analysis by FTIR spectroscopy. The amount of NO formed in reaction (2) was determined from the yield of HNO_3 formed by total oxidation and hydration of NO_x products, corrected for losses to the wall. The value of k_2/k obtained from the experimental data was 0.57 ± 0.08 ; the value given in the table was obtained by averaging the experimental value with selected literature data.
- (b) Based on the measurements of Amimoto *et al.*,⁴ Wine and Ravishankara,⁵ and Davidson *et al.*⁶

$$\Delta(E_1/R)=(E_2/R)=\pm 100 \text{ K.}$$

Comments on Preferred Values

The data and recommendation for the branching ratio at room temperature of $k_2/k=0.61\pm0.08$ given by Cantrell *et al.*¹ are completely in accord with our previous evaluation ($k_2/k=0.62\pm0.09$).² The preferred values for the rate coefficients are therefore unchanged from our previous evaluation, IUPAC, 1992.² The values at room temperature are the average of the results of Amimoto *et al.*,⁴ Wine and Ravishankara,⁵ and Davidson *et al.*,⁶ all of which are in close agreement. The temperature independence reported by Davidson *et al.*⁶ is accepted.

Preferred Values

$k_1=4.4\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–350 K.

$k_2=7.2\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–350 K.

$k_3<1\times10^{-12}$, independent of temperature over the range 200–350 K.

Reliability

$$\Delta\log k_1=\Delta\log k_2=\pm 0.1 \text{ at } 298 \text{ K.}$$

References

- ¹C. A. Cantrell, R. E. Shetter, and J. G. Calvert, *J. Geophys. Res.* **99**, 3739 (1994).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
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- ⁵P. H. Wine and A. R. Ravishankara, *Chem. Phys. Lett.* **77**, 103 (1981).
- ⁶J. A. Davidson, H. I. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltzekopf, and C. J. Howard, *J. Chem. Phys.* **67**, 5021 (1977).

$$\Delta H^\circ = -49.8 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.5 \times 10^{-12} \exp(-925/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–450 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The results of Diau *et al.*¹ are in excellent agreement with the previously recommended Arrhenius expression, which was based on the results of Stuhl,² Smith and Zellner,³ Perry *et al.*,⁴ Silver and Kolb,⁵ and Stephens.⁶ There is no change in the preferred value resulting from the inclusion of the new data of Diau *et al.*¹ The many high temperature studies have

been considered by Jeffries and Smith⁷ to derive a modified Arrhenius expression over an extended temperature range of $k = 1.58 \times 10^{-17} T^{1.8} \exp(-250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the temperature range of 225–2350 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁸

References

- ¹E. W.-G. Diau, T.-L. Tso, and Y.-P. Lee, *J. Phys. Chem.* **94**, 5261 (1990).
- ²F. Stuhl, *J. Chem. Phys.* **59**, 635 (1973).
- ³I. W. M. Smith and R. Zellner, *Int. J. Chem. Kinet. Symp.* **1**, 341 (1975).
- ⁴R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.* **64**, 3237 (1976).
- ⁵J. A. Silver and C. E. Kolb, *Chem. Phys. Lett.* **75**, 191 (1980).
- ⁶R. D. Stevens, *J. Phys. Chem.* **88**, 3308 (1984).
- ⁷J. B. Jeffries and G. P. Smith, *J. Phys. Chem.* **90**, 487 (1986).
- ⁸IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -168.4 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-12} \exp[(260 \pm 140)/T]$ $(7.05 \pm 0.26) \times 10^{-12}$	298–373 298	Burkholder <i>et al.</i> , 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.8 \times 10^{-11} \exp(-390/T)$	280–340	IUPAC, 1992 ²	(b)
$1.8 \times 10^{-11} \exp(-390/T)$	200–300	NASA, 1994 ³	(b)

Comments

- (a) Laser flash photolysis system with LIF detection of HO radicals. HO radicals were produced from the 266 nm photolysis of O₃ in the presence of excess H₂O, and HONO was prepared from acidified NaNO₂ solution and its concentration, together with that of NO₂, was monitored by *in situ* diode-array spectroscopy. Pseudo first-order decays of OH radicals in excess HONO were measured. The reported error limit is the 95% confidence limit.
- (b) Based on the measurements of Jenkin and Cox⁴ and Cox *et al.*⁵

Preferred Values

$k = 6.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.7 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 260 \text{ K}$.

Comments on Preferred Values

The new direct measurements of this rate coefficient from Burkholder *et al.*¹ agree well with the earlier relative rate determination of Cox *et al.*⁵ at 296 K [$k = (6.3 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$], but are higher than the direct measurements of Jenkin and Cox⁴ using the molecular modulation technique [$k = (4.5 \pm 1.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K]. The new measurements show a small negative temperature dependence whilst the earlier work⁴ gave a positive dependence with an activation energy of 3.2 kJ mol⁻¹. The new measurements have substantially better precision and accuracy and the temperature dependence is consistent with that observed for the analogous reaction of HO radicals with HONO₂. The preferred value is a weighted average of the reported values of Cox *et al.*,⁵ Jenkin and Cox,⁴ and Burkholder *et al.*,¹ at 298 K combined with the temperature dependence of Burkholder *et al.*¹

References

¹J. B. Burkholder, A. Mellouki, R. Talukdar, and A. R. Ravishankara, *Int. J. Chem. Kinet.* **24**, 711 (1992).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴M. E. Jenkin and R. A. Cox, *Chem. Phys. Lett.* **137**, 548 (1987).

⁵R. A. Cox, R. D. Derwent, and P. M. Holt, *J. Chem. Soc. Faraday Trans. 1*, **72**, 2031 (1976).

$$\Delta H^\circ(1) = \Delta H^\circ(2) = -72.4 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$$k = 1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K and } 1 \text{ bar.}$$

See comments for expression to be used under other conditions of temperature and pressure.

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

There is now understanding of the kinetics and mechanism of this complex reaction. There is general consensus on the following major features of the data: (a) a strong negative temperature dependence below room temperature with a much weaker temperature dependence above room temperature which appears to level off near 500 K, and (b) a small but measurable pressure dependence at room temperature which increases at low temperatures. The pressure dependence from 20–100 Torr and 225–298 K was determined by Margitan and Watson,¹ and Stachnik *et al.*² measured rate coefficients over the range 10–730 Torr at 297 K and 248 K. These studies agree on a 50 increase in the rate constant at the highest pressure studied at room temperature and a doubling of the low pressure limit at 240 K.

Lamb *et al.*³ have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex. This mechanism gives a rate coefficient expression which combines a low pressure limiting rate constant (k_1) and a Lindemann-Hinshelwood expression for the pressure dependence. This mechanism has been used in the NASA evaluation,⁴ and the expression derived in the NASA panel's analysis⁴ has been adopted for the evaluation. The overall rate constant can be expressed as:

$$k = k_1(T) + k_2(M, T)$$

where

$$k_2(M, T) = k_3[M]/(1 + k_3[M]/k_4).$$

The expressions for the elementary rate constants are:

$$k_1 = 7.2 \times 10^{-15} \exp(785/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k_3 = 1.9 \times 10^{-33} \exp(725/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, \text{ and}$$

$$k_4 = 4.1 \times 10^{-16} \exp(1440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1};$$

all expressions are valid over the temperature range 220–300 K. This expression has been evaluated for the conditions of 298 K and 1 atm pressure to yield the preferred value given here. The reader is referred to Ref. 4 for a more detailed discussion of this reaction. Bossard *et al.*⁵ and Singleton *et al.*⁶ have reported a pressure and temperature dependence, respectively, of the rate constant for the related reaction $\text{DO} + \text{DNO}_3$. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

¹J. J. Margitan and R. T. Watson, *J. Phys. Chem.* **86**, 3819 (1982).

²R. A. Stachnik, L. T. Molina, and M. J. Molina, *J. Phys. Chem.* **90**, 2777 (1986).

³J. J. Lamb, M. Mozurkewich, and S. W. Benson, *J. Phys. Chem.* **88**, 6441 (1984).

⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

⁵A. R. Bossard, G. Paraskevopoulos, and D. L. Singleton, *Chem. Phys. Lett.* **134**, 583 (1987).

⁶D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, *J. Phys. Chem.* **95**, 694 (1991).

⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -191 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -44.9 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.5 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = {}^{+300}_{-600} \text{ K}$.

Comments on Preferred Values

The preferred value is based on a least-squares fit to the data of Trevor *et al.*,¹ Smith *et al.*,² and Barnes *et al.*³ Trevor *et al.*¹ studied this reaction from 246–324 K at low pressure (3–15 Torr) and recommended a temperature-independent value, but also reported an Arrhenius expression with $E/R = 193 \pm 194 \text{ K}$. In contrast, Smith *et al.*² report data from 240–340 K at one atmosphere pressure and report a negative temperature dependence with $E/R = -(650 \pm 30) \text{ K}$. It is possible that the difference may be due to the reaction being complex with different temperature dependences at low and at high pressure. The error limits on the recommended E/R

value encompass the results of both studies. At 220 K the values deduced from these studies differ by a factor of three. The recent study of Barnes *et al.*,³ the first study over an extended pressure range, found the rate coefficient to be independent of pressure from 5–300 Torr at 278 K and also report the same value at 295 K (low pressure) and at 268 K (100 Torr He). They also report no change with synthetic air as buffer gas. A TST calculation by Lamb *et al.*⁴ suggests that the pressure dependence for this rate coefficient will be much less than that for the corresponding reaction of HO with HNO_3 . These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

- ¹P. L. Trevor, G. Black, and J. R. Barker, *J. Phys. Chem.* **86**, 1661 (1982).
- ²C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina, *Int. J. Chem. Kinet.* **16**, 41 (1984).
- ³I. Barnes, V. Bastian, K. H. Becker, E. H. Fink, and F. Zabel, *Chem. Phys. Lett.* **83**, 459 (1981).
- ⁴J. J. Lamb, M. Mozurkewich, and S. W. Benson, *J. Phys. Chem.* **88**, 6441 (1984).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + NO + M → HONO + M

$\Delta H^\circ = -209.0 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients**Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$5.0 \times 10^{-31} [\text{Ar}]$	298–422	Zabarnick, 1993 ¹	(a)
$1.5 \times 10^{-30} [\text{SF}_6]$	298–430		
$3.9 \times 10^{-31} (T/300)^{-2.4} [\text{He}]$	250–400	Forster <i>et al.</i> , 1995 ²	(b)
Reviews and Evaluations			
$7.4 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2]$	200–300	IUPAC, 1992 ³	(c)
$7.0 \times 10^{-31} (T/300)^{-2.6} [\text{air}]$	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) HO radicals were generated by photodissociation of HNO_3 at 248 nm and monitored by LIF at 310 nm. The bath gases Ar (50–400 Torr), N_2 (100 Torr), and SF_6 (50–400 Torr) were employed. Extrapolations were performed with a Lindemann–Hinshelwood expression.
- (b) Laser flash photolysis system with saturated LIF detection of HO radicals. Measurements were made over the pressure range 1–110 bar. Falloff extrapolations were carried out with $F_c = 0.9$ at 250 K and $F_c = 0.8$ at 400 K.
- (c) The preferred values have not been changed since 1984, because the data base appears fairly complete and consistency with theoretical analysis was obtained. The new high pressure measurements² put the falloff extrapolation on a sounder basis.
- (d) The recommended value is a weighted average of the data from Refs. 5–15, with heavy weighting to Ref. 14.

Preferred Values

$k_0 = 7.4 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The measurements from Refs. 1 and 2 appear consistent with our earlier recommendation,³ which remains unchanged.

High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
8.4×10^{-12}	298–422	Zabarnick, 1993 ¹	(a)
3.0×10^{-11}	298		
8.0×10^{-11}	430		
4.5×10^{-11}	250–400	Forster <i>et al.</i> , 1995 ²	(b)
<i>Reviews and Evaluations</i>			
3.2×10^{-11}	200–400	IUPAC, 1992 ³	(c)
1.5×10^{-11}	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) See comment (a) on k_0 . The first value was obtained in M=Ar, while the other values were extrapolated from measurements in M=SF₆.
- (b) See comment (b) on k_0 .
- (c) Based on preliminary data from Ref. 2.
- (d) The recommended value is a weighted average of the data of Anastasi and Smith¹⁴ and Anderson *et al.*⁹

Preferred Values

$k_{\infty} = 4.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.2$ over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are from Ref. 2, where a major part of the falloff curves was measured (up to 100 bar of M=He) at 250, 300, and 400 K. Falloff curves are constructed with $F_c=0.9$ at 250 K and 0.8 at 400 K.

References

- ¹S. Zabarnick, Chem. Phys. **171**, 265 (1993).
- ²R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlegel, and J. Troe, J. Chem. Phys. **103**, 2949 (1995).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
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- ⁶F. Stuhl and H. Niki, J. Chem. Phys. **57**, 3677 (1972).
- ⁷C. Morley and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **68**, 1016 (1972).
- ⁸A. A. Westenberg and N. deHaas, J. Chem. Phys. **57**, 5375 (1972).
- ⁹J. G. Anderson, J. J. Margitan, and F. Kaufman, J. Chem. Phys. **60**, 3310 (1974).
- ¹⁰C. J. Howard and K. M. Evenson, J. Chem. Phys. **61**, 1943 (1974).
- ¹¹G. W. Harris and R. P. Wayne, J. Chem. Soc. Faraday Trans. 1, **71**, 610 (1975).
- ¹²R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., J. Chem. Phys. **62**, 3284 (1975).
- ¹³R. P. Overend, G. Paraskevopoulos, and C. Black, J. Chem. Phys. **64**, 4149 (1976).
- ¹⁴C. Anastasi and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2, **74**, 1056 (1978).
- ¹⁵J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **79**, 111 (1983).

$$\Delta H^\circ = -207.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.5 \times 10^{-30} (T/300)^{-3.0} [\text{He}]$	268–400	Forster <i>et al.</i> , 1995 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.6 \times 10^{-30} (T/300)^{-2.9} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$2.6 \times 10^{-30} (T/300)^{-3.2} [\text{air}]$	200–400	NASA, 1994 ³	(c)

Comments

- (a) Laser flash photolysis system with saturated LIF detection of HO radicals. Measurements were made between 1 and 150 bar. Falloff curves were constructed with $F_c=0.46$ at 270 K, 0.43 at 300 K, and 0.37 at 400 K.
- (b) The data base is large. This evaluation was based on a calculated value of $F_c=0.43$ at 300 K.
- (c) The values are from Refs. 4–8. The temperature dependence was based on $(-\langle\Delta E\rangle)=2.3 \text{ kJ mol}^{-1}$ for $M=N_2$.

Reliability

$$\Delta \log k_0 = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.3.$$

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.² The new measurements for $M=He$ from Ref. 1 appear consistent with this recommendation.

Preferred Values

$$k_0 = 2.6 \times 10^{-30} (T/300)^{-2.9} [N_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

High-pressure rate coefficients**Rate coefficient data**

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.7 \times 10^{-11} (T/300)^{-0.6}$	260–400	Forster <i>et al.</i> , 1995 ¹	(a)
<i>Reviews and Evaluations</i>			
6.0×10^{-11}	200–300	IUPAC, 1992 ²	(b)
$2.4 \times 10^{-11} (T/300)^{-1.3}$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 .
- (b) Based on preliminary data from Ref. 1.
- (c) The recommended values were from a RRKM model of Smith and Golden.⁹

Preferred Values

$$k_\infty = 6.7 \times 10^{-11} (T/300)^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The preferred values are from the measurements of Ref. 1, which covered the largest part of the falloff curves.

References

- ¹R. Forster, M. Frost, D. Fulle, H. F. Hamann, H. Hippler, A. Schlegel, and J. Troe, *J. Chem. Phys.* **103**, 2949 (1995).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴J. G. Anderson, J. J. Margitan, and F. Kaufman, *J. Chem. Phys.* **60**, 3310 (1974).
- ⁵C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **61**, 1943 (1974).
- ⁶C. Anastasi and I. W. M. Smith, *J. Chem. Soc. Faraday Trans. 2*, **72**, 1459 (1976).
- ⁷P. H. Wine, N. M. Kreutter, and A. R. Ravishankara, *J. Phys. Chem.* **83**, 3191 (1979).
- ⁸J. P. Burrows, T. J. Wallington, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **79**, 111 (1983).
- ⁹G. P. Smith and D. M. Golden, *Int. J. Chem. Kinet.* **10**, 489 (1978).

$$\Delta H^\circ = -65.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.22 \pm 0.35) \times 10^{-11}$	298	Becker, Rahman, and Schindler, 1992 ¹	(a)
$(2.1 \pm 1.0) \times 10^{-11}$	297	Mellouki <i>et al.</i> , 1993 ²	(b)
<i>Reviews and Evaluations</i>			
2.3×10^{-11}	298	IUPAC, 1992 ³	(c)
2.2×10^{-11}	298	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with resonance fluorescence detection of HO radicals. NO₃ and HO₂ radical concentrations were measured by mass spectrometry. The HO radical time-dependence was followed in the presence of excess NO₃ radical concentrations. The rate coefficients obtained with HO radical production *in situ* from the H + NO₂ reaction and with injection of HO radicals from either the H + NO₂ or F + H₂O reactions were the same within the experimental errors. A complex kinetic analysis was required to extract the rate coefficients by computer simulation using a complex mechanism, taking account of secondary reactions of the HO₂ radical product. The average value is reported and the cited error refers to precision only.
- (b) Discharge flow system with LMR detection of HO and HO₂ radicals and NO₂. The H + NO₂ reaction was used to generate HO radicals, and NO₃ radicals were produced by the thermal decomposition of N₂O₅. NO₃ radicals were detected by titration with NO, monitoring the NO₂ product. The rate coefficient was determined by a pseudo first-order analysis with NO₃ in excess over HO. The average value of k is reported.
- (c) Mean of the data of Mellouki *et al.*⁵ and Boodaghians *et al.*⁶
- (d) Weighted average of the data from Refs. 1, 2, 5, and 6.

Preferred Values

$$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3.$$

Comments on Preferred Values

The two new measurements^{1,2} of this rate constant using the discharge flow technique at room temperature are not in good agreement. The rate coefficient reported by Mellouki *et al.*² is in good agreement with the two earlier determinations,^{5,6} but less accuracy is claimed. The rate coefficient of Becker *et al.*¹ is a factor of 2 lower and the discrepancy is well outside the claimed accuracy. In all systems corrections for secondary reactions were required, but the reasons for the discrepancies are not clear. The preferred value for k is a simple average of the 4 reported values.^{1,2,5,6} In the absence of experimental data a temperature dependence cannot be recommended. Consistent with other radical + radical reactions, a small negative temperature coefficient is expected.

References

- ¹E. Becker, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 776 (1992).
- ²A. Mellouki, R. K. Talukdar, A. M. R. P. Bopeggedera, and C. J. Howard, Int. J. Chem. Kinet. **25**, 25 (1993).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **92**, 2229 (1988).
- ⁶R. B. Boodaghians, C. E. Canosa-Mas, P. J. Carpenter, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2, **84**, 931 (1988).

$$\Delta H^\circ = -32.4 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.7 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–500 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The preferred value at 298 K is a mean of the five determinations of Hack *et al.*,¹ Howard,² Leu,³ Howard and Evenson,⁴ and Jemi-Alade and Thrush.⁵ The value reported by Glaschick-Schimpf *et al.*⁶ of $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is high, but in agreement within the stated uncertainty. The temperature dependence is that reported by Howard⁷ for the combined temperature range 232–1271 K, based on high

temperature data⁷ and the low temperature data of Howard.² This temperature dependence measured over a very large temperature range is preferred to that reported by Leu³ ($E/R = 130 \text{ K}$) obtained over a much smaller temperature range. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁸

References

- ¹W. Hack, A. W. Preuss, F. Temps, H. Gg. Wagner, and K. Hoyermann, *Int. J. Chem. Kinet.* **12**, 851 (1980).
- ²C. J. Howard, *J. Chem. Phys.* **71**, 2352 (1979).
- ³M.-T. Leu, *J. Chem. Phys.* **70**, 1662 (1979).
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- ⁵A. A. Jemi-Alade and B. A. Thrush, *J. Chem. Soc. Faraday Trans.* **86**, 3355 (1990).
- ⁶I. Glaschick-Schimpf, A. Leiss, P. B. Monkhouse, U. Schurath, K. H. Becker, and E. H. Fink, *Chem. Phys. Lett.* **67**, 318 (1979).
- ⁷C. J. Howard, *J. Am. Chem. Soc.* **102**, 6937 (1980).
- ⁸IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -105 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.8 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.10$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The latest data of Jemi-Alade and Thrush¹ are consistent with the series of earlier measurements reviewed in Refs. 2 and 3. Refinement of F_c by calculations will lead to minor modifications of k_0 .

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

A temperature independent value of k_∞ is chosen in agreement with other reaction systems. Improved falloff extrapolations would require measurements above 1 bar and the use of a calculated value of F_c different from a fixed $F_c = 0.6$. The preferred values of k_0 and k_∞ are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹A. A. Jemi-Alade and B. A. Thrush, *J. Chem. Soc. Faraday Trans.* **86**, 3355 (1990).
- ²CODATA, 1980 (see references in Introduction).
- ³IUPAC, Supplement III, 1989 (see references in Introduction).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 105 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.3 \times 10^{-20} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 5 \times 10^{-6} \exp(-10000/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 260\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

More studies of the dissociation reaction appear desirable. By combining the preferred values with the corresponding recombination results, an equilibrium constant of $K_c = 1.8 \times 10^{-27} \exp(10900/T) \text{ cm}^3 \text{ molecule}^{-1}$ is obtained, in close agreement with the evaluation of Ref. 1.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 0.34 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_\infty = 2.6 \times 10^{15} \exp(-10900/T) \text{ s}^{-1} \text{ over the temperature range } 260\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500.$$

responding high-pressure limit for the recombination reaction with the equilibrium constant K_c (see comment to preferred values of k_0) to obtain k_∞ . Since $F_c = 0.6$ was used for the falloff extrapolation of the recombination, an even larger value of k_∞ is expected if $F_c = 0.4$ is used.² These preferred values of k_0 and k_∞ are identical to our previous evaluation, IUPAC, 1992.³

References

Comments on Preferred Values

Because the falloff curves for recombination have been determined more systematically, we have combined the cor-

¹NASA Evaluation No. 11, 1994 (see references in Introduction).

²CODATA, Supplement I, 1982 (see references in Introduction).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -223.4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -15.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (1.9 \pm 0.8) \times 10^{-12}$	298	Becker, Rahman, and Schindler, 1992 ¹	(a)
$k_2 = (2.5 \pm 0.7) \times 10^{-12}$	298		
$(3.0 \pm 0.7) \times 10^{-12}$	297 ± 2	Mellouki <i>et al.</i> , 1993 ²	(b)
<i>Branching Ratios</i>			
$k_2/k = 1.0^{+0.0}_{-0.3}$	297	Mellouki <i>et al.</i> , 1993 ²	(b)
<i>Reviews and Evaluations</i>			
4.3×10^{-12}	298	IUPAC, 1992 ³	(c)
3.5×10^{-12}	298	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with resonance fluorescence detection of HO radicals. NO₃ and HO₂ radical concentrations were measured by mass spectrometry. The O₂ + CH₂OH reaction was used to generate HO₂ radicals, and NO₃ radicals were produced by the F + HNO₃ reaction. The HO₂ and HO radical time-dependence was monitored in the presence of excess concentrations of NO₃ radicals. The rate coefficient k_1 was inferred from the enhanced loss of HO₂ radicals following the attainment of a quasi-steady state of HO₂ and HO radicals due to secondary reactions of HO radicals with NO₃ radicals reforming HO₂ radicals. Rate coefficients k were obtained by computer simulation using a complex mechanism, taking account of secondary reactions of HO and HO₂ radicals including wall loss. The average values from 10 experiments is reported and the error limits refer to precision only.
- (b) Discharge flow system with LMR detection of HO and HO₂ radicals and NO₂. The H + O₂ + M reaction was used to generate HO₂ radicals. NO₃ radicals were produced by three methods: F + HNO₃, Cl + ClNO₃, and thermal decomposition of N₂O₅ and detected by titration with NO and monitoring the NO₂ product. NO₃ radicals were in >30 fold excess over HO₂ radicals and C₂F₃Cl was added to scavenge the HO radical product. The rate coefficient k was determined under pseudo first-order conditions. The average value of k was reported with estimated overall accuracy. The branching ratio is based on computer simulation of absolute time-dependencies of HO and HO₂ radicals using a simple mechanism.

- (c) Mean of the values from Mellouki *et al.*⁵ and Hall *et al.*⁶
- (d) Weighted average of data from Mellouki *et al.*,^{2,5} Hall *et al.*⁶ and Becker *et al.*¹

Preferred Values

$$k = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2.$$

Comments on Preferred Values

The two new measurements of this rate constant, using discharge flow techniques at room temperature, are in reasonably good agreement. While the measurement of the overall rate constant (k_1+k_2) by Becker *et al.*¹ is in good agreement with the two earlier determinations of $(4.5 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ⁵ and $4.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁶ the result of Mellouki *et al.*² is 30% lower. The three earlier studies^{1,5,6} propose that both channels (1) and (2) occur, but the branching ratio from the HO yields measured by Mellouki *et al.*,² which appears to be the most direct determination, suggests near a 100% reaction via the second channel. The preferred value for k is a weighted average of the 4 reported values.^{1,2,5,6} No recommendation is made for the branching ratio because of the experimental uncertainties. A temperature dependence was reported by Hall *et al.*,⁶ with $k = 2.3 \times 10^{-12} \exp[(170 \pm 270)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, but because of the large uncertainty no recommendation is given. In line with other radical + radical reactions, a small negative temperature coefficient is expected.

References

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²A. Mellouki, R. K. Talukdar, A. M. R. P. Bopegedera, and C. J. Howard, *Int. J. Chem. Kinet.* **25**, 25 (1993).
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⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
⁵A. Mellouki, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **92**, 2229 (1988).
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NH₂ + O₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$<6 \times 10^{-21}$	296	Tyndall <i>et al.</i> , 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$<3 \times 10^{-18}$	298	IUPAC, 1992 ²	(b)
$<6 \times 10^{-21}$	298	NASA, 1994 ³	(c)

Comments

- (a) Photolysis of NH₃ in the presence and absence of excess O₂. NO, NO₂, and N₂O products were measured by FTIR spectroscopy. The upper limit to the rate coefficient was based on a computer simulation with a complex reaction mechanism.
 (b) Based on the measurements of Lesclaux and Demissy,⁴ Cheskis and Sarkisov,⁵ Patrick and Golden,⁶ Lozovsky *et al.*,⁷ and Michael *et al.*⁸
 (c) Based on the data of Tyndall *et al.*¹

Preferred Values

$$k = <6 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

This reaction has several energetically feasible product channels, including NO + H₂O and HNO + HO. The new measurements of Tyndall *et al.*¹ of the upper limit to the rate

coefficient for all channels leading directly or indirectly to NO, NO₂ and N₂O confirm earlier conclusions that the reaction is very slow,^{4–8} and reduces the upper limit by three orders of magnitude. Systematic uncertainties in the system were identified which would cause an overestimate of the rate coefficient. The new upper limit is recommended, making this reaction unimportant in the atmosphere.

References

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NH₂ + O₃ → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.9 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}380 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred value is taken as the average of the results reported by Kurasawa and Lesclaux,¹ Bulatov *et al.*,² Hack *et al.*,³ Patrick and Golden,⁴ and Cheskis *et al.*⁵ The temperature dependence averages the values reported by Kurasawa and Lesclaux,¹ Hack *et al.*,³ and Patrick and Golden.⁴ Although the products of this reaction have not been determined, the most likely process is abstraction of an oxygen atom by NH₂ to give NH₂O + O₂. While it has been

suggested^{2,3} that NH_2 may be regenerated by reaction of NH_2O with O_3 , the study of Patrick and Golden⁴ indicates that this reaction must be slow. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁶

References

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⁵S. G. Cheskis, A. A. Iogansen, O. M. Sarkisov, and A. A. Titov, Chem. Phys. Lett. **120**, 45 (1985).
⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -517.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -18.4 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2+k_3$)

$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.6 \times 10^{-11} \exp(T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210–500 K.
 $(k_2+k_3)/k = 0.1$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta n = \pm 0.5$.
 $\Delta(k_2+k_3)/k = \pm 0.03$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is the average of the determinations of Atakan *et al.*¹ and Bulatov *et al.*² together with the values reported in Refs. 3–13. The temperature dependence is based on the data below 500 K in the six temperature dependence studies of Silver and Kolb,⁵ Stief *et al.*,⁶ Lesclaux *et al.*,¹² Hack *et al.*,¹³ Atakan *et al.*,¹ and Bulatov *et al.*²

The direct measurements of the branching ratio reported by Atakan *et al.*¹ are the basis for the recommendation for $(k_2+k_3)/k$. Other, less direct, rate coefficient ratio determinations are consistent with the value recommended, with the exception of the results of Andresen *et al.*⁷ who report that the production of HO dominates; this discrepancy has not been explained. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.¹⁴

References

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¹¹O. M. Sarkisov, S. G. Cheskis, and E. A. Sviridenkov, Bull. Acad. Sci. USSR, Chem. Ser. **27**, 2336, Eng. Trans. (1978).
¹²R. Lesclaux, P. V. Khe, P. Dezaudier, and J. C. Soullignac, Chem. Phys. Lett. **35**, 493 (1975).
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¹⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -378 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -355 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$k=2.0 \times 10^{-11} (T/298)^{-2.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.7$.

Comments on Preferred Values

The preferred value at 298 K is the average of the values from Bulatov *et al.*,¹ Whyte and Phillips,² Kurasawa and Leclaux,³ Xiang *et al.*,⁴ and Hack *et al.*⁵ The temperature dependence is the average from Refs. 1, 3, and 5. Hack *et al.*,⁵ using mass spectrometric analysis, determined that the predominant reaction channel is channel (1) to give N_2O

+ H_2O , with at least 95% of the reaction proceeding by this channel. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁶

References

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- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -114.1 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k=2.0 \times 10^{-38} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at 298 K.

$k=3.3 \times 10^{-39} \exp(530/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ over the temperature range 273–600 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

This evaluation accepts the recommendation given in the evaluation by Baulch *et al.*¹ Olbregts² observed non-Arrhenius behavior over the entire temperature range studied and expressed k by a modified Arrhenius expression and also as the sum of two Arrhenius expressions. However, from 250

K to about 600 K the total rate coefficient of Olbregts² is in good agreement with the value calculated from the expression recommended here. Olbregts² interpreted his results in terms of a multi-step mechanism involving NO_3 or the dimer $(\text{NO})_2$ as intermediates. For atmospheric modeling purposes, the expression recommended here is adequate. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹D. L. Baulch, D. D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Homogeneous Gas Phase Reactions of the H_2 - N_2 - O_2 System Vol. 2 (Butterworths, London, 1973).
- ²J. Olbregts, *Int. J. Chem. Kinet.* **17**, 835 (1985).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -199.8 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.8 \times 10^{-12} \exp(-1370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
the temperature range 195–304 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred Arrhenius expression is based on least-squares analysis of the data at and below room temperature reported by Michael *et al.*,¹ Borders and Birks,² Lippmann *et al.*,³ Ray and Watson,⁴ and Birks *et al.*,⁵ with data at closely spaced temperatures reported by Borders and Birks² and Lippmann *et al.*,³ being grouped to give equal weight to each of the five studies. The preferred expression fits these data to within 20%. Only data between 195 and 304 K were used due to the nonlinear Arrhenius behavior observed by Michael *et al.*,¹ Borders and Birks,² Birks *et al.*,⁵ Clyne *et al.*,⁶ and Clough and Thrush.⁷ Michael *et al.*,¹ Birks *et al.*,⁵ Clyne *et al.*,⁶ and Schurath *et al.*⁸ have reported individual Arrhenius parameters for each of two primary reaction

channels (one to produce NO₂ in the ground electronic state and the other to produce electronically excited NO₂). Earlier room-temperature results of Stedman and Niki⁹ and Bemand *et al.*¹⁰ are in good agreement with the preferred value. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.¹¹

References

- 1 J. V. Michael, J. E. Allen, Jr., and W. D. Brobst, *J. Phys. Chem.* **85**, 4109 (1981).
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- 11 IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -40.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.6 \pm 0.15) \times 10^{-33} [\text{He}]$	208	Smith and Yarwood, 1986 ¹	(a)
$(5.5 \pm 0.8) \times 10^{-33} [\text{Ar}]$	208		
$(4.2 \pm 0.3) \times 10^{-33} [\text{He}]$	206	Smith and Yarwood, 1987 ²	(b)
$(6.7 \pm 0.6) \times 10^{-33} [\text{Ar}]$	207		
$(5.0 \pm 0.4) \times 10^{-33} [\text{Ne}]$	203	Markwalder, Gozel, and van den Bergh, 1993 ³	(c)
$(9.1 \pm 0.7) \times 10^{-33} [\text{N}_2]$	208		
$(13.9 \pm 1.0) \times 10^{-33} [\text{CF}_4]$	208		
$(2.8 \pm 1.4) \times 10^{-33} [\text{Ar}]$	227		
$(2.8 \pm 2.8) \times 10^{-15} T^{-(7.7 \pm 0.8)} [\text{Ar}]$	227–260		

Comments

- Partial photolysis of N₂O₃ in equilibrium NO₂-N₂O₄-NO-N₂O₃-He (or Ar) mixtures. The relaxation to equilibrium was monitored by observing the transmittance of a cw CO laser selected to coincide with the ν_1 band of N₂O₃ at 1829.59 cm⁻¹. The total pressure was 190–660 Torr.
- Flash photolysis perturbation of NO₂-N₂O₄-N₂O₃ mixtures in excess of NO. N₂O₃ was monitored at the ν_1 band using a CO laser. Pressure was varied between 190–6970 Torr (He), 190–500 Torr (Ar), 248–6970 Torr (Ne), 166–401 Torr (N₂), and 132–441 Torr

(CF₄). Falloff curves were extrapolated using $F_c = 0.53, 0.60, 0.58, 0.62,$ and 0.65 for He, Ar, Ne, N₂, and CF₄, respectively. Collision efficiencies $\beta_c(\text{He}) = 0.14$, $\beta_c(\text{Ar}) = 0.33$, $\beta_c(\text{Ne}) = 0.26$, $\beta_c(\text{N}_2) = 0.42$, and $\beta_c(\text{CF}_4) = 0.60$ were derived from theoretical analysis of the data.

- CO₂ laser-induced temperature jump measurements with NO₂-N₂O₄-N₂O₃-NO-SiF₄-Ar mixtures. Temperature jumps of 0.5–3 K displace the equilibrium towards NO and NO₂. The subsequent relaxation toward equilibrium was monitored by UV absorption of N₂O₃ at 253 nm. Ar concentrations were varied from

0.5 to 200 bar. Extrapolations towards the limiting rate coefficients were made using $F_c=0.6$. A collisional efficiency of $\beta_c(\text{Ar})=0.3$ was derived by theoretical analysis.

Preferred Values

$k_0=2.3 \times 10^{-34} (T/300)^{-7.7} [\text{Ar}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 208–300 K.
 $k_0=3.1 \times 10^{-34} (T/300)^{-7.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 208–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values for $M=\text{Ar}$ are from Markwalder *et al.*³ The data recommended for $M=\text{N}_2$ are from rate coefficients of Ref. 3 for $M=\text{Ar}$ after conversion by the ratio $k_0(\text{N}_2)/k_0(\text{Ar})=1.36$ of Smith and Yarwood.²

High-pressure rate coefficients

Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.4 \pm 1) \times 10^{-12}$	208	Smith and Yarwood, 1987 ²	(a)
$(5.8 \pm 1.6) \times 10^{-12}$	227	Markwalder, Gozel, and van den Bergh, 1993 ³	(b)
$(2.7 \pm 0.9) \times 10^{-15} T^{(1.4 \pm 0.2)}$	227–260		

Comments

- (a) See comment (b) for k_0 .
 (b) See comment (c) for k_0 .

Comments on Preferred Values

The preferred values are those from Ref. 3 because larger pressure ranges were investigated. At 208 K, the k_∞ values from Refs. 2 and 3 are in reasonable agreement.

Preferred Values

$k_\infty=7.9 \times 10^{-12} (T/300)^{1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 208–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 0.5$.

References

- ¹I. W. M. Smith and G. Yarwood, Chem. Phys. Lett. **130**, 24 (1986).
²I. W. M. Smith and G. Yarwood, Faraday Discuss. Chem. Soc. **84**, 205 (1987).
³B. Markwalder, P. Gozel, and H. van den Bergh, J. Phys. Chem. **97**, 5260 (1993).

$$\Delta H^\circ = 40.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

k_0 / s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$5.0 \times 10^{14} T^{-(8.7 \pm 0.9)} \exp(-4880/T) [\text{Ar}]$	225–260	Markwalder, Gozel, and van den Bergh, 1993 ¹	(a)

Comments

- (a) CO_2 laser-induced temperature jump measurements with $\text{NO}_2\text{-N}_2\text{O}_4\text{-N}_2\text{O}_3\text{-NO-SiF}_4\text{-Ar}$ mixtures. Temperature jumps of 0.5–3 K displace the equilibrium towards NO and NO_2 . The subsequent relaxation toward equilibrium was monitored by UV absorption of

N_2O_3 at 253 nm. Ar concentrations were varied from 0.5 to 200 bar. Extrapolations towards the limiting recombination rate coefficients were made using $F_c=0.6$. A collisional efficiency of $\beta_c(\text{Ar})=0.3$ was derived by theoretical analysis. Dissociation rate coefficients were derived from the measured recombination rate coefficients and the equilibrium constant from

Chao *et al.*² of $K_c = 1.8 \times 10^{29} T^{-1} \exp(-4880/T)$ molecule cm^{-3} .

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.

$\Delta n = \pm 1$.

$\Delta(E/R) = \pm 200$ K.

Preferred Values

$k_0 = 1.6 \times 10^{-14} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

$k_0 = 1.4 \times 10^{-7} (T/300)^{-8.7} \exp(-4880/T) [\text{Ar}] \text{ s}^{-1}$ over the temperature range 225–300 K.

$k_0 = 1.9 \times 10^{-7} (T/300)^{-8.7} \exp(-4880/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 225–300 K.

Comments on Preferred Values

The rate coefficients of Ref. 1 are adopted here for $M = \text{Ar}$. The preferred values for $M = \text{N}_2$ are obtained by converting $k_0(\text{Ar})$ into $k_0(\text{N}_2)$ using $k_0(\text{N}_2)/k_0(\text{Ar}) = 1.36$ from Smith and Yarwood³ (see reaction $\text{NO} + \text{NO}_2 + M \rightarrow \text{N}_2\text{O}_3 + M$).

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{14} T^{(0.4 \pm 0.1)} \exp(-4880/T)$	225–260	Markwalder, Gozel, and van den Bergh, 1993 ¹	(a)

Comments

(a) See comment (a) for k_0 .

Comments on Preferred Values

The preferred values are from Ref. 1, using the equilibrium constant of Ref. 2.

Preferred Values

$k_\infty = 3.6 \times 10^8 \text{ s}^{-1}$ at 298 K.

$k_\infty = 4.7 \times 10^{15} (T/300)^{0.4} \exp(-4880/T) \text{ s}^{-1}$ over the temperature range 225–300 K.

References

¹B. Markwalder, P. Gozel, and H. van den Bergh, *J. Phys. Chem.* **97**, 5260 (1993).

²J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *Thermochim. Acta* **10**, 359 (1974).

³I. W. M. Smith and G. Yarwood, *Faraday Discuss. Chem. Soc.* **84**, 205 (1987).

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

$\Delta(E/R) = \pm 100$ K.

$$\Delta H^\circ = -97.6 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.8 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature values reported by Hammer *et al.*,¹ Sander and Kircher,² and Tyndall *et al.*,³ which are in excellent agreement. The preferred temperature dependence is the average of the temperature dependences reported by Sander and Kircher² and by Tyndall *et al.*,³ which are in excellent agreement. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

References

- ¹P. D. Hammer, E. J. Dlugokencky, and C. J. Howard, *J. Phys. Chem.* **90**, 2491 (1986).
- ²S. P. Sander and C. C. Kircher, *Chem. Phys. Lett.* **126**, 149 (1986).
- ³G. S. Tyndall, J. J. Orlando, C. A. Cantrell, R. E. Shetter, and J. G. Calvert, *J. Phys. Chem.* **95**, 4381 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -102.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.2 \times 10^{-13} \exp(-2450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–360 K.

The results of Verhees and Adema⁵ show a similar temperature dependence but a higher preexponential factor. It was shown that wall reactions played an important role in this study.⁵ The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁶

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
 $\Delta(E/R) = \pm 150 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the data on the three temperature-dependent studies of Davis *et al.*,¹ Graham and Johnston,² and Huie and Herron.³ The results of Cox and Coker⁴ are in excellent agreement with this recommendation.

References

- ¹D. D. Davis, J. Prusazcyk, M. Dwyer, and P. Kim, *J. Phys. Chem.* **78**, 1775 (1974).
- ²R. A. Graham and H. S. Johnston, *J. Chem. Phys.* **60**, 4628 (1974).
- ³R. E. Huie and J. T. Herron, *Chem. Phys. Lett.* **27**, 411 (1974).
- ⁴R. A. Cox and G. B. Coker, *J. Atmos. Chem.* **1**, 53 (1983).
- ⁵P. W. C. Verhees and E. H. Adema, *J. Atmos. Chem.* **2**, 387 (1985).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -57.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.4 \pm 0.2) \times 10^{-33} [\text{N}_2]$	298	Borrell, Cobos, and Luther, 1988 ¹	(a)
$(2.4 \pm 0.5) \times 10^{-34} [\text{He}]$	224	Bunning, Frost, and Smith, 1988 ²	(b)
$(1.0 \pm 0.1) \times 10^{-33} [\text{N}_2]$	224		
$(1.8 \pm 0.3) \times 10^{-33} [\text{CF}_4]$	224		
$(2.1 \pm 0.2) \times 10^{-12} T^{(-9.0 \pm 0.9)} [\text{He}]$	255–273	Markwalder, Gozel, and van den Bergh, 1992 ³	(c)
<i>Reviews and Evaluations</i>			
$4.7 \times 10^{-35} \exp(860/T) [\text{N}_2]$	250–350	Baulch, Drysdale, and Horne, 1973 ⁴	(d)

Comments

- (a) Relaxation of NO_2 - N_2O_4 - N_2 mixtures after laser flash photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was observed by measuring the change in N_2O_4 absorption at 220 nm. Falloff curves (1–207 bar) were extrapolated with $F_c = 0.40$ and $N = 1.26$. From a theoretical analysis in terms of the unimolecular rate theories, an average energy transferred per collision of -560 cm^{-1} was derived.
- (b) Perturbation of equilibrium mixtures of N_2O_4 and NO_2 by photolysis of a fraction of the N_2O_4 . The relaxation rate was monitored by IR absorption of N_2O_4 at 1565.5 cm^{-1} . Relative collisional efficiencies of $\beta_c(\text{He}) : \beta_c(\text{N}_2) : \beta_c(\text{CF}_4) = 0.2 : 1 : 1.9$ were reported.
- (c) Temperature jumps of the order of 1 K were induced

by IR absorption of SiF₄ in equilibrium mixtures of NO₂-N₂O₄-He-SiF₄. The kinetics of the relaxation to equilibrium were followed by measuring the NO₂ and N₂O₄ concentrations by absorption spectroscopy at 420 and 250 nm, respectively. Falloff curves (0.3–200 bar) were extrapolated with $F_c=0.52$ and $N=1.10$.

- (d) Based on data for the reverse reaction previous to 1970 and their tabulated equilibrium constant.⁴

Preferred Values

$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–500 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from the most extensive data of Ref. 1, where a complete falloff curve was measured. Earlier less extensive measurements are in reasonable agreement with this curve, which uses $F_c=0.40$. The temperature dependence given is from the theoretical modeling of Ref. 1, rather than the limited experimental information of Ref. 3.

High-pressure rate coefficients

Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(8.3 \pm 1.0) \times 10^{-13}$	298	Borrell, Cobos, and Luther, 1988 ¹	(a)
$(3.7 \pm 0.3) \times 10^{-18} T^{(2.3 \pm 0.2)}$	255–273	Markwalder, Gozel, and van den Bergh, 1992 ³	(b)

Comments

- (a) See comment (a) for k_0 .
(b) See comment (b) for k_0 .

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient is the mean of the values of Borrell *et al.*¹ and Markwalder *et al.*³ The temperature dependences of k_0 and k_∞ derived from the measurements of Ref. 3 appear unrealistic and are due to fitting of incomplete falloff curves.

Preferred Values

$k_\infty = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–300 K.

Intermediate falloff range

Rate coefficient data

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
3.3×10^{-15}	60	Ar	258	Gozel, Calpini, and van den Bergh, 1984 ⁵	(a)
1.7×10^{-14}	770	Ar	258		

Comments

- (a) Temperature-jump relaxation study, similar to Comment (c) for k_0 .

References

¹P. Borrell, C. J. Cobos, and K. Luther, *J. Phys. Chem.* **92**, 4377 (1988).

²J. Brunning, M. J. Frost, and I. W. M. Smith, *Int. J. Chem. Kinet.* **20**, 957 (1988).

³B. Markwalder, P. Gozel, and H. van den Bergh, *J. Chem. Phys.* **97**, 5472 (1992).

⁴D. L. Baulch, D. D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System Vol. 2 (Butterworths, London, 1973).

⁵P. Gozel, B. Calpini, and H. van den Bergh, *Isr. J. Chem.* **24**, 210 (1984).

$$\Delta H^\circ = 57.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.29 \times 10^{-5} (T/300)^{-3.8} \exp(-6460/T) [\text{N}_2]$	300–500	Borrell, Cobos, and Luther, 1988 ¹	(a)
$1.6 \times 10^{19} T^{(-10.0 \pm 1.0)} \exp[-(6790 \pm 700)/T] [\text{He}]$	255–273	Markwalder, Gozel, and van den Bergh, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
$4.2 \times 10^{-7} \exp(-5550/T) [\text{N}_2]$	250–350	Baulch, Drysdale, and Horne, 1973 ³	(c)

Comments

- (a) Relaxation of NO_2 - N_2O_4 - N_2 mixtures after laser flash photolysis of N_2O_4 at 248 nm. The relaxation to equilibrium was observed by measuring the change in N_2O_4 absorption at 220 nm. Falloff curves (1–207 bar) were extrapolated with $F_c=0.40$ and $N=1.26$. The equilibrium constant from Ref. 4 was employed.
- (b) Temperature jumps of the order 1 K were induced by IR absorption of SiF_4 in equilibrium mixtures of NO_2 - N_2O_4 -He- SiF_4 . The kinetics of the relaxation to equilibrium were followed by measuring the NO_2 and N_2O_4 concentrations by absorption spectroscopy at 420 and 250 nm, respectively. Falloff curves (0.3–200 bar) were extrapolated with $F_c=0.52$ and $N=1.10$. Equilibrium constants from Ref. 5 were employed.
- (c) Based on the shock-wave studies of Refs. 6 and 7.

Preferred Values

$$k_0 = 6.1 \times 10^{-15} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.3 \times 10^{-5} (T/300)^{-3.8} \exp(-6400/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 300\text{--}500 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred values are from the measurements of Ref. 1 in combination with the equilibrium constants from Ref. 4. These data are based on the most complete falloff curve at 300 K, using $F_c=0.40$. The temperature dependence is from a theoretical analysis, in good agreement with the evaluation from Ref. 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
<i>Reviews and Evaluations</i>			
$7.7 \times 10^{15} (T/300)^{-1.1} \exp(-6460/T)$	300–600	Borrell, Cobos, and Luther, 1988 ¹	(a)
$2.8 \times 10^{13} T^{(1.3 \pm 0.2)} \exp[-(6790 \pm 700)/T]$	255–273	Markwalder, Gozel, and van den Bergh, 1992 ²	(b)

Comments

- (a) See comment (a) for k_0 .
- (b) See comment (b) for k_0 .

Reliability

$$\Delta \log k_\infty = \pm 0.4 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred rate coefficient at room temperature is the average of the values of Borrell *et al.*¹ and Markwalder *et al.*² The recommended temperature coefficient corresponds to a temperature-independent value of k_∞ for the reverse recombination.

Preferred Values

$$k_\infty = 4.4 \times 10^6 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_\infty = 1.15 \times 10^{16} \exp(-6460/T) \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Intermediate falloff range

Rate coefficient data

k/s^{-1}	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
6.1×10^{-15}	760	NO ₂ /N ₂ O ₄	298	Fiedler and Hess, 1990 ⁸	(a)
$(4.3 \pm 0.8) \times 10^{-15}$	2.2–6.5	NO ₂ /N ₂ O ₄	298	Van Roozendaal and Herman, 1990 ⁸	(b)

Comments

- (a) Chemical relaxation of N₂O₄ was studied by Ar ion laser excited acoustic resonances of a cylindrical cavity. The reaction was investigated by measuring resonances profiles of the first radial mode. An activation energy of 36 kJ mol⁻¹ was derived between 273 and 317 K. The efficiency of collision varied between 0.96 and 0.5 over the range 273–317 K.
- (b) Nonresonant optoacoustic experiments in NO₂-N₂O₄ mixtures. NO₂ was monitored by IR absorption at 1601 cm⁻¹.

References

- ¹P. Borrell, C. J. Cobos, and K. Luther, *J. Phys. Chem.* **92**, 4377 (1988).
²B. Markwalder, P. Gozel, and H. van den Bergh, *J. Chem. Phys.* **97**, 5472 (1992).
³D. L. Baulch, D.D. Drysdale, and D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions*, Homogeneous Gas Phase Reactions of the H₂-N₂-O₂ System Vol. 2 (Butterworths, London, 1973).
⁴J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *Thermochim. Acta* **10**, 359 (1974).
⁵A. J. Vosper, *J. Chem. Soc.* **A1**, 625 (1970).
⁶T. Carrington and N. Davidson, *J. Phys. Chem.* **57**, 418 (1953).
⁷E. Zimet, *J. Chem. Phys.* **53**, 315 (1970).
⁸M. Fiedler and P. Hess, *J. Chem. Phys.* **93**, 8693 (1990).
⁹M. Van Roozendaal and M. Herman, *Chem. Phys. Lett.* **166**, 233 (1990).

$$\Delta H^\circ = -95.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 2.7 \times 10^{-30} (T/300)^{-3.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–400 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.10 \text{ at 298 K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The results of Orlando *et al.*¹ are in excellent agreement with our previous recommended values,² which are also adopted here.

High-pressure rate coefficients

Preferred Values

$$k_\infty = 2.0 \times 10^{-12} (T/300)^{0.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–500 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.2 \text{ at 298 K.}$$

$$\Delta n = \pm 0.6.$$

Comments on Preferred Values

Very good agreement between the rate coefficients reported by Orlando *et al.*¹ and our previously recommended values² are observed. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹J. J. Orlando, G. S. Tyndall, C. A. Cantrell, and J. G. Calvert, *J. Chem. Soc. Faraday Trans.* **87**, 2345 (1991).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 95.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.04 \times 10^{-3} (T/300)^{-3.5} \exp(-11000/T) [\text{N}_2]$	253–384	Cantrell <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.2 \times 10^{-3} (T/300)^{-4.4} \exp(-11080/T) [\text{N}_2]$	220–300	IUPAC, 1992 ²	(b)
$8.2 \times 10^{-4} (T/300)^{-3.9} \exp(-11000/T) [\text{air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Thermal decomposition of N_2O_5 in the presence of NO in N_2 . FTIR analysis of N_2O_5 in a stainless steel cell equipped with multiple path optics. Falloff curves over the gas density 4.3×10^{14} to 1.1×10^{20} molecule cm^{-3} were analyzed using $F_c = [2.5 \exp(-1950/T) + 0.9 \exp(-T/430)]$. In the analysis, data from Refs. 4 and 5 were also taken in account.
- (b) Based on the recommendation of a previous evaluation.⁶
- (c) Rate coefficients evaluated from the recommended rate coefficients for the reverse reaction and the equilibrium constant.

$k_0 = 1.0 \times 10^{-3} (T/300)^{-3.5} \exp(-11000/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The recommended values of the previous evaluation² have been slightly modified according to the recent study of Cantrell *et al.*¹ In this way both the preferred values of the recombination and dissociation low-pressure rate coefficients and the recommended values for the recombination and dissociation high-pressure rate coefficients are internally consistent through the same equilibrium constant. The equilibrium constant at room temperature of $2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ compares well with other recently reported values.^{7,8}

Preferred Values

$$k_0 = 9.5 \times 10^{-20} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.22 \times 10^{14} (T/300)^{-0.2} \exp(-11000/T)$	253–384	Cantrell <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$9.7 \times 10^{14} (T/300)^{0.1} \exp(-11080/T)$	200–300	IUPAC, 1992 ²	(b)
$5.5 \times 10^{14} (T/300)^{-0.7} \exp(-11000/T)$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 .
- (b) See comment (b) for k_0 .
- (c) See comment (c) for k_0 .

$k_\infty = 9.7 \times 10^{14} (T/300)^{0.1} \exp(-11080/T) \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.2$.

Preferred Values

$$k_\infty = 6.9 \times 10^{-2} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992,² and agree well with the recent

determination.¹ For the equilibrium constant, see comments on preferred values for k_0 .

References

¹C. A. Cantrell, R. E. Shetter, J. G. Calvert, G. S. Tyndall, and J. J. Orlando, *J. Phys. Chem.* **97**, 9141 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴P. Connell and H. S. Johnston, *Geophys. Res. Lett.* **6**, 553 (1979).

⁵A. A. Viggiano, J. A. Davidson, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.* **74**, 6113 (1981).

⁶CODATA, Supplement I, 1982 (see references in Introduction).

⁷J. Hjorth, J. Notholt, and G. Restelli, *Int. J. Chem. Kinet.* **24**, 51 (1992).

⁸H. O. Pritchard, *Int. J. Chem. Kinet.* **26**, 61 (1994).

$$\Delta H^\circ = -39.6 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k < 2 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

This upper limit is based on the data of Tuazon *et al.*,¹ Atkinson *et al.*,² Hjorth *et al.*,³ and Hatakeyama and Leu.⁴ It is possible that the observed decays proceed only by heterogeneous processes. While the lower value of Sverdrup *et al.*⁵ may in fact be closer to the value of the rate coefficient for the homogeneous gas phase reaction, because it is less direct we prefer the more conservative recommendation given here. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.⁶

References

¹E. C. Tuazon, R. Atkinson, C. N. Plum, A. M. Winer, and J. N. Pitts, Jr., *Geophys. Res. Lett.* **10**, 953 (1983).

²R. Atkinson, E. C. Tuazon, H. Mac Leod, S. M. Aschmann, and A. M. Winer, *Geophys. Res. Lett.* **13**, 117 (1986).

³J. Hjorth, G. Ottobriani, F. Cappellani, and G. Restelli, *J. Phys. Chem.* **91**, 1565 (1987).

⁴S. Hatakeyama and M.-T. Leu, *J. Phys. Chem.* **93**, 5784 (1989).

⁵G. M. Sverdrup, C. W. Spicer, and G. F. Ward, *Int. J. Chem. Kinet.* **19**, 191 (1987).

⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{HONO} + h\nu \rightarrow \text{HO} + \text{NO}$ (1)	209	572
$\rightarrow \text{H} + \text{NO}_2$ (2)	331	361
$\rightarrow \text{HNO} + \text{O}(^3\text{P})$ (3)	428	280

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(\text{H})$	355	Burkholder <i>et al.</i> , 1992 ¹	(a)

Comments

- (a) Relative yield of H atoms inferred from secondary HO production observed in the laser photolysis of HONO

at 355 nm. HO radicals were produced via the reaction: $\text{H} + \text{NO}_2 \rightarrow \text{HO} + \text{NO}$, involving impurity NO_2 . The data obtained were consistent with $\phi_2=0.1$ at 355 nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
190	127	260	8.0	330	10.9
195	172	265	5.2	335	7.7
200	197	270	3.4	340	19.7
205	220	275	2.5	345	11.2
210	214	280	-	350	13.4
215	179	285	-	355	27.6
220	146	290	-	360	9.4
225	120	295	-	365	18.8
230	86	300	0.0	370	24.0
235	60	305	0.8	375	5.7
240	42	310	1.9	380	10.8
245	30	315	2.9	385	16.9
250	18.5	320	5.2	390	2.8
255	12.4	325	5.8	395	0.7

Quantum Yields

$\phi_1 + \phi_2 + \phi_3 = 1.0$ throughout this wavelength range.

$\phi_1 = 1.0$ at $\lambda > 366$ nm, decreasing to 0.4 at $\lambda = 310$ nm.

$\phi_2 = 0.0$ at $\lambda > 366$ nm, increasing to 0.6 at $\lambda = 310$ nm.

Comments on Preferred Values

The preferred values for the cross-sections in the 300–395 nm range, which are unchanged from our previous IUPAC evaluation,² are obtained from the data of Bongartz *et al.*³ by averaging their 0.5 nm intervals centered on the wavelengths specified in the table.

The laser photolysis experiments of Burkholder *et al.*¹ in the first absorption band at 355 nm show strong indirect evidence for the production of H atoms in HONO photolysis

at wavelengths below the threshold for reaction (2), as originally proposed by Cox.⁴ Further evidence for an increasing contribution from reaction (2) with decreasing wavelength in the first absorption band comes from a comparison of the relative absorption spectra determined by conventional light absorption methods and by laser photofragment spectroscopy of the HO radical product from channel (1). When the spectra are normalized to peaks at $\lambda > 370$ nm, the cross-section values of Vasudev⁵ at $\lambda < 350$ nm obtained from the HO radical yield are consistently smaller than those measured in absorption by Bongartz *et al.*³ The difference increases approximately linearly to approximately 60% at 310 nm. This difference could be attributed to a decrease in $\phi(\text{HO})$ from unity at 366 nm to 0.4 at 310 nm. The balance could be attributed to H atom production, ϕ_2 , with $\phi_1 + \phi_2 = 1.0$ in the first absorption band.

In the second absorption band, cross-sections over the range 185–275 nm are based on the data of Kenner *et al.*,⁶ which also show that reaction (1) is the main photodissociation channel in this region. However, in view of the clear indication of H atom production in the first absorption band a contribution from reaction (2) at shorter wavelengths seems likely.

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HONO₂ + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HONO ₂ + $h\nu \rightarrow$ HO + NO ₂	(1)	200	598
$\rightarrow$ HONO + O(³ P)	(2)	298	401
$\rightarrow$ H + NO ₃	(3)	418	286
$\rightarrow$ HONO + O(¹ D)	(4)	488	245
$\rightarrow$ HO + NO + O(³ P)	(5)	499	239

Absorption cross-section data

Wavelength range/nm	References	Comments
195–350	Burkholder <i>et al.</i> , 1993 ¹	(a)

Comments

- (a) The temperature dependence of HNO_3 absorption cross-sections were measured using a diode array spectrometer with a resolution of <0.4 nm between 240–360 K. Absorption cross-sections were determined using both absolute pressure measurements at 298 K and

a dual cell arrangement to measure absorption at various temperatures relative to 298 K. A review of all previous experimental values was given together with an assessment of temperature-dependence effects on the stratospheric photolysis rates of HNO_3 .

Quantum yield data

Measurement	Wavelength/nm	Reference	Comment
ϕ [HO], ϕ [$\text{O}({}^3\text{P})$], ϕ [$\text{O}({}^1\text{D})$], ϕ [$\text{H}({}^2\text{S})$]	248, 222, 193	Turnipseed <i>et al.</i> , 1992 ²	(b)
ϕ [HO]	248, 193	Schiffman, Nelson, and Nesbitt, 1993 ³	(c)
$\phi(1)$, $\phi(4)$, $\phi(5)$	193	Felder, Yang, and Huber, 1993 ⁴	(d)

Comments

- (a) Quantum yields for HO radicals, $\text{O}[({}^3\text{P})+({}^1\text{D})]$ atoms, $\text{O}({}^1\text{D})$ atoms and H atoms were measured in pulsed laser photolysis systems at 248, 222, and 193 nm, using LIF detection for $\text{HO}(\text{X}^2\Pi)$ radicals and atomic resonance fluorescence for $\text{O}({}^3\text{P})$ and $\text{H}({}^2\text{S})$ atoms. ϕ [HO] was measured relative to the yield of HO radicals from H_2O_2 photolysis (ϕ [HO]=2.0 at 248 nm⁴ and ϕ [HO]=1.5 at 193 nm⁵). ϕ [$\text{O}({}^3\text{P})+({}^1\text{D})$] was measured relative to the O atom yield from ozone photolysis at 248 nm ($\phi=1$) and 193 nm ($\phi=1.2$).⁶ ϕ [$\text{H}({}^2\text{S})$] was measured relative to the H atom yield from the photolysis of O_3/H_2 mixtures where the H atoms are produced in the $\text{O}({}^1\text{D}) + \text{H}_2$ reaction. Measurements gave: ϕ [HO]= 0.95 ± 0.09 at 248 nm, 0.90 ± 0.11 at 222 nm, and 0.33 ± 0.06 at 193 nm. ϕ [$\text{O}({}^3\text{P})+({}^1\text{D})$] was observed to be 0.031 ± 0.010 , 0.20 ± 0.03 , 0.81 ± 0.13 at 248, 222, and 193 nm respectively, with exclusively $\text{O}({}^3\text{P})$ production at 248 nm. ϕ [$\text{O}({}^1\text{D})$] was 0.074 ± 0.03 at 222 nm and 0.28 ± 0.13 at 193 nm. H atom yields were very low; only at 193 nm were any H atoms detected with ϕ [$\text{H}({}^2\text{S})$] < 0.012 .
- (b) Absolute quantum yields were measured for HO radical production from 248 nm and 193 nm pulsed laser photolysis of HNO_3 and H_2O_2 in a flow tube. HO radicals were detected by tunable diode laser absorption. ϕ [HO] was measured to be 0.47 ± 0.06 and 0.75 ± 0.10 at 193 and 248 nm, respectively. Equivalent values for HO radical yields from H_2O_2 photolysis were $\phi=1.22 \pm 0.13$ and $\phi=1.58 \pm 0.23$, respectively.
- (c) Photofragment translation spectroscopy investigation

of HONO_2 photolysis at 193 nm. The primary processes and their relative yields were deduced from photofragment time-of-flight signals at masses 16 (O^+), 17 (OH^+), 30 (NO^+), and 46 (NO_2^+). Relative yields for reactions (1) and (4) of 0.6 ± 0.1 and 0.4 ± 0.1 , respectively, were obtained. Hot NO_2 photofragments were produced in reaction (1) in the ratio 2:1, relative to stable NO_2 , leading to production of $\text{O}({}^3\text{P})$ atoms via reaction channel (5).

Preferred Values

Absorption cross-sections at 298 K^a

λ/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$	λ/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
190	1360	0	270	1.62	1.45
195	1016	0	275	1.38	1.60
200	588	1.66	280	1.12	1.78
205	280	1.75	285	0.858	1.99
210	104	1.97	290	0.615	2.27
215	36.5	2.17	295	0.412	2.61
220	14.9	2.15	300	0.263	3.10
225	8.81	1.90	305	0.150	3.64
230	5.75	1.80	310	0.081	4.23
235	3.75	1.93	315	0.041	5.20
240	2.58	1.97	320	0.020	6.45
245	2.11	1.68	325	0.0095	7.35
250	1.97	1.34	330	0.0043	9.75
255	1.95	1.16	335	0.0022	10.1
260	1.91	1.14	340	0.0010	11.8
265	1.80	1.20	345	0.0006	11.2
			350	0.0004	9.30

^aTemperature dependence given by the expression: $\log_e \sigma = \log_e \sigma(298) + B(T-298)$ with T in K.

Quantum yields

	λ/nm		
	≥ 248	222	193
$\phi(1) + \phi(5)$	> 0.97	0.90 ± 0.10	0.60 ± 0.20
$\phi(2)$	0.03 ± 0.03		
$\phi(3)$	< 0.01	< 0.01	0.01
$\phi(4)$		0.10 ± 0.10	0.39 ± 0.20
$\phi(5)$		0.13 ± 0.03	0.40 ± 0.20

Comments on Preferred Values

The new results of Burkholder *et al.*¹ for the cross-section provide a high quality and comprehensive data set over the range of temperatures and wavelengths of significance for the atmospheric photolysis of HNO_3 . Over the wavelength range 205–310 nm there is good agreement with the earlier studies of Rattigan *et al.*,⁵ Biaume,⁶ Molina and Molina,⁷ and Johnston and Graham.⁸ At $\lambda < 205$ nm, the data from different studies show small but unexplained discrepancies. At $\lambda > 310$ nm the room temperature results¹ are increasingly higher than all previously reported data except that of Rattigan *et al.*,⁵ which is in good agreement. Values recommended previously by NASA⁹ and IUPAC¹⁰ on the basis of earlier data are therefore too low. The preferred values are those given by Burkholder *et al.*¹

The temperature dependence reported by Burkholder *et al.*¹ is weaker than that reported previously by Rattigan *et al.*⁵ However, if the data at the lowest temperature (239 K) from Ref. 5 is omitted the agreement is good, and Burkholder *et al.*¹ give values for the temperature coefficient, B , based on the two data sets^{1,5} (excluding the 239 K data from Ref. 5), and these are adopted here.

The new data for the quantum yield confirm that, although reaction (1) is the dominant channel at $\lambda \geq 260$ nm with $\phi(1)$ close to unity, other channels become important at shorter wavelengths as suggested by the earlier work of Kenner *et al.*¹¹ The results of Turnipseed *et al.*² and Schiffman *et al.*³ are in excellent agreement at 248 nm when the relative measurements of Turnipseed *et al.*² are normalized to the same value of the quantum yield for HO radical production from H_2O_2 . The agreement is less good at 193 nm, where the direct measurements of Schiffman *et al.*³ give an HO radical yield higher by about 50%. The value of $\phi(\text{H}_2\text{O}_2)$ obtained by Schiffman *et al.*³ is about 25% lower at both 248 and 193 nm than the values obtained by Vaghjiani *et al.*¹² (2.0 at 248 nm and 1.5 at 193 nm) which are recommended in the present evaluation.

The preferred values of the quantum yields $\phi(1) + \phi(5)$ [HO production] are based on the indirect studies of Johnston *et al.*¹³ and the direct observations of Jolly *et al.*¹⁴

at 222 nm, Turnipseed *et al.*,² and Felder *et al.*⁴ The data of Schiffman *et al.*³ are not used in view of the inconsistency of their absolute $\phi(\text{HO})$ values for H_2O_2 dissociation. At 193 nm, O-atom production becomes a major channel but HO and O production is not mutually exclusive since reaction (5) can occur at $\lambda \leq 239$ nm, either through excited NO_2^* or HONO^* . Felder *et al.*⁴ show that $\phi(5) = 0.4$ at 193 nm. Ground state HONO is the likely co-product of $\text{O}(^1\text{D})$ atoms and hence the data of Turnipseed *et al.*² imply $\phi(4) = 0.28$ at 193 nm and 0.074 at 222 nm, which is consistent within the experimental uncertainty with the results of Felder *et al.*⁴ In the absence of direct measurements of HONO at longer wavelengths, $\phi(2)$ cannot be determined; this channel is probably responsible for the small amount of O-atom production at $\lambda \geq 239$ nm, as measured, for example, by Margitan and Watson¹⁵ with $\phi[\text{O}(^3\text{P})] = 0.03$ at 266 nm. The data of Turnipseed *et al.*² show that H atom production, and hence $\phi(3)$, is significant only at 193 nm with $\phi(3) = < 0.012$.

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HO₂NO₂ + *hν* → products**Primary photochemical transitions**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HO ₂ NO ₂ + <i>hν</i> → HO ₂ + NO ₂ (1)	105	1141
→ HO + NO ₃ (2)	170	704

Preferred Values**Absorption cross-sections at 296 K**

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
190	1010	260	28.4
195	816	265	22.9
200	563	270	18.0
205	367	275	13.3
210	239	280	9.3
215	161	285	6.2
220	118	290	3.9
225	93.2	295	2.4
230	78.8	300	1.4
235	68.0	305	0.85
240	57.9	310	0.53
245	49.7	315	0.39
250	41.1	320	0.24
255	34.9	325	0.15
		330	0.09

Quantum Yields

$$\phi_1 = 0.61.$$

$$\phi_2 = 0.39.$$

Comments on Preferred Values

The preferred absorption cross-section values are based on the data of Singer *et al.*¹ and Molina and Molina,² which are in excellent agreement at wavelengths between 210–300 nm. Between 300 and 320 nm the cross-sections of Singer *et al.*¹ are approximately a factor of 2 lower. A simple mean of the two data sets is taken over the whole range.

For the quantum yield we recommend values based on the measurements of Mac Leod *et al.*,³ with a small upward revision to take into account the present recommendation for the absorption cross-section for H₂O₂. The uncertainties on the quantum yields are large and it should be noted that they are based on data at a single wavelength. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

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NO₂ + *hν* → products**Primary photochemical transitions**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
NO ₂ + <i>hν</i> → NO + O(³ P) (1)	300	398
→ NO + O(¹ D) (2)	490	244

Absorption cross-section data

Wavelength range/nm	Reference	Comments
440–460	Amoruso <i>et al.</i> , 1993 ¹	(a)
310–570	Harwood and Jones, 1994 ²	(b)

Comments

- (a) Measurements of the NO₂ absorption cross-section in a limited wavelength range, with estimates of the NO₂-N₂O₄ equilibrium constant.
- (b) Cross-sections measured over the temperature range of 213–298 K and with NO₂ concentrations of (1.5–20.0) × 10¹⁵ molecule cm⁻³ using a diode array spectrometer. Absorption due to N₂O₄ was corrected for using data for the cross-sections for N₂O₄ and K_p for dimerization of NO₂ determined simultaneously in the same experiments. The spectral resolution was 0.54 nm FWHM. Averaged cross-sections over 5 nm intervals were given as well as high-resolution data.

Preferred Values

Absorption cross-sections^a

λ/nm	10 ²⁰ σ/cm ²	λ/nm	10 ²⁰ σ/cm ²	λ/nm	10 ²⁰ σ/cm ²
190		315	21.53	440	45.52
195		320	24.77	445	46.58
200		325	28.07	450	47.58
205	43.06	330	31.33	455	40.02
210	47.20	335	34.25	460	41.85
215	49.54	340	37.98	465	39.65
220	45.61	345	40.65	470	32.38
225	37.88	350	43.13	475	36.78
230	27.39	355	47.17	480	31.97
235	16.69	360	48.33	485	24.19
240	9.31	365	51.66	490	28.95
245	4.74	370	53.15	495	27.09
250	2.48	375	55.08	500	17.22
255	1.95	380	56.44	505	22.48
260	2.24	385	57.57	510	21.61
265	2.73	390	59.27	515	14.95
270	4.11	395	58.45	520	15.00
275	4.90	400	60.21	525	16.58
280	5.92	405	57.81	530	14.18
285	7.39	410	59.99	535	9.88
290	9.00	415	56.51	540	10.10
295	10.91	420	58.12	545	11.83
300	13.07	425	53.81	550	10.17
305	15.73	430	50.81	555	7.34
310	18.61	435	51.70	560	5.62
				565	7.87

^aAbsorption cross-sections in the range 190–565 nm, averaged over 5 nm intervals, are independent of temperature.

Quantum Yields

λ/nm	φ	λ/nm	φ	λ/nm	φ
<310	1.00	370	0.98	406	0.29
315	0.99	375	0.98	408	0.18
320	0.99	380	0.97	410	0.13
325	0.99	385	0.97	412	0.09
330	0.99	390	0.96	414	0.07
335	0.99	392	0.96	416	0.05
340	0.99	394	0.95	418	0.03
345	0.99	396	0.92	420	0.02
350	0.99	398	0.82	422	0.01
355	0.99	400	0.82	424	0.00
360	0.98	402	0.69		
365	0.98	404	0.42		

Comments on Preferred Values

The new absorption cross-sections of Harwood and Jones² are in very good agreement with the earlier data of Davidson *et al.*,³ Bass *et al.*,⁴ and Schneider *et al.*⁵ at room temperature. The agreement in the 5 nm-averaged cross-sections for the range 320–435 nm is within ±4% of the data of Davidson *et al.*,³ which were recommended previously.

No significant temperature dependence of the 0.5 nm-averaged cross-sections was observed in the wavelength region 320–535 nm (Davidson *et al.*³ observed a very weak temperature dependence, in contrast to earlier studies which showed a larger effect). The new measurements support the suggestion of Davidson *et al.*³ that the discrepancies observed by Bass *et al.*,⁴ Davenport *et al.*,⁶ and Hicks *et al.*⁷ can be accounted for by incorrect compensation for N₂O₄. Roscoe and Hind⁸ have reached similar conclusions in their recent critical review of the implications of the NO₂ ⇌ N₂O₄ equilibrium for earlier determinations of NO₂ absorption cross-sections and their temperature dependence.

Cross-sections measured by Harwood and Jones² at higher resolution showed a sharpening of the spectral features of the NO₂ spectrum as the temperature was decreased, but no shift in wavelength was observed. The apparent shifts in wavelength with temperature observed in certain regions by Davidson *et al.*³ and Schneider *et al.*⁵ were probably due to calibration errors.

The preferred values for the cross-sections at 298 K, averaged over 5 nm intervals for the range 270–410 nm, are mean values from the data of Harwood and Jones² and Davidson *et al.*³ and are virtually unchanged from the previously recommended values for 273 K. The averaged values in the range 410–565 nm (not previously given in the IUPAC evaluations) are taken from Harwood and Jones.² The preferred values for the wavelength range 185–265 nm, also averaged over 5 nm wavelength intervals, are taken from Table 4 of Schneider *et al.*⁵ The averaged values are independent of temperature over the whole range.

The preferred quantum yields are those recommended by Gardner *et al.*⁹ (see previous IUPAC evaluation¹⁰). They are based on a best fit to the data of Gardner *et al.*⁹ from 334–404 nm, Jones and Bayes¹¹ for 297–412 nm, Davenport⁶ for

400–420 nm, and Harker *et al.*¹² (corrected for cross-sections) for 397–420 nm. The results of Gardner *et al.*⁹ support the results of Jones and Bayes¹¹ showing that the primary quantum yield is nearly unity throughout the entire wavelength region from 290–390 nm, and that the low values reported by Harker *et al.*¹² for the 375–396 nm region must be in error. Possible reasons for these low values are discussed in Ref. 9.

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NO₃ + *hν* → products

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
NO ₃ + <i>hν</i> → NO + O ₂ (³ Σ) (1)	10.9	11000
→ NO + O ₂ (¹ Δ) (2)	105.2	1137
→ NO + O ₂ (¹ Σ) (3)	167.8	712
→ NO ₂ + O(³ P) (4)	203.9	587

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(\text{NO}+\text{O}_2)$, $\phi(4)$	532–662	Davis <i>et al.</i> , 1993 ¹	(a)
$\phi(\text{NO}+\text{O}_2)$, $\phi(4)$	570–635	Orlando <i>et al.</i> , 1993 ²	(b)

Comments

- (a) The photodissociation of NO₃ was studied using molecular beam photofragment translational spectroscopy. For internally cold NO₃, $\phi(\text{NO} + \text{O}_2) = (0.70 \pm 0.10)$ at 588 nm falling off rapidly at $\lambda \leq 587$ nm to reach < 0.01 at 583 nm. $\phi(4)$ increased from 0.3 to > 0.99 over this range of wavelength. Both channels appear to result from dissociation from the same vibrationally excited ground state, excited by crossing from the NO₃ (²E') state formed on excitation. The dissociation energy $D_0(\text{O}-\text{NO}_2)$ was measured as 203.7 ± 1.0 kJ mol⁻¹ and corresponding values of $\Delta H_f^\circ(\text{NO}_3) = 78.95 \pm 1.38$ and 73.72 ± 1.38 kJ mol⁻¹ at 0 K and 298 K, respectively, were determined.

- (b) The photodissociation of NO₃ was studied at 298 K using pulsed laser photolysis, with resonance fluorescence detection of O(³P) atoms and NO(X²Π). $\phi[\text{O}(\text{³P})]$ was 1.0 from 570–585 nm, decreasing to a value < 0.1 at 635 nm. $\phi(\text{NO})$ was < 0.1 at 580 nm and about 0.20 ± 0.10 at 590 nm. These data were combined with earlier results of Magnotta and Johnston⁶ to provide quantum yields $\phi(\text{NO} + \text{O}_2)$ and $\phi(4)$ as a function of wavelength (586–639 nm) and to calculate photolysis rates for overhead sun at the earth's surface, with $J(\text{NO}_2 + \text{O}) = 0.19$ s⁻¹; $J(\text{NO} + \text{O}_2) = 0.016$ s⁻¹.

Preferred Values

Absorption cross-sections at 298 K and 230 K

λ/nm	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K
400	0.0	0.4	500	11.3	11.5	600	27.6	27.8
401	0.0	0.5	501	11.1	10.7	601	28.6	28.5
402	0.0	0.5	502	11.1	10.4	602	33.2	33.4
403	0.2	0.5	503	11.1	11.1	603	38.0	40.3
404	0.0	0.3	504	12.6	12.5	604	43.7	48.1
405	0.3	0.7	505	12.8	13.1	605	43.6	49.8
406	0.2	0.6	506	13.4	14.1	606	33.2	37.1
407	0.1	0.5	507	12.8	13.1	607	24.0	24.8
408	0.3	0.5	508	12.7	12.2	608	18.5	17.9
409	0.0	0.7	509	13.5	13.2	609	17.1	16.6
410	0.1	0.5	510	15.1	15.5	610	17.7	17.3
411	0.2	0.7	511	17.3	18.7	611	19.1	19.4
412	0.5	0.4	512	17.7	19.8	612	22.3	23.6
413	0.5	0.7	513	16.0	18.0	613	26.3	30.0
414	0.2	1.1	514	15.8	16.2	614	25.5	28.6
415	0.6	0.7	515	15.8	15.9	615	22.6	24.2
416	0.6	0.7	516	15.6	16.4	616	20.9	21.1
417	0.7	1.0	517	14.9	14.4	617	21.1	20.6
418	0.5	1.0	518	14.4	14.0	618	23.9	22.9
419	0.8	1.0	519	15.4	14.9	619	25.6	25.4
420	0.8	1.3	520	16.8	16.2	620	32.7	33.5
421	0.8	1.2	521	18.3	17.7	621	52.4	58.9
422	0.9	1.2	522	19.3	19.3	622	101.8	113.6
423	1.1	1.2	523	17.7	17.9	623	147.3	163.5
424	0.9	1.3	524	16.4	15.7	624	120.5	129.9
425	0.7	1.6	525	15.8	15.0	625	83.8	94.3
426	1.4	1.5	526	16.3	15.7	626	73.0	82.6
427	1.4	1.2	527	18.1	18.1	627	75.3	90.0
428	1.2	1.5	528	21.0	22.3	628	73.7	88.3
429	1.1	1.3	529	23.9	25.6	629	69.8	84.6
430	1.7	1.6	530	22.3	23.1	630	67.6	84.0
431	1.3	1.7	531	20.9	21.3	631	48.4	57.1
432	1.5	1.7	532	20.2	20.6	632	32.7	37.3
433	1.8	1.9	533	19.5	19.8	633	21.7	23.5
434	1.8	2.1	534	20.4	21.3	634	16.4	16.2
435	1.6	2.2	535	23.0	24.9	635	14.4	13.1
436	1.5	2.2	536	25.7	28.7	636	16.9	15.2
437	1.8	1.9	537	25.8	28.6	637	20.7	18.8
438	2.1	2.1	538	23.4	24.4	638	20.3	17.7
439	2.0	2.6	539	20.4	21.0	639	15.8	13.3
440	1.9	2.2	540	21.0	21.2	640	12.3	10.6
441	1.8	2.3	541	20.4	20.4	641	10.0	8.9
442	2.1	2.2	542	18.8	18.5	642	9.2	7.9
443	1.8	2.2	543	16.8	16.4	643	9.7	7.6
444	1.9	2.2	544	17.0	16.2	644	9.5	7.9
445	2.0	2.7	545	19.6	20.0	645	8.6	7.5
446	2.4	2.7	546	24.2	24.8	646	7.5	6.5
447	2.9	3.1	547	29.1	30.9	647	7.0	6.4
448	2.4	3.4	548	29.8	31.3	648	6.2	5.9
449	2.8	3.1	549	27.1	27.8	649	5.4	5.0
450	2.9	3.1	550	24.8	26.0	650	5.0	4.7
451	3.0	3.5	551	24.3	25.9	651	5.5	5.2
452	3.3	3.7	552	24.7	26.7	652	6.1	6.2
453	3.1	3.5	553	25.3	27.5	653	7.1	7.4
454	3.6	3.7	554	27.8	31.0	654	8.2	8.6
455	3.6	3.8	555	31.1	35.6	655	9.8	10.3
456	3.6	3.4	556	32.6	36.7	656	13.3	13.5
457	4.0	3.9	557	32.9	36.8	657	17.1	17.3
458	3.7	4.4	558	35.1	39.5	658	24.2	24.3

Absorption cross-sections at 298 K and 230 K—Continued

λ/nm	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K	λ/nm	$10^{19}\sigma/\text{cm}^2$ 298 K	$10^{19}\sigma/\text{cm}^2$ 230 K
459	4.2	4.2	559	37.2	42.4	659	40.7	40.0
460	4.0	4.3	560	33.2	36.1	660	74.5	74.0
461	3.9	4.0	561	29.8	31.7	661	144.8	156.9
462	4.0	3.7	562	29.0	30.6	662	210.0	250.0
463	4.1	4.5	563	28.0	30.1	663	174.4	215.2
464	4.8	4.8	564	27.2	28.8	664	112.9	136.3
465	5.1	5.1	565	27.3	29.0	665	74.1	87.0
466	5.4	5.3	566	28.5	30.9	666	49.6	58.9
467	5.7	5.6	567	28.1	29.4	667	30.4	35.0
468	5.6	5.5	568	28.5	29.9	668	19.0	21.8
469	5.8	5.6	569	28.9	30.5	669	12.5	13.6
470	5.9	5.3	570	27.9	29.1	670	9.5	10.5
471	6.2	5.8	571	27.6	28.9	671	7.9	8.8
472	6.4	6.1	572	27.4	28.6	672	7.6	9.1
473	6.2	6.1	573	27.8	28.9	673	6.4	7.6
474	6.2	6.0	574	28.6	29.9	674	5.2	5.9
475	6.8	6.9	575	30.8	33.7	675	4.8	5.2
476	7.8	7.8	576	32.7	36.2	676	4.9	4.9
477	7.7	7.7	577	33.8	37.0	677	5.9	5.8
478	7.3	6.9	578	33.1	36.1	678	7.5	6.7
479	7.3	6.9	579	32.4	35.9	679	7.8	6.8
480	7.0	7.0	580	33.4	37.4	680	6.9	6.0
481	7.1	6.9	581	35.5	41.1	681	5.3	5.0
482	7.1	6.8	582	32.8	37.0	682	4.0	4.1
483	7.2	6.7	583	29.3	32.4	683	3.0	3.0
484	7.7	6.9	584	28.2	30.7	684	2.6	2.6
485	8.2	7.7	585	28.9	31.8	685	1.8	2.2
486	9.1	8.9	586	33.2	37.2	686	1.6	1.4
487	9.2	8.8	587	41.6	48.5	687	1.2	2.2
488	9.5	8.6	588	50.4	59.8	688	1.2	1.9
489	9.6	9.9	589	61.3	72.4	689	1.2	1.8
490	10.3	10.5	590	59.6	67.3	690	1.0	2.0
491	9.9	9.6	591	54.4	60.5	691	0.7	1.6
492	9.9	9.9	592	51.1	56.4			
493	10.1	10.2	593	45.8	49.8			
494	10.1	9.5	594	41.9	47.0			
495	10.6	10.4	595	42.9	49.5			
496	12.1	12.1	596	46.2	54.4			
497	12.2	13.1	597	43.6	50.6			
498	12.0	12.4	598	36.7	40.9			
499	11.7	11.8	599	31.0	34.2			

Quantum Yields

$\phi(4)=1.0$ for $\lambda \leq 583$ nm.

Comments on Preferred Values

No new data have been reported on the absorption cross-sections for NO_3 radical absorption since our previous 1992 IUPAC evaluation.³ The preferred values are based on the peak value of the cross-section at 662 nm of $2.1 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, adopted from the evaluation of Wayne *et al.*⁴ The values of σ in the wavelength range 400–691 nm are calculated from the data of Sander,⁵ normalized to the preferred peak value. The absorption cross-sections obtained by Sander⁵ at 230 K in the range 400–700 nm were normalized to the value of $2.50 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ at 662 nm to provide the preferred values given in the table for 230 K, following the recommendation of Wayne *et al.*⁴ The follow-

ing expression is recommended for the temperature dependence of the 662 nm band:

$$\sigma(T) = 3.63 \times 10^{-17} - (5.13 \times 10^{-20} T) \text{ cm}^2 \text{ molecule}^{-1} \text{ at } 662 \text{ nm}$$

The measurements of Orlando *et al.*² confirm qualitatively the wavelength dependence of $\phi(\text{NO} + \text{O}_2)$ and $\phi(4)$ observed in the earlier room temperature measurements of Magnotta and Johnston,⁶ and provide more accurate values for $\phi(4)$. The earlier problem⁶ of total quantum yields in excess of 1.4 was not encountered in the work of Orlando *et al.*,² which confirms that NO_3 radical dissociation is exclusively to $\text{NO}_2 + \text{O}(^3\text{P})$ at wavelengths < 585 nm.

The new molecular beam study¹ has revealed considerable new insight into the photodissociation of the NO_3 radical. There is a very sharp threshold for channel (4) at 587 nm for

internally cold NO_3 . Any dissociation at longer wavelengths via channel (4) must occur from photolysis of internally excited NO_3 . At $\lambda \geq 588$ nm this process competes with photodissociation of NO_3 to form $\text{NO} + \text{O}_2$ via a 3-center transition state from the vibrationally excited ground state. The yield of this process falls off above 600 nm and may only occur from hot band absorption above 605 nm. These facts imply that the branching ratio for bulk, thermally equilibrated, NO_3 radicals will depend very strongly on temperature, especially near the threshold for the NO_2 -forming channel, where higher temperatures will tend to favor dissociation via the simple bond fission channel (4).

The atmospheric photodissociation rates suggested by Orlando *et al.*² for an overhead sun at the earth's surface and the wavelength range 470–700 nm [$J(\text{NO}_2 + \text{O}) = 0.19 \text{ s}^{-1}$; $J(\text{NO} + \text{O}_2) = 0.016 \text{ s}^{-1}$] agree well with those of Magnotta and Johnston⁶ which were recommended previously by IUPAC³, i.e., $J(\text{NO}_2 + \text{O}) = 0.18 \pm 0.06 \text{ s}^{-1}$; $J(\text{NO} + \text{O}_2) = 0.022 \pm 0.007 \text{ s}^{-1}$. The new values of J are preferred for

atmospheric calculations. The new knowledge from the molecular beam experiments¹ dictates that these expressions only apply for temperatures near room temperature. Further measurements of the quantum yields for NO_3 radical photolysis in bulk samples at low temperature are required before a recommendation can be made for atmospheric photolysis rates at stratospheric temperatures.

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$\text{N}_2\text{O} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O}(^3\text{P})$ (1)	161	742
$\rightarrow \text{N}_2 + \text{O}(^1\text{D})$ (2)	351	341
$\rightarrow \text{N} + \text{NO}$ (3)	475	252
$\rightarrow \text{N}_2 + \text{O}(^1\text{S})$ (4)	565	212

Preferred Values

Absorption cross-sections

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
175	12.6	210	0.755
180	14.6	215	0.276
185	14.3	220	0.092
190	11.1	225	0.030
195	7.57	230	0.009
200	4.09	235	0.003
205	1.95	240	0.001

Temperature dependence of absorption cross-sections

$$\ln \sigma(\lambda, T) = A_1 + A_2\lambda + A_3\lambda^2 + A_4\lambda^3 + A_5\lambda^4 + (T - 300) \times \exp(B_1 + B_2\lambda + B_3\lambda^2 + B_4\lambda^3)$$

where

$$\begin{aligned} A_1 &= 68.21023, & B_1 &= 123.4014, \\ A_2 &= -4.071805, & B_2 &= -2.116255, \\ A_3 &= 4.301146 \times 10^{-2}, & B_3 &= 1.111572 \times 10^{-2}, \\ A_4 &= -1.777846 \times 10^{-4}, & B_4 &= -1.881058 \times 10^{-5}, \\ A_5 &= 2.520672 \times 10^{-7}. \end{aligned}$$

Quantum yields

$$\phi_2 = 1.0 \text{ for } \lambda = 185\text{--}230 \text{ nm.}$$

Comments on Preferred Values

The preferred absorption cross-sections and the expression for $\ln \sigma(\lambda, T)$ in (σ, T) are from Selwyn *et al.*¹ These cross-section values have been confirmed both at room temperature and at 208 K by the results of Hubrich and Stuhl² and Merienne *et al.*³ who also determined the temperature dependence. Several publications with additional information on this process have appeared since the original evaluation. Selwyn and Johnston⁴ studied the ultraviolet absorption spectrum of nitrous oxide and its ^{15}N isotopes over the wavelength range 172–197 nm and the temperature range 150–500 K. Lee and Suto⁵ measured the photoabsorption and fluorescence cross-sections in the 106–160 nm region and studied the production and quenching of excited photofragments. Yoshino *et al.*⁶ made high-resolution room temperature cross-section measurements in the 170–222 nm range. Recent state-resolved photofragment spectroscopy studies of N_2O photodissociation at 193 nm⁷ and 205 nm⁸ show that 43% of the energy deposited in the molecule appears as translational energy of the $\text{O}(^1\text{D})$ atom fragment.

The preferred value of the quantum yield ($\phi_2=1.0$) is based on the results reported by Paraskevopoulos and Cvetanovic,⁹ Preston and Barr,¹⁰ and Greiner.¹¹ Greenblatt and Ravishankara¹² have measured the quantum yield for production of NO(²I) and N(⁴S) atoms at 193 nm to be $<8 \times 10^{-3}$.

The recommendations are unchanged from those given in our previous evaluation, IUPAC, 1992.¹³

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N₂O₅ + hν → products

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
N ₂ O ₅ + hν → NO ₃ + NO ₂ (1)	89	1340
→ NO ₃ + NO + O (2)	390	307
→ NO ₃ + NO ₂ * (3)		
→ NO ₃ + NO ₂ + hν (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–420	Harwood <i>et al.</i> , 1993 ¹	(a)

Comments

- (a) Measurements at 233–313 K using a dual-beam diode array spectrometer. Absolute cross-sections were based on pressure measurements and determination of NO₂

and HNO₃ impurities by UV and IR spectroscopic methods. For 260–380 nm, a pronounced temperature dependence was observed and the results were expressed in the form $\log_{10}(\sigma) = A + 1000 B/T$.

Absorption cross-section at 298 K

λ/nm	$10^{20}\sigma_{298}/\text{cm}^2$	B/K
200	920	
205	820	
210	560	
215	370	
220	220	
225	144	
230	99	
235	77	
240	62	
245	52	
250	40	
255	32	
260	26.3	-0.091
265	20.5	-0.100
270	16.5	-0.104
275	13.3	-0.112
280	11.4	-0.112
285	8.72	-0.126
290	6.80	-0.135
295	5.15	-0.152
300	3.90	-0.170
305	2.93	-0.194
310	2.19	-0.226
315	1.63	-0.253
320	1.22	-0.294
325	0.90	-0.338
330	0.68	-0.388
335	0.50	-0.409
340	0.38	-0.492
345	0.280	-0.530
350	0.217	-0.583
355	0.167	-0.719
360	0.126	-0.770
365	0.095	-0.801
370	0.074	-0.885
375	0.054	-0.765
380	0.042	-0.992
385	0.033	-0.992
390	0.0234	-0.949
395	0.0174	-0.845
400	0.0135	-0.966
405	0.0103	-1.00
410	0.0080	-1.16

Temperature dependence: $\log_{10}\sigma_T (\text{cm}^2 \text{ molecule}^{-1}) = \log_{10}\sigma_{298} + 1000 B(1/T - 1/298)$.

Quantum Yields

$\phi_1 + \phi_2 + \phi_3 = 1.0$ for
 $\lambda = 248\text{--}350 \text{ nm}$

λ/nm	ϕ_2
248	0.72 ± 0.17
266	0.38 ± 0.10
287	0.21 ± 0.05
289	0.15 ± 0.05

Comments on Preferred Values

The new absorption cross-section values reported by Harwood *et al.*¹ show good agreement with previously recommended values,² which were based on the data of Yao *et al.*³ For wavelengths less than 280 nm, the σ values¹ are 7% lower than Yao *et al.*³ and within 5% of the earlier values of Graham and Johnston.⁴ No significant temperature dependence was observed at $\lambda \leq 260 \text{ nm}$,¹ but for the region 265–410 nm there is a significant temperature dependence. In general, the temperature dependence from Harwood *et al.*¹ agrees well with that of Yao *et al.*³ except at the longest wavelengths where the new results show a slightly larger dependence, leading to σ values at 380 nm about 30% lower at 233 K than predicted from the earlier parameterization. The preferred values for the cross-section at room temperature were obtained by averaging the results from Harwood *et al.*¹ and Yao *et al.*,³ and the temperature dependence parameters are taken from Harwood *et al.*¹

The preferred quantum yield of unity for NO_3 radical production is based on the results of Swanson *et al.*⁵ at 249 and 350 nm, those of Ravishankara *et al.*⁶ at 248 nm, and those of Barker *et al.*⁷ at 290 nm. The preferred quantum yield values for O atom production are those reported by Ravishankara *et al.*⁶ The study of Oh *et al.*⁸ indicates that electronically excited NO_2 in the $^2\text{B}_1$ state is produced, and photolysis induced fluorescence (PIF) quantum yield values are reported. For calculation of photodissociation rates in the atmosphere, channel (3) is equivalent to channel (1). In summary, it appears that NO_3 radicals are produced with unit quantum yield throughout the region 248–350 nm, and that the quantum yield for oxygen atom production decreases at longer wavelengths and appears to be approaching zero in the neighborhood of the thermodynamic threshold for O atom production at 307 nm.

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4.4. Organic Species

$$\Delta H^\circ(1) = -285.8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -287.7 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.4 \pm 0.3) \times 10^{-10}$	294–900	Slagle, Sarzynski, and Gutman, 1987 ¹	(a)
<i>Branching Ratios</i>			
$k_2/k = 0.4 \pm 0.1$	298	Seakins and Leone, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
1.4×10^{-10}	300–2500	Baulch <i>et al.</i> , 1992 ³	(c)
1.4×10^{-10}	200–900	IUPAC, 1992 ⁴	(d)
1.1×10^{-10}	200–300	NASA, 1994 ⁵	(e)

Comments

- (a) Flow system with generation of CH_3 radicals and $\text{O}(^3\text{P})$ atoms from simultaneous *in situ* photolysis of CH_3COCH_3 and SO_2 , and determination of $[\text{CH}_3]$ and $[\text{O}]$ by photoionization MS. Experiments were performed under conditions such that $[\text{O}]/[\text{CH}_3] > 20$, and rate coefficients were determined from the decay of CH_3 radicals. The rate coefficient k was found to be independent of pressure over the range 1–11 Torr, and its value was confirmed by measurement of the rate of formation of HCHO, the sole observable product.
- (b) Laser flash photolysis with time-resolved FTIR emission from the vibrationally excited products, HCHO and CO.
- (c) Based on the data of Slagle *et al.*¹
- (d) See Comments on Preferred Values.
- (e) Weighted average of the measurements of Washida and Bayes,⁶ Washida,⁷ and Plumb and Ryan.⁸

Preferred Values

$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–900 K.

$k_2/k = 0.4$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

Our previous recommendation⁴ for the overall rate coefficient, based on the results of Slagle *et al.*,¹ remains unaltered. The recent experiments of Seakins and Leone² show that the reaction has a second channel yielding CO and, presumably, $\text{H}_2 + \text{H}$, and that the branching ratio for this channel is significant.

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$$\Delta H^\circ(1) = -178.8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -472.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published on the overall k or the branching ratio of this reaction since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

$k_1/k = 0.9$; $k_3/k = 0.1$; $k_2/k = 0$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta k_1/k = \Delta k_3/k = \pm 0.1$ over the temperature range 200–300 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

This data sheet is largely based on our previous evaluation,¹ but includes additional comments from a later evaluation.² The most recent data³ on this reaction are in excellent agreement with the previous recommendation,² which is unaltered. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴ Casavecchia *et al.*⁵ have

carried out a molecular beam study which indicates an alternative reaction channel yielding CH_3O (or CH_2OH) + H. Further work is needed to confirm this observation.

A study⁶ of the 248 nm laser flash photolysis of O_3 - CH_4 mixtures, with low-pressure FTIR emission spectroscopy to monitor the HO product, has provided evidence that the partitioning of energy in the vibrationally excited HO radical (up to $n=4$, the maximum allowable according to the energetics of the reaction) is non-statistical.

References

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$$\Delta H^\circ = -60.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$4.0 \times 10^{-12} \exp[-(1944 \pm 114)/T]$	278–378	Finlayson-Pitts <i>et al.</i> , 1992 ¹	(a)
5.87×10^{-15}	298		
$(2.62 \pm 0.27) \times 10^{-14}$	378	Lancar, Le Bras, and Poulet, 1992 ²	(b)
$(4.27 \pm 0.18) \times 10^{-14}$	422		
$< 3 \times 10^{-16}$	178	Sharkey and Smith, 1993 ³	(c)
$(1.65 \pm 0.2) \times 10^{-15}$	216		
$(7.6 \pm 0.3) \times 10^{-15}$	298		
$9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$	293–800	Dunlop and Tully, 1993 ⁴	(c,d)
$(5.62 \pm 0.43) \times 10^{-15}$	293		
$(5.4 \pm 0.2) \times 10^{-15}$	292	Saunders <i>et al.</i> , 1994 ⁵	(c)
$2.56 \times 10^{-12} \exp[-(1765 \pm 146)/T]$	233–343	Mellouki <i>et al.</i> , 1994 ⁶	(c)
$(6.34 \pm 0.88) \times 10^{-15}$	298		
Reviews and Evaluations			
$3.9 \times 10^{-12} \exp(-1885/T)$	240–300	IUPAC, 1992 ⁷	(e)
$7.44 \times 10^{-18} T^2 \exp(-1361/T)$	223–1512	Atkinson, 1994 ⁸	(f)
$2.65 \times 10^{-12} \exp(-1800/T)$	223–400	NASA, 1994 ⁹	(g)

Comments

- (a) Discharge flow system with resonance fluorescence detection of HO radicals.
- (b) Discharge flow system with EPR detection of HO radicals.
- (c) Pulsed laser photolysis system with LIF detection of HO radicals.
- (d) The temperature-dependent expression cited⁴ is that for the rate coefficients of Dunlop and Tully⁴ combined with those of Vaghjiani and Ravishankara¹⁰ and as such covers the temperature range 223–800 K⁴.

- (e) Derived from the absolute rate coefficient data of Dixon-Lewis and Williams,¹¹ Margitan *et al.*,¹² Howard and Evenson,¹³ Ernst *et al.*,¹⁴ Tully and Ravishankara,¹⁵ Madronich and Felder,¹⁶ Smith *et al.*,¹⁷ Bott and Cohen,¹⁸ and Vaghjiani and Ravishankara.¹⁰ The three parameter equation $k = CT^2 \exp(-D/T)$ was fitted to these data,^{10–18} resulting in $k = 7.44 \times 10^{-18} T^2 \exp(-1355/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 223–1512 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

- (f) Derived from the absolute rate coefficient data of Dixon-Lewis and Williams,¹¹ Margitan *et al.*,¹² Howard and Evenson,¹³ Ernst *et al.*,¹⁴ Tully and Ravishankara,¹⁵ Madronich and Felder,¹⁶ Smith *et al.*,¹⁷ Bott and Cohen,¹⁸ Vaghjiani and Ravishankara,¹⁰ and Finlayson-Pitts *et al.*,¹ using the three parameter expression $k = CT^2 \exp(-D/T)$.
- (g) The 298 K rate coefficient is based on the absolute rate coefficient data of Vaghjiani and Ravishankara,¹⁰ Finlayson-Pitts *et al.*,¹ Dunlop and Tully,⁴ Saunders *et al.*,⁵ and Mellouki *et al.*,⁶ and the temperature dependence is derived from those of Vaghjiani and Ravishankara,¹⁰ Finlayson-Pitts *et al.*,¹ Dunlop and Tully,⁴ and Mellouki *et al.*⁶ at temperatures <400 K.

Preferred Values

$k = 6.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.3 \times 10^{-12} \exp(-1765/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Finlayson-Pitts *et al.*,¹ Dunlop and Tully,⁴ and Mellouki *et al.*⁶ are in good agreement with those of Vaghjiani and Ravishankara.¹⁰ However, over the temperature range ~250–420 K these rate coefficients of Vaghjiani and Ravishankara,¹⁰ Finlayson-Pitts *et al.*,¹ Dunlop and Tully,⁴ and Mellouki *et al.*⁶ are ~20% lower than most of the previously reported absolute rate coefficients.^{8,9} While Vaghjiani and Ravishankara¹⁰ concluded that a number of earlier studies^{19–21} gave rise to erroneously high measured rate coefficients due to the use of lower CH₄/OH concentration ratios and the occurrence of secondary reactions, Finlayson-Pitts *et al.*¹ used a CH₄/OH concentration ratio significantly lower than employed by Vaghjiani and Ravishankara.¹⁰

The preferred values are derived from the absolute rate coefficient data of Vaghjiani and Ravishankara¹⁰ and Dunlop and Tully,⁴ both conducted over significant, and overlapping, temperature ranges. The temperature-dependent expression obtained by Dunlop and Tully⁴ from a fit of their data⁴ and

those of Vaghjiani and Ravishankara¹⁰ to the three parameter equation $k = CT^n \exp(-D/T)$ is accepted, of $k = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 223–800 K. The preferred Arrhenius expression, $k = A \times \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = Ce^n T^n$ and $B = D + nT$. The recommended three-parameter expression leads to a calculated rate coefficient at 1234 K which is within 15% of the value measured by Bott and Cohen.¹⁸

The absolute rate coefficients of Lencar *et al.*² at 378 and 422 K and of Sharkey and Smith³ and Saunders *et al.*⁵ at 298 K are within 25% of the preferred values, and the upper limit obtained by Sharkey and Smith³ at 178 K is also consistent with the rate coefficient calculated from the preferred rate coefficient expression. However, the rate coefficient reported by Sharkey and Smith³ at 216 K is a factor of 2.5 higher than that calculated from the preferred Arrhenius expression.

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$$\Delta H^\circ = -152 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 5 \times 10^{-30} (T/300)^{-1.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1.5$.

Comments on Preferred values

The preferred 298 K rate coefficient is based on the ex-

perimental data of Schmidt *et al.*¹ and Wahner and Zetzsch² and the theoretical analysis of Smith *et al.*,³ and the temperature dependence is based on the data of Perry *et al.*,⁴ Michael *et al.*,⁵ and Perry and Williamson,⁶ as discussed and evaluated by Atkinson.⁷ At temperatures above ~500 K another component of the rate coefficient with a much stronger temperature dependence also has to be taken into account.⁷ The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁸

High-pressure rate coefficients

Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(7.0 \pm 1.5) \times 10^{-13}$	297	Arnts, Seila, and Bufalini, 1989 ⁹	(a)
<i>Reviews and Evaluations</i>			
$9.0 \times 10^{-13} (T/300)^2$	200–300	IUPAC, 1992 ⁸	(b)
$8.3 \times 10^{-13} (T/300)^2$	220–300	NASA, 1994 ¹⁰	(c)
$9.4 \times 10^{-12} \exp(-700/T)$	230–500	Atkinson, 1994 ¹¹	(d)

Comments

- HO radicals were generated by the photolysis of methyl nitrite in the presence of NO. The concentrations of C_2H_2 and C_2H_6 were measured by GC. The rate coefficient k was measured relative to that of the reaction $\text{HO} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{C}_2\text{H}_5$, using a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 2.46 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation). Experiments were carried out in 760 Torr of air.
- See Comments on Preferred Values.
- Based on the analysis of Smith *et al.*³
- The previous recommendations⁷ were unchanged.

Preferred Values

$k_\infty = 9.0 \times 10^{-13} (T/300)^2 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 298 K.

$\Delta n = \sim 1$.

Comments on Preferred Values

The preferred values are based on the evaluation of Atkinson⁷ of the experimental data of Perry *et al.*,⁴ Michael *et al.*,⁵ Perry and Williamson,⁶ Atkinson and Aschmann,¹² Schmidt *et al.*,¹ Wahner and Zetzsch,² Hatakeyama *et al.*¹³ and Liu *et al.*¹⁴ Falloff curves are constructed with $F_c = 0.69$ at 228 K and 0.62 at 298 K, as derived by Smith *et al.*³ The preferred values are identical to those in our previous evaluation, IUPAC, 1992,⁸ and the rate coefficient of Arnts *et al.*⁹ at room temperature and atmospheric pressure of air is in good agreement with the preferred values.

Intermediate falloff range

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>					
$1.1 \times 10^{-13} \exp[(1460 \pm 500)/T]$	414–864	He	627–713	Lai, Hsu, and Lee, 1992 ¹⁵	(a)

Comments

- (a) HO radicals were formed by 193 nm photolysis of N_2O in the presence of H_2O , and monitored by LIF at 310 nm. The rate coefficients for the forward and reverse $\{k = (2.2 \pm 0.4) \times 10^{12} \exp[-(15100 \pm 600)] \text{ s}^{-1}\}$ reactions did not change appreciatively with pressure, although they had not reached the high pressure limit. From the temperature dependence of the equilibrium constant, a value of $\Delta H_0^\circ = -(140.6 \pm 5.0) \text{ kJ mol}^{-1}$ was derived.

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$$\Delta H^\circ = -126 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Reviews and Evaluations</i>			
$7 \times 10^{-29} (T/300)^{-3.1} [\text{N}_2]$	200–300	IUPAC, 1992 ¹	(a)
$1.0 \times 10^{-28} (T/300)^{-0.8} [\text{air}]$	200–300	NASA, 1994 ²	(b)
$3.0 \times 10^{-29} (T/300)^{-4} [\text{He}]$	295–420	Atkinson, 1994 ³	(c)
$6 \times 10^{-29} (T/300)^{-4} [\text{N}_2, \text{O}_2]$	295–420		

Comments

- (a) Based on a series of earlier data. Because of the smallest scatter, heavier weight was given to the results of Ref. 4. Falloff extrapolation was carried out with a calculated value of $F_c = 0.7$ from Ref. 5.
- (b) Based on a series of earlier data, in particular on the data of Ref. 5.
- (c) Detailed review of all available earlier data. The temperature dependence based on the work of Kuo and Lee⁴ and a previous evaluation⁶ was adopted.

Preferred Values

$$k_0 = 7 \times 10^{-29} (T/300)^{-3.1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 2.$$

Comments on Preferred Values

No new measurements have been reported. The values recommended by Atkinson³ in a recent review are similar to those preferred earlier.¹

High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(7.7 \pm 1.0) \times 10^{-12}$	298	Becker, Geiger, and Wiesen, 1991 ⁷	(a)
<i>Reviews and Evaluations</i>			
9.0×10^{-12}	200–300	IUPAC, 1992 ¹	(b)
8.8×10^{-12}	200–300	NASA, 1994 ²	(c)
$9.0 \times 10^{-12}(T/300)^{-1.1}$	290–525	Atkinson, 1994 ³	(d)

Comments

- (a) HO radicals were generated by 248 nm laser photolysis of H_2O_2 and monitored in real time by LIF at 308 nm. Experiments were carried out at a total pressure of 760 Torr of synthetic air. Numerical simulation with a mechanism formed by 12 reactions.
- (b) Based on results from Ref. 8 which are in good agreement with the value preferred earlier. The temperature coefficient is uncertain because of extensive falloff at temperatures above 300 K and the possibility of a small activation barrier.
- (c) See comment (b) for k_0 .
- (d) The previous recommendations⁶ were unchanged.

Preferred Values

$k_{\infty} = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred value is similar to those reported in Refs. 3 and 6. The temperature dependence is uncertain due to the possibility of a small electronic barrier. These preferred values of k_0 and k_{∞} are identical to those in our previous evaluation, IUPAC, 1992.¹

Intermediate falloff range

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
4.4×10^{-12}	790	Ar	1197	Bott and Cohen, 1991 ⁹	(a)
$4.3 \times 10^{-13} \exp[(1200 \pm 800)/T]$	500–616	He	544–590	Diau and Lee, 1992 ¹⁰	(b)

Comments

- (a) Shock wave experiments. HO radicals were generated by dissociation of *t*-butyl hydroperoxide and detected by UV absorption at 309 nm.
- (b) HO radicals were generated by photolysis of N_2O in the presence of H_2O at 193 nm and detected by LIF at 310 nm. Experiments were carried out between 544–673 K and 276–616 Torr He.

References

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$$\Delta H^\circ = -75.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.74 \pm 0.40) \times 10^{-13}$	298	Dóbé <i>et al.</i> , 1991, ¹ 1992 ²	(a)
$(1.54 \pm 0.24) \times 10^{-11}$	1225	Bott and Cohen, 1991 ³	(b)
$(1.3 \pm 0.2) \times 10^{-14}$	138	Sharkey and Smith, 1993 ⁴	(c)
$(2.5 \pm 0.3) \times 10^{-14}$	178		
$(7.85 \pm 0.4) \times 10^{-14}$	216		
$(2.95 \pm 0.14) \times 10^{-13}$	298		
$1.03 \times 10^{-11} \exp[-(1108 \pm 40)/T]$	231–377	Talukdar <i>et al.</i> , 1994 ⁵	(c)
$(2.43 \pm 0.13) \times 10^{-13}$	298		
Relative Rate Coefficients			
$6.5 \times 10^{-12} \exp(-943/T)$	298–373	Finlayson-Pitts, Hernandez, and Berko, 1993 ⁶	(d)
2.76×10^{-13}	298		
Reviews and Evaluations			
$7.8 \times 10^{-12} \exp(-1020/T)$	240–300	IUPAC, 1992 ⁷	(e)
$1.51 \times 10^{-17} T^2 \exp(-492/T)$	226–800	Atkinson, 1994 ⁸	(f)
$8.7 \times 10^{-12} \exp(-1070/T)$	226–298	NASA, 1994 ⁹	(g)

Comments

- (a) Pulsed laser photolysis system with resonance fluorescence detection of HO radicals.
- (b) HO radicals were generated from the thermal decomposition of *t*-butyl hydroperoxide in a shock tube and monitored by UV absorption at 309 nm.
- (c) Pulsed laser photolysis system with LIF detection of HO radicals.
- (d) Relative rate method. HO radicals were generated from the photolysis of O₃-H₂O-ethane-propane mixtures and from the dark reactions of O₃ in the presence of ethane and propane.⁶ The rate coefficient ratios $k(\text{HO} + \text{ethane})/k(\text{HO} + \text{propane})$ were placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{propane}) = 8.0 \times 10^{-12} \exp(-590/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (e) Derived using the absolute rate coefficient data of Howard and Evenson,¹⁰ Leu,¹¹ Margitan and Watson,¹² Tully *et al.*,^{13,14} Smith *et al.*,¹⁵ Baulch *et al.*,¹⁶ Devolder *et al.*,¹⁷ Stachnick *et al.*,¹⁸ Wallington *et al.*,¹⁹ Bourmada *et al.*,²⁰ Zabarnick *et al.*,²¹ and Abbatt *et al.*²² The absolute rate coefficient data used in the evaluation^{10–22} were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.51 \times 10^{-17} T^2 \exp(-492/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 226–800 K. The Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.
- (f) Derived from the absolute rate coefficient data of Howard and Evenson,¹⁰ Leu,¹¹ Margitan and Watson,¹² Tully *et al.*,^{13,14} Smith *et al.*,¹⁵ Baulch *et al.*,¹⁶ Devolder *et al.*,¹⁷ Stachnik *et al.*,¹⁸ Wallington *et al.*,¹⁹

Bourmada *et al.*,²⁰ Zabarnick *et al.*,²¹ and Abbatt *et al.*²² These data were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$.

- (g) The 298 K rate coefficient was derived from the data of Tully *et al.*,¹⁴ Wallington *et al.*,¹⁹ Abbatt *et al.*,²² Schiffman *et al.*,²³ Talukdar *et al.*,⁵ and Anderson and Stephens (unpublished data, 1994), using a temperature dependence of $E/R = 1070 \text{ K}$ to recalculate the reported room temperature data to 298 K. The temperature dependence was derived from the data of Wallington *et al.*,¹⁹ Talukdar *et al.*,⁵ and Anderson and Stephens (unpublished data, 1994).

Preferred Values

$$k = 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.9 \times 10^{-12} \exp(-1030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The absolute rate coefficients of Dóbé *et al.*,^{1,2} Bott and Cohen³ (from an apparently limited study), Sharkey and Smith,⁴ and Talukdar *et al.*⁵ and the relative rate coefficients of Finlayson-Pitts *et al.*⁶ are in good agreement (within 20% except for the 138 K rate coefficient of Sharkey and Smith⁴) with the three-parameter expression obtained in the previous IUPAC evaluation.⁷ The preferred values were obtained by using the absolute rate coefficient data of Howard and Evenson,¹⁰ Leu,¹¹ Margitan and Watson,¹² Tully *et al.*,^{13,14} Smith *et al.*,¹⁵ Baulch *et al.*,¹⁶ Devolder *et al.*,¹⁷ Stachnick

et al.,¹⁸ Wallington *et al.*,¹⁹ Bourmada *et al.*,²⁰ Zabarnick *et al.*,²¹ Abbatt *et al.*,²² and Talukdar *et al.*⁵

The absolute rate coefficient data used in the evaluation^{5,10–22} were fitted to the three parameter equation $k = CT^2 \times \exp(-D/T)$, resulting in $k = 1.52 \times 10^{-17} T^2 \exp(-499/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 226–800 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The room temperature (the temperature not being specified) absolute rate coefficient of Schiffman *et al.*²³ is in good agreement with the preferred 298 K rate coefficient, as are the relative rate coefficients of Baulch *et al.*²⁴ and Edney *et al.*²⁵

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$$\Delta H^\circ = -134 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 8 \times 10^{-27} (T/300)^{-3.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 1.0 \text{ at 298 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, because the reaction is close to the high-pressure limit at pressures of 1 bar. The preferred values follow the falloff extrapolations from Refs. 1 and 2 which show the smallest scatter. Falloff extrapolations are made using $F_c = 0.5$ at 300 K. The temperature coefficient of k_0 is estimated by analogy to the reaction $\text{HO} + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_2\text{H}_4\text{OH} + \text{M}$. The recommendation of our previous evaluation, IUPAC, 1992³ are unchanged.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.1 \text{ over the temperature range 200–300 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The preferred values are based on Refs. 1, 2, and 4–7. There is an uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small activation barrier, as in the reaction $\text{HO} + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{C}_2\text{H}_2\text{OH} + \text{M}$. We here prefer a temperature independent value of k_∞ in contrast to the recommendation of Ref. 8. The recommendations of our previous evaluation, IUPAC, 1992,³ are unchanged.

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$$\Delta H^\circ(1) = -79.1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -86.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.40 \pm 0.30) \times 10^{-12}$	298	Dóbcé <i>et al.</i> , 1991 ¹	(a)
$9.81 \times 10^{-12} \exp[-(650 \pm 30)/T]$	233–363	Mellouki <i>et al.</i> , 1994 ²	(b)
$(1.05 \pm 0.09) \times 10^{-12}$	295		
$1.01 \times 10^{-11} \exp[-(657 \pm 46)/T]$	233–376	Talukdar <i>et al.</i> , 1994 ³	(b)
$(1.11 \pm 0.04) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(1.10 \pm 0.05) \times 10^{-12}$	298 ± 2	Nielsen <i>et al.</i> , 1994 ⁴	(c)
$(1.15 \pm 0.06) \times 10^{-12}$	298	Finlayson-Pitts, Hernandez, and Berko, 1993 ⁵	(d)
$(1.14 \pm 0.19) \times 10^{-12}$	298	Finlayson-Pitts, Hernandez, and Berko, 1993 ⁵	(e)
<i>Reviews and Evaluations</i>			
$9.8 \times 10^{-12} \exp(-640/T)$	270–340	IUPAC, 1992 ⁶	(f)
$1.50 \times 10^{-17} T^2 \exp(-44/T)$	293–1220	Atkinson, 1994 ⁷	(g)
$1.0 \times 10^{-11} \exp(-660/T)$	200–300	NASA, 1994 ⁸	(h)

Comments

- (a) Pulsed laser photolysis system with resonance fluorescence detection of HO radicals.
- (b) Pulsed laser photolysis system with LIF detection of HO radicals.
- (c) Relative rate method. HO radicals generated by the dark reaction of N_2H_4 with O_3 in air. The concentrations of propane and 2-methylpropane were measured during the experiments by GC and a rate constant ratio of $k(\text{OH} + \text{propane})/k(\text{OH} + 2\text{-methylpropane}) = 0.47 \pm 0.02$ determined. This rate constant ratio is placed on an absolute basis by use of $k(\text{OH} + 2\text{-methylpropane}) = 2.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.⁷
- (d) Relative rate method. HO radicals generated by the photolysis of $\text{O}_3\text{-H}_2\text{O-O}_2$ mixtures and by the dark reaction of $\text{O}_3\text{-propane-}n\text{-butane-H}_2\text{O-O}_2$ mixtures. The propane and n -butane concentrations were measured during the experiments by GC and rate constant ratios of $k(\text{OH} + \text{propane})/k(\text{OH} + n\text{-butane}) = 0.452 \pm 0.023$

and 0.453 ± 0.021 were obtained for the photolytic and dark reactions, respectively. These rate constant ratios are placed on an absolute basis by use of $k(n\text{-butane}) = 2.54 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.⁷

- (e) Relative rate method. HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO-air}$ mixtures, photolysis of $\text{O}_3\text{-H}_2\text{O-O}_2$ mixtures, and the dark reaction of $\text{O}_3\text{-propane-2-methylpropane-H}_2\text{O-O}_2$ mixtures. The concentrations of propane and 2-methylpropane were measured during the experiments by GC. Rate constant ratios $k(\text{OH} + \text{propane})/k(\text{OH} + 2\text{-methylpropane})$ of 0.448 ± 0.026 , 0.522 ± 0.015 and 0.496 ± 0.025 , respectively, were obtained. The average of these rate constant ratios is placed on an absolute basis by use of $k(2\text{-methylpropane}) = 2.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.⁷
- (f) Derived from the absolute rate coefficient data of Greiner,⁹ Bott and Cohen,¹⁰ Smith *et al.*,¹¹ Baulch *et al.*,¹² Droege and Tully,¹³ Abbatt *et al.*,¹⁴ and MacLeod *et al.*¹⁵ and the relative rate coefficients of Baker

et al.^{16,17} and Atkinson *et al.*¹⁸ These data^{9–18} were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.48 \times 10^{-17} T^2 \exp(-39/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 293–1220 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 300 K, and was derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

- (g) Derived from the absolute rate coefficient data of Greiner,⁹ Bott and Cohen,¹⁰ Smith *et al.*,¹¹ Baulch *et al.*,¹² Droege and Tully,¹³ Abbatt *et al.*,¹⁴ and MacLeod *et al.*¹⁵ and the relative rate coefficients of Baker *et al.*^{16,17} and Atkinson *et al.*¹⁸ These data^{9–18} were fitted to the three parameter equation $k = CT^2 \times \exp(-D/T)$.
- (h) The room temperature rate coefficients of Greiner,⁹ Bradley *et al.*,¹⁹ Tully *et al.*,²⁰ Baulch *et al.*,¹² Schmidt *et al.*,²¹ Droege and Tully,¹³ Abbatt *et al.*,¹⁴ Schiffman *et al.*,²² Talukdar *et al.*,³ Mellouki *et al.*,² and Anderson and Stephens (unpublished data, 1994) were used to derive the 298 K value. The temperature dependence was derived from a least-squares analysis of the rate coefficients of Droege and Tully¹³ at temperatures <400 K, Talukdar *et al.*,³ Mellouki *et al.*,² and Anderson and Stephens (unpublished data, 1994), with the A factor being adjusted to fit the 298 K value.

Preferred Values

$k = 1.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 8.0 \times 10^{-12} \exp(-590/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 150 \text{ K}$.

Comments on Preferred Values

The room temperature absolute and relative rate coefficients of Dóbé *et al.*,¹ Mellouki *et al.*,² Talukdar *et al.*,³ Nielsen *et al.*,⁴ and Finlayson-Pitts *et al.*⁵ are in good¹ or excellent^{2–5} agreement with the previous IUPAC evaluation.⁶ The absolute rate coefficient data of Greiner,⁹ Bott and Cohen,¹⁰ Smith *et al.*,¹¹ Baulch *et al.*,¹² Droege and Tully,¹³ Abbatt *et al.*,¹⁴ MacLeod *et al.*,¹⁵ Mellouki *et al.*,² and Talukdar *et al.*³ and the relative rate coefficients of Baker *et al.*^{16,17} and Atkinson *et al.*¹⁸ were used to derive the preferred value. These data were fitted to the three-parameter

equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.54 \times 10^{-17} T^2 \exp(-60/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 233–1220 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The relative rate coefficients of Baulch *et al.*²³ and Edney *et al.*²⁴ are in good agreement with the recommended expression, as is the absolute rate coefficient of Schiffman *et al.*²² at room temperature (which was not specified).

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$$\Delta H^\circ(1) = -104.3 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -129 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$k_{01} = 1.3 \times 10^{-13}$	298	Forster <i>et al.</i> , 1995 ¹	(a)
$k_{02} = 4.1 \times 10^{-33} [\text{He}]$	298		
$k_{\infty 2} = 9.7 \times 10^{-13}$	298		
$k_{01} = 1.8 \times 10^{-12} \exp(-2720/T) + 1.6 \times 10^{-13} \exp(-60/T)$	90–3000	Fulle <i>et al.</i> , 1996 ²	(b)
$k_{02} = \{2.0 \times 10^{-32} (T/300)^{-2.7} \exp(-490/T)\} [\text{He}]$	90–3000		
$k_{\infty 2} = 1.8 \times 10^{-11} \exp(-1850/T) + 1.5 \times 10^{-12} \exp(-130/T)$	90–3000		
Reviews and Evaluations			
$1.5 \times 10^{-13} [1 + 0.6 \text{ P/bar}]$	200–300	IUPAC, 1992 ³	(c)
$1.5 \times 10^{-13} [1 + 0.6 \text{ P/bar}]$	200–300	NASA, 1994 ⁴	(c)

Comments

- (a) Laser flash photolysis experiments up to 150 bar of the bath gas He. Detection of HO radicals was by saturated LIF. The pressure dependence of k_1 and k_2 were represented by $k_1 = k_{01} \{1 - [x/(x+1)] F_c^{[1+(\log x)^2]^{-1}}\}$ and $k_2 = k_{02} \{(1+y)/(1+x)\} F_c^{[1+(\log x)^2]^{-1}}$ with $x = k_{02}/(k_{\infty 2} - k_{01})$, $y = k_{01}/(k_{\infty 2} - k_{01})$ and $F_c(298 \text{ K}) = 0.69$.
- (b) Laser flash photolysis experiments over the range 80–900 K between 1 and 700 bar of the bath gas He. Detection of HO radicals was by saturated LIF. The data representation was consistent with statistical unimolecular rate theory in the form of comment (a), with $F_c = 0.84$ at 100 K, 0.77 at 200 K, 0.73 at 250 K, and 0.69 at 300 K. Rate data for other bath gases will have to be analyzed by analogy to the He data, leading to different k_{02} and F_c values. The reaction enthalpy for reaction (2) was derived from experiments between 600 and 900 K.
- (c) Weighted average of earlier data in $\text{M} = \text{N}_2$ at pressures below 1 bar. These experiments all require reanalysis with respect to the partitioning of k into k_1 and k_2 and the respective pressure dependences which, at temperatures near 200 K, are marked at pressures far below 1 bar.

Preferred Values

$$k = 1.3 \times 10^{-13} [1 + (0.6 \text{ P/bar})(300/T)^{1.0}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K and the pressure range 0–1 bar of N}_2 \text{ or air.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at 298 K.}$$

$$\Delta \log k = \pm 0.2 \text{ over the temperature range 200–300 K.}$$

Comments on Preferred Values

The preferred values at 298 K are only slightly changed from previous evaluations. However, the partitioning of the product channels between reactions (1) and (2) is included on the basis of the studies of Forster *et al.*¹ and Fulle *et al.*² Also, marked changes with decreasing temperature are accounted for, consistent with the recent experiments.²

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$$\Delta H^\circ(1) = -130.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -91.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.94 \pm 0.30) \times 10^{-11}$	1205 $\pm$ 16	Bott and Cohen, 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$8.8 \times 10^{-12} \exp(25/T)$	240–300	IUPAC, 1992 ²	(b)
$1.20 \times 10^{-14} T \exp(287/T)$	228–1205	Atkinson, 1994 ³	(c)
1.0×10^{-11}	228–576	NASA, 1994 ⁴	(d)

Comments

- (a) HO radicals generated from thermal decomposition of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm.
- (b) Derived from the absolute rate coefficients determined by Atkinson and Pitts,⁵ Stief *et al.*,⁶ Temps and Wagner,⁷ Zabarnick *et al.*,⁸ and Yetter *et al.*⁹ and the relative rate coefficient of Niki *et al.*¹⁰ These rate coefficients^{5–10} were fitted to the three parameter equation $k=CT^2 e^{-D/T}$, yielding $k=1.69 \times 10^{-17} T^2 \times \exp(557/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 228–572 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, was centered at 265 K and was derived from the three parameter expression with $A=C e^2 T^2$ and $B=D+2T$.
- (c) Derived from the absolute rate coefficients of Atkinson and Pitts,⁵ Stief *et al.*,⁶ Temps and Wagner,⁷ Yetter *et al.*,⁹ and Bott and Cohen¹ and the relative rate coefficient of Niki *et al.*¹⁰ (for ¹³CH₂O), using the expression $k=CT \exp(-D/T)$.
- (d) The 298 K rate coefficient was the average of the absolute rate coefficients determined by Atkinson and Pitts,⁵ Stief *et al.*,⁶ Temps and Wagner,⁷ and Zabarnick *et al.*⁸ The combined data set yielded no evidence for any temperature dependence of the rate coefficient.

Preferred Values

$$k=9.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k=8.6 \times 10^{-12} \exp(20/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}300 \text{ K.}$$

$$k_1/k=1.0 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

$$\Delta(k_1/k) = \pm 0.10 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The absolute rate coefficients of Atkinson and Pitts,⁵ Stief *et al.*,⁶ Temps and Wagner,⁷ Yetter *et al.*,⁹ and Bott and Cohen¹ and the relative rate coefficient of Niki *et al.*¹⁰ (for formaldehyde-¹³C) were fitted to the three parameter expressions $k=CT \exp(-D/T)$ and $k=CT^2 \exp(-D/T)$, resulting in

$$k=8.24 \times 10^{-18} T^2 \exp(753/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k=1.20 \times 10^{-14} T \exp(287/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 228–1205 K. The expression $k=CT \exp(-D/T)$ gave a better fit to the data, and the preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter expression with $A=C e T$ and $B=D+T$.

The product data of Temps and Wagner⁷ and Niki *et al.*¹⁰ and the kinetic/modeling results of Yetter *et al.*⁹ show that at 298 K this reaction proceeds via pathway (1) to yield H₂O + HCO.

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$$\Delta H^\circ = -139.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(1.62 \pm 0.10) \times 10^{-11}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$5.6 \times 10^{-12} \exp(310/T)$	240–530	IUPAC, 1992 ²	(b)
$5.55 \times 10^{-12} \exp(311/T)$	244–528	Atkinson, 1994 ³	(b)
$6.0 \times 10^{-12} \exp(250/T)$	244–528	NASA, 1994 ⁴	(c)

Comments

- (a) Relative rate method. HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of CH_3CHO and ethane measured during the experiments by GC. The measured rate constant ratio was placed on an absolute basis by use of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁵
- (b) Derived from the absolute rate coefficient data of Atkinson and Pitts⁶ and Michael *et al.*,⁷ and the relative rate coefficient of Niki *et al.*⁸ at 298 K. The data of Semmes *et al.*⁹ were not used in the evaluation because of their reported difficulties⁹ in determining the acetaldehyde concentration.
- (c) The 298 K rate coefficient was based upon the rate coefficient data of Morris *et al.*,¹⁰ Niki *et al.*,⁸ Atkinson and Pitts,⁶ Kerr and Sheppard,¹¹ Semmes *et al.*,⁹ and Michael *et al.*⁷ The temperature dependence was the average of those measured by Atkinson and Pitts,⁶ Semmes *et al.*,⁹ and Michael *et al.*⁷

Preferred Values

$$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 5.6 \times 10^{-12} \exp(310/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}530 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred values were obtained from a least-squares analysis of the absolute rate coefficient data of Atkinson and Pitts⁶ and Michael *et al.*,⁷ and the relative rate coefficient of Niki *et al.*⁸ at 298 K. The absolute and relative rate data of Morris *et al.*,¹⁰ Cox *et al.*,¹² Kerr and Sheppard,¹¹ Balestra-

Garcia *et al.*,¹³ and Scollard *et al.*¹ are in agreement with the preferred 298 K value. The data of Semmes *et al.*,⁹ which are lower than the preferred values by up to $\sim 25\%$, were not used in the evaluation because of their reported difficulties in accurately determining the acetaldehyde concentrations.

While the absolute rate coefficients measured by Dóbé *et al.*¹⁴ for CH_3CHO are in good agreement with the preferred values, their measured rate coefficients for the reactions of the HO radical with the higher aldehydes $(\text{CH}_3)_2\text{CHCHO}$ and $(\text{CH}_3)_3\text{CCHO}$ are significantly higher, by factors of $\sim 1.5\text{--}2.3$, than the rate coefficients of Kerr and Sheppard¹¹ and Semmes *et al.*⁹ (which are in good agreement). Accordingly, the rate coefficient data of Dóbé *et al.*¹⁴ have not been used in the evaluation.

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HO + C₂H₅CHO → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred rate coefficient is derived from the mean of the absolute rate coefficient of Semmes *et al.*¹ and the relative rate coefficients of Niki *et al.*² and Kerr and Sheppard³ and is identical to our previous evaluation, IUPAC, 1992.⁴ The upper limit to the rate coefficient obtained by Kerr and Stocker⁵ is consistent with the preferred value. The relative rate coefficient of Audley *et al.*⁶ was not used in the evaluation, due to questions concerning the applicability of the experimental technique used.^{1,7} The rate coefficient derived by Kaiser⁸ at 553 K relative to those for ethene, propene and *trans*-2-butene of $\leq 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, though

of only semi-quantitative value, suggests a zero or close to zero temperature dependence, as expected by analogy with HCHO and CH₃CHO. The major reaction channel is expected⁷ to be H-atom abstraction from the -CHO group to form H₂O + C₂H₅CO.

References

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HO + (CHO)₂ → H₂O + CHOCO

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred rate coefficient is based on the study of Plum *et al.*,¹ with increased uncertainty limits, and is identical to our previous evaluation, IUPAC, 1992.² The rate coefficient at 298 K is similar to those for other aldehydes. A close to zero temperature dependence is expected at around 298 K. The reaction is assumed to proceed via overall H-atom abstraction to yield H₂O + HC(O)CO. Niki *et al.*³ showed from a study of the Cl atom-initiated reaction of

glyoxal that at 298 K and 700 Torr total pressure the HC(O)CO radical reacts by the pathways,

with $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{18} \text{ molecule cm}^{-3}$.

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No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1/k = 0.80$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is taken from the study of Niki *et al.*,¹ with the error limits increased accordingly, and is identical to our previous evaluation, IUPAC, 1992.²

References

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$8.4 \times 10^{-13} \exp[(830 \pm 300)/T]$ $(1.32 \pm 0.30) \times 10^{-11}$	273–333 298	Tyndall <i>et al.</i> , 1995 ¹	(a)
<i>Reviews and Evaluations</i>			
1.7×10^{-11}	298	IUPAC, 1992 ²	(b)

Comments

- (a) Discharge flow system with LIF detection of HO radicals.
- (b) Based on the relative rate coefficient of Plum *et al.*³

Preferred Values

$k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the relative rate coefficient of Plum *et al.*³ and the absolute rate coefficient of Tyndall *et al.*¹ The absolute rate coefficient measured by Kleindienst *et al.*⁴ may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal. The data of Tyndall *et al.*¹ indicate a

significant negative temperature dependence; while no recommendation is made concerning the magnitude of the temperature dependence for this reaction a negative temperature dependence is expected at around room temperature (see, for example, the $\text{HO} + \text{CH}_3\text{CHO}$ reaction in this evaluation). The reaction is assumed to proceed via H-atom abstraction to form $\text{H}_2\text{O} + \text{CH}_3\text{COCO}$. Green *et al.*⁵ have shown that the dominant fate of this CH_3COCO radical under atmospheric conditions is decomposition to form $\text{CH}_3\text{CO} + \text{CO}$.

References

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$$\Delta H^\circ = -87.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(8.80 \pm 1.32) \times 10^{-12}$	1217	Bott and Cohen, 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.7 \times 10^{-12} \exp(-600/T)$	240–440	IUPAC, 1989 ² , 1992 ³	(b)
$5.34 \times 10^{-18} T^2 \exp(-230/T)$	240–1217	Atkinson, 1994 ⁴	(c)

Comments

- (a) HO radicals were generated by the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, and monitored by resonance absorption at 309 nm.
- (b) Derived from the absolute rate coefficient study of Wallington and Kurylo.⁵
- (c) Derived from the absolute rate coefficients of Wallington and Kurylo⁵ and Bott and Cohen¹ and the relative rate constant of Kerr and Stocker,⁶ using the expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$$k = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.8 \times 10^{-12} \exp(-760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient data of Wallington and Kurylo⁵ and Bott and Cohen¹ and the relative rate constant of Kerr and Stocker.⁶ These data^{1,5,6} have been fitted to the three-parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 5.34 \times 10^{-18} T^2 \times \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–1217 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The 298 K rate coefficient is similar to that for the HO radical reaction with ethane (this evaluation) and the present recommendation for the temperature dependence is more similar to that for ethane than was the previous IUPAC (1989, 1992) evaluation.^{2,3}

References

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$$\Delta H^\circ(1) = -88.5 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -61.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(8.64 \pm 1.30) \times 10^{-12}$	1205 ± 16	Bott and Cohen, 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$3.3 \times 10^{-12} \exp(-380/T)$	240–300	IUPAC, 1992 ²	(b)
$6.01 \times 10^{-18} T^2 \exp(170/T)$	240–1205	Atkinson, 1994 ³	(c)
$6.7 \times 10^{-12} \exp(-600/T)$	240–400	NASA, 1994 ⁴	(d)

Comments

- (a) HO radicals were generated from the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, and monitored by resonance absorption at 309 nm.
- (b) Derived from the absolute rate coefficients of Overend and Paraskevopoulos,⁵ Ravishankara and Davis,⁶ Wallington and Kurylo,⁷ McCaully *et al.*,⁸ Hess and Tully,⁹ and Nelson *et al.*¹⁰ and the relative rate coefficient of Tuazon *et al.*¹¹ These data^{5–11} were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 6.37 \times 10^{-18} T^2 \exp(150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–866 K. The Arrhenius expression is centered at 265 K and was derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.
- (c) Derived from the absolute rate coefficients of Overend and Paraskevopoulos,⁵ Ravishankara and Davis,⁶ Wallington and Kurylo,⁷ McCaully *et al.*,⁸ Hess and Tully,⁹ Nelson *et al.*,¹⁰ and Bott and Cohen¹ and the relative rate coefficient of Tuazon *et al.*,¹¹ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (d) The 298 K rate coefficient was the average of the absolute rate coefficients of Overend and Paraskevopoulos,⁵ Ravishankara and Davis,⁶ Hägele *et al.*,¹² Meier *et al.*,¹³ Greenhill and O'Grady,¹⁴ Wallington and Kurylo,⁷ and Hess and Tully.⁹ The temperature dependence was derived from those reported by Greenhill and O'Grady¹⁴ and Wallington and Kurylo.⁷

Preferred Values

$k = 9.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.1 \times 10^{-12} \exp(-360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.
 $k_2/k = 0.15$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.
 $\Delta k_2/k = \pm 0.10$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Overend and Paraskevopoulos,⁵ Ravishankara and Davis,⁶ Wallington and Kurylo,⁷ McCaully *et al.*,⁸ Hess and Tully,⁹ Nelson *et al.*,¹⁰ and Bott and Cohen¹ and the relative rate coefficient of Tuazon *et al.*¹¹ to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.01 \times 10^{-18} T^2 \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–1205 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The kinetic⁸ and product^{12,13} studies show that the reaction proceeds mainly by step (1) at room temperature, as expected from the thermochemistry of the reaction steps (1) and (2).

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$\Delta H^\circ(1) = -80 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H^\circ(2) = -109.9 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H^\circ(3) = -63.5 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_2 + k_3 = (8.80 \pm 1.32) \times 10^{-12}$	1204 ± 16	Bott and Cohen, 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$4.1 \times 10^{-12} \exp(-70/T)$	270–340	IUPAC, 1992 ²	(b)
$6.18 \times 10^{-18} T^2 \exp(532/T)$	293–599	Atkinson, 1994 ³	(c)
$7.0 \times 10^{-12} \exp(-235/T)$	240–600	NASA, 1994 ⁴	(d)

Comments

- HO radicals were generated by the thermal desorption of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm. The measured rate coefficient corresponds to $(k_2 + k_3)$ because of the rapid thermal decomposition of the $\text{CH}_2\text{CH}_2\text{OH}$ radical formed in reaction channel (1) (this is the same radical as formed from the addition of HO radicals to ethene).
- Derived from the HO^{18} radical and (for temperatures < 500 K) the HO^{16} radical rate coefficients of Hess and Tully.⁵ These data⁵ were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 6.18 \times 10^{-18} T^2 \exp(532/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 293–599 K. The Arrhenius expression, $k = A \exp(-B/T)$, was centered at 300 K and was derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.
- Derived from the HO^{18} rate coefficients and the < 500 K HO^{16} rate coefficients measured by Hess and Tully,⁵ using the three parameter equation $k = CT^2 \exp(-D/T)$. This expression is expected to be the overall rate constant $k = k_1 + k_2 + k_3$.
- The 298 K rate coefficient was the average of the room temperature rate coefficients of Campbell *et al.*,⁶ Overend and Paraskevopoulos,⁷ Ravishankara and Davis,⁸ Cox and Goldstone,⁹ Kerr and Stocker,¹⁰ Wallington and Kurylo,¹¹ and Hess and Tully.⁵ The temperature dependence was obtained by averaging the temperature dependencies of the rate coefficients reported by Wallington and Kurylo¹¹ and Hess and Tully.⁵

Preferred Values

$k = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.1 \times 10^{-12} \exp(-70/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.
 $k_1/k = 0.05$ at 298 K.
 $k_3/k = 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 200$ K.
 $\Delta k_1/k = \begin{smallmatrix} +0.10 \\ -0.05 \end{smallmatrix}$ at 298 K.
 $\Delta k_3/k = \begin{smallmatrix} +0.10 \\ -0.05 \end{smallmatrix}$ at 298 K.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.² There is substantial scatter in the room temperature rate coefficients measured to date. The most definite study to date is that of Hess and Tully.⁵ The preferred rate coefficient is derived from fitting the HO^{18} and (for temperatures < 500 K) the HO^{16} rate coefficient data of

Hess and Tully⁵ to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.18 \times 10^{-18} T^2 \exp(532/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 293–599 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$ is centered at 300 K and is derived from this three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The rate coefficients calculated from the preferred Arrhenius expression are $\sim 10\%$ higher than the lowest temperature rate coefficients reported by Greenhill and O'Grady¹² (at 255 K) and Wallington and Kurylo¹¹ (at 240 K). The preferred 298 K rate coefficient is in good agreement with the absolute and relative rate coefficients of Nelson *et al.*¹³ The rate coefficient measured by Bott and Cohen¹ at 1204 K, and ascribed to $(k_2 + k_3)$, is consistent with the value of $(k_1 + k_2 + k_3)$ calculated from the recommended three parameter expression and with the rate coefficient k_1 at 1204 K estimated using the procedure of Atkinson.¹⁴

Meier *et al.*¹⁵ determined that at room temperature the reaction proceeds mainly ($75 \pm 15\%$) via formation of the CH_3CHOH radical, consistent with the expected thermochemistry of the reaction steps. The kinetic data of Hess and Tully⁵ for the reactions of the HO^{16} and HO^{18} radicals with ethanol indicate that channel (1) accounts for $\sim 15\%$ of the overall reaction at 600 K, in agreement with the calculated value of $\sim 20\%$ from the estimation procedure of Atkinson.¹⁴ This agreement allows a rate coefficient ratio of $k_1/k = 0.05$ at 298 K to be estimated. Assuming that H-atom abstraction from the -OH group in ethanol [channel (3)] has a similar rate coefficient to the analogous channel for methanol (this evaluation) allows $k_3/k = 0.05$ at 298 K to be estimated. The resulting value of $k_2/k = 0.90$ at 298 K is just consistent with the product data of Meier *et al.*¹⁵

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- R. Atkinson, *Int. J. Chem. Kinet.* **19**, 799 (1987).
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HO + *n*-C₃H₇OH → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The experimental technique of Campbell *et al.*¹ was possibly prone to unrecognized problems,² and hence this rate coefficient was not used in deriving the preferred values. The 298 K value is the mean of the absolute rate coefficients of Overend and Paraskevopoulos,³ Wallington and Kurylo,⁴ and

Nelson *et al.*⁵ and the relative rate coefficient of Nelson *et al.*⁵ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

References

- ¹I. M. Campbell, D. F. McLaughlin, and B. J. Handy, *Chem. Phys. Lett.* **38**, 362 (1976).
- ²R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 1**, 1 (1989).
- ³R. Overend and G. Paraskevopoulos, *J. Phys. Chem.* **82**, 1329 (1976).
- ⁴T. J. Wallington and M. J. Kurylo, *Int. J. Chem. Kinet.* **19**, 1015 (1987).
- ⁵L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 1111 (1990).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -60.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.044 \times 10^{-17} T^{1.86} \exp(736/T)$ $(5.10 \pm 0.21) \times 10^{-12}$	293–587 293	Dunlop and Tully, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
5.7×10^{-12}	240–440	IUPAC, 1992 ²	(b)
$4.06 \times 10^{-18} T^2 \exp(788/T)$	293–587	Atkinson, 1994 ³	(c)

Comments

- (a) Pulsed laser photolysis system with LIF detection of HO radicals. The reactions of HO¹⁶ radicals were studied over the temperature range 293–745 K and the reactions of HO¹⁸ radicals were studied at 548 K and 587 K. Non-exponential decays of HO¹⁶ radicals were observed over the temperature range 504–600 K¹ and, while exponential HO¹⁶ radical decays were observed above 600 K,¹ the rate coefficients were significantly lower than expected from extrapolation of the lower temperature data.¹ These observations are consistent with thermal decomposition of the CH₃CH(OH)CH₂ radical formed in reaction channel (3) [the same radical as formed from HO radical addition to propene] at temperatures ≥ 500 K. Hence using HO¹⁶ radicals, values of $k_1 + k_2 + k_3$ were measured at temperatures ≤ 500 K and $k_1 + k_2$ at temperatures ≥ 600 K. No regeneration of HO¹⁸ radicals from thermal decomposition of the

CH₃CH(¹⁶OH)CH₂ radical can occur, and hence the measured HO¹⁸ rate coefficients are those for ($k_1 + k_2 + k_3$).

- (b) The preferred 298 K rate coefficient was the average of the room temperature absolute rate coefficients of Overend and Paraskevopoulos,⁴ Wallington and Kurylo,⁵ and Nelson *et al.*⁶ and the relative rate coefficient of Nelson *et al.*⁶ A zero temperature dependence was used, consistent with the data of Wallington and Kurylo.⁵
- (c) Derived from the HO¹⁸ radical and (for temperatures ≤ 502 K) HO¹⁶ radical rate coefficients of Dunlop and Tully.¹ These rate coefficients¹ were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$$k = 5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.7 \times 10^{-12} \exp(190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 270\text{--}340 \text{ K.}$$

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred rate coefficients are derived from the data obtained by Dunlop and Tully.¹ The HO¹⁸ rate coefficients at 548 K and 587 K and the HO¹⁶ rate coefficients at ≤ 502 K were fitted to the three parameter expression $k = CT^2 \times \exp(-D/T)$, resulting in $k = 4.06 \times 10^{-18} T^2 \exp(788/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 293–587 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is

centered at 300 K and is derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The preferred rate coefficients are $\sim 10\%$ lower than those of Wallington and Kurylo⁵ over the temperature range 270–340 K.

References

- ¹J. R. Dunlop and F. P. Tully, *J. Phys. Chem.* **97**, 6457 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁴R. Overend and G. Paraskevopoulos, *J. Phys. Chem.* **82**, 1329 (1978).
- ⁵T. J. Wallington and M. J. Kurylo, *Int. J. Chem. Kinet.* **19**, 1015 (1987).
- ⁶L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 1111 (1990).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.29 \times 10^{-11} \exp[-(388 \pm 151)/T]$ $(3.50 \pm 0.35) \times 10^{-12}$	299–424 298.9	Perry, Atkinson, and Pitts, 1977 ¹	(a)
$1.04 \times 10^{-11} \exp[-(372 \pm 34)/T]$ $(2.95 \pm 0.12) \times 10^{-12}$	295–442 295	Tully and Droegge, 1987 ²	(b)
$6.7 \times 10^{-12} \exp[-(300 \pm 70)/T]$ $(2.49 \pm 0.22) \times 10^{-12}$ $(2.35 \pm 0.24) \times 10^{-12}$	240–440 296 298 $\pm$ 2	Wallington <i>et al.</i> , 1988 ³ Nelson <i>et al.</i> , 1990 ⁴	(a) (c)
<i>Relative Rate Coefficients</i>			
$(2.30 \pm 0.23) \times 10^{-12}$ $(3.19 \pm 0.70) \times 10^{-12}$	295 $\pm$ 3 298 $\pm$ 2	Wallington <i>et al.</i> , 1989 ⁵ Nelson <i>et al.</i> , 1990 ⁴	(d) (e)
<i>Reviews and Evaluations</i>			
$1.04 \times 10^{-11} \exp(-372/T)$	295–442	Atkinson, 1994 ⁶	(f)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (b) Laser photolysis system with LIF detection of HO radicals.
- (c) Pulsed radiolysis system with resonance absorption detection of HO radicals.
- (d) Relative rate method. HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at atmospheric pressure. Concentrations of dimethyl ether and *n*-butane measured during the experiment by GC and the rate coefficient ratio of $k(\text{CH}_3\text{OCH}_3)/k(\textit{n}\text{-butane}) = 0.918 \pm 0.090$ placed on an absolute basis by using $k(\textit{n}\text{-butane}) = 2.50 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.⁶
- (e) Relative rate method. HO radicals generated by the photolysis of CH₃ONO-NO-air mixtures at atmospheric pressure. Concentrations of dimethyl ether and cyclohexane measured during the experiments by GC, and the rate coefficient ratio $k(\text{CH}_3\text{OCH}_3)/$

$k(\text{cyclohexane})$ placed on an absolute basis by use of $k(\text{cyclohexane}) = 7.49 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.⁶

- (f) Based on the absolute rate coefficient data of Tully and Droegge.²

Preferred Values

$k = 2.9 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k = 1.0 \times 10^{-11} \exp(-370/T)$ cm³ molecule⁻¹ s⁻¹ over the temperature range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The reported room temperature absolute^{1–4} and relative^{4,5} rate coefficients exhibit appreciable scatter, covering a range of a factor of 1.5. The measured temperature dependencies^{1–3} are in good agreement. The preferred values are based on the absolute rate coefficient study of Tully and

Droege,² the data of which are between those of the other two absolute temperature-dependent studies of Perry *et al.*¹ and Wallington *et al.*³

References

¹R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.* **67**, 611 (1977).

²F. P. Tully and A. T. Droege, *Int. J. Chem. Kinet.* **19**, 251 (1987).

³T. J. Wallington, R. Liu, P. Dagaut, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 41 (1988).

⁴L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 1111 (1990).

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⁶R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

HO + CH₃COCH₂OH → products

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

Based on the sole study of Dagaut *et al.*,¹ with expanded

uncertainty limits. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

¹P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, *J. Phys. Chem.* **93**, 7838 (1989).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ(2) = -140 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.9 \times 10^{-12} \exp(190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–430 K.

$k_1/k = 0.35$ over the temperature range 220–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 150 \text{ K}$.

$\Delta(k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values are those of Vaghjiani and Ravishankara.¹ The preferred branching ratio, also taken from the absolute rate coefficient study of Vaghjiani and Ravishankara,¹ is in good agreement with the earlier measurement of Niki *et al.*² The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

¹G. L. Vaghjiani and A. R. Ravishankara, *J. Phys. Chem.* **93**, 1948 (1989).

²H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **87**, 2190 (1983).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + HCOOH → products

No new data have been published since our last evaluation.

Preferred Values

$k = 4.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 250$ K.

Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HCOOH. The studies of Wine *et al.*,¹ Jolly *et al.*,² and Singleton *et al.*³ monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies^{1–3} agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut *et al.*⁴ The data of Wine *et al.*¹ and Singleton *et al.*³ show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficient data of Wine *et al.*,¹ Jolly *et al.*,² and Singleton *et al.*³ has been used to derive the preferred rate coefficient. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

The studies of Wine *et al.*¹ and Jolly *et al.*² showed that H atoms are produced in this reaction, with a yield of 0.75

± 0.25 .¹ Furthermore, Wine *et al.*¹ and Singleton *et al.*³ showed that within the experimental uncertainties the rate coefficient for the reaction of the HO radical with DCOOH is identical to that for HCOOH at 298 K. Also, the room temperature rate coefficients for the reactions of the DO radical with HCOOH and DCOOH are significantly lower than those for the reactions of the HO radical with HCOOH and DCOOH.³ This reaction then appears to proceed by

with overall abstraction of the H (or D) atom from the -OH (or -OD) group being the major pathway at room temperature.

References

- ¹P. H. Wine, R. J. Astalos, and R. L. Mauldin, III, *J. Phys. Chem.* **89**, 2620 (1985).
- ²G. S. Jolly, D. J. McKenney, D. L. Singleton, G. Paraskevopoulos, and A. R. Bossard, *J. Phys. Chem.* **90**, 6557 (1986).
- ³D. L. Singleton, G. Paraskevopoulos, R. S. Irwin, G. S. Jolly, and D. J. McKenney, *J. Am. Chem. Soc.* **110**, 7786 (1988).
- ⁴P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 331 (1988).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH₃COOH → products

No new data have been published since our last evaluation.

Preferred Values

$k = 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

At 298 K, the rate coefficients of Dagaut *et al.*¹ and Singleton *et al.*² are in reasonable agreement. However, at temperatures above 298 K, Dagaut *et al.*¹ observed the rate coefficient to increase with increasing temperature, while Singleton *et al.*² observed the rate coefficient to decrease in a non-Arrhenius manner with increasing temperature. At 400–440 K, the rate coefficients of Dagaut *et al.*¹ and Singleton *et al.*² disagree by a factor of 2.2.

The preferred 298 K rate coefficient is an average of the data of Dagaut *et al.*¹ and Singleton *et al.*² No recommenda-

tion is made regarding the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC, 1992.³ The rate coefficient data of Singleton *et al.*³ for the reactions of the HO radical with CH₃COOH, CD₃COOH, and CD₃COOD indicate that at room temperature the major reaction channel involves overall H atom abstraction from the -OH bond:

References

- ¹P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 331 (1988).
- ²D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, *J. Am. Chem. Soc.* **111**, 5248 (1989).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-12} \exp[-(120 \pm 30)/T]$	298–440	Dagaut <i>et al.</i> , 1988 ¹	(a)
$(1.22 \pm 0.12) \times 10^{-12}$	298		
$(1.07 \pm 0.05) \times 10^{-12}$	298–445	Singleton, Paraskevopoulos, and Irwin, 1989 ²	(b)
$(1.02 \pm 0.55) \times 10^{-12}$	298		
<i>Reviews and Evaluations</i>			
1.16×10^{-12}	298–445	Atkinson, 1994 ³	(c)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (b) Pulsed laser photolysis system with resonance absorption detection of HO radicals.
- (c) Derived from an average of all of the rate coefficients of Dagaut *et al.*¹ and Singleton *et al.*² These data^{1,2} indicate that the rate coefficient is independent of temperature over the range 298–445 K.

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The rate coefficients measured by Dagaut *et al.*¹ and Singleton *et al.*² are in good agreement and indicate that the rate coefficient for this reaction is independent of temperature over the range 298–445 K. The preferred value is an average of all of the rate coefficients of Dagaut *et al.*¹ and Singleton *et al.*² combined with a zero temperature dependence. The reaction is expected to proceed by H-atom abstraction from the C-H bonds of the -CH₃ group and the O-H bond of the -C(O)OH group.

References

- ¹P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 331 (1988).
²D. L. Singleton, G. Paraskevopoulos, and R. S. Irwin, *J. Am. Chem. Soc.* **111**, 5248 (1989).
³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

No new data have been published since our last evaluation.

Preferred Values

$k = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar.
 $k = 1.0 \times 10^{-14} \exp(1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–400 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K (1 bar).
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

At room temperature, the absolute and relative rate coefficients of Nielsen *et al.*¹ and Kerr and Stocker² measured at 1 bar pressure are in good agreement, but are an order of magnitude higher than the rate coefficient measured by Gaffney *et al.*³ at 0.003–0.004 bar pressure. This may indicate that the rate coefficient is pressure dependent and hence that the reaction proceeds by H-atom abstraction and OH

radical addition (and by ~90% OH radical addition at 298 K and 1 bar). This conclusion is supported by the observed negative temperature dependence.¹ The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Nielsen *et al.*¹ and Kerr and Stocker² (note that formation of CH₃ONO₂ in the photolysis of CH₃ONO-NO-air mixtures could have led to a low measured rate coefficient in the relative rate coefficient study of Nielsen *et al.*,¹ although the agreement of this relative rate coefficient¹ with the absolute rate coefficient of Nielsen *et al.*¹ and the relative rate coefficient of Kerr and Stocker² suggests that any such formation of CH₃ONO₂ was small). The temperature dependence is derived from the absolute rate coefficient data of Nielsen *et al.*,¹ and is applicable only at 1 bar pressure. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **178**, 163 (1991).
- ²J. A. Kerr and D. W. Stocker, *J. Atmos. Chem.* **4**, 253 (1986).
- ³J. S. Gaffney, R. Fajer, G. I. Senum, and J. H. Lee, *Int. J. Chem. Kinet.* **18**, 399 (1986).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + C₂H₅ONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar.
 $k = 4.4 \times 10^{-14} \exp(720/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–380 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K (1 bar).
 $\Delta(E/R) = \pm 500 \text{ K}$ (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker¹ and Nielsen *et al.*² are in good agreement at room temperature. All three rate coefficients have been determined

at ~ 1 bar pressure, and it is possible that the rate coefficient is pressure dependent at low total pressures. The preferred 298 K rate coefficient is the average of those determined by Kerr and Stocker¹ and Nielsen *et al.*² The preferred temperature dependence is that of Nielsen *et al.*² The preferred values are applicable to 1 bar pressure and are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹J. A. Kerr and D. W. Stocker, *J. Atmos. Chem.* **4**, 253 (1986).
- ²O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **178**, 163 (1991).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + *n*-C₃H₇ONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 7.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–370 K (1 bar).

Reliability

$\Delta \log k = \pm 0.15$ at 298 K (1 bar).
 $\Delta(E/R) = \pm 500 \text{ K}$ (1 bar).

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker,¹ Atkinson and Aschmann,² and Nielsen *et al.*³ are in reasonable agreement at room temperature. All studies have been carried out at ~ 1 bar pressure. The reaction may proceed by H-atom abstraction and OH radical addition, and the rate coefficient may be pressure dependent at low total pres-

ures. The preferred 298 K rate coefficient is the average of those measured by Kerr and Stocker,¹ Atkinson and Aschmann,² and Nielsen *et al.*³ A zero temperature dependence is assumed, consistent with the data of Nielsen *et al.*³ The preferred rate coefficients are applicable to 1 bar pressure, and are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹J. A. Kerr and D. W. Stocker, *J. Atmos. Chem.* **4**, 253 (1986).
- ²R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **21**, 1123 (1989).
- ³O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **178**, 163 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + *i*-C₃H₇ONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K (1 bar).

Comments on Preferred Values

The study of Atkinson and Aschmann,¹ carried out in a 6400 liter reaction chamber, supersedes the earlier study of Atkinson *et al.*² carried out in a 50 liter chamber and in which wall losses were concluded (probably erroneously) to have occurred. The relative rate coefficients of Becker and Wirtz³ and Atkinson and Aschmann¹ are in reasonable agree-

ment. The preferred 298 K rate coefficient is the average of those of Becker and Wirtz³ and Atkinson and Aschmann,¹ and is identical to our previous evaluation, IUPAC, 1992.⁴ As for the other alkyl nitrates, this reaction may proceed by H-atom abstraction and OH radical addition, and the preferred rate coefficient is applicable to 1 bar pressure.

References

- ¹R. Atkinson and S. M. Aschmann, *Int. J. Chem. Kinet.* **21**, 1123 (1989).
- ²R. Atkinson, S. M. Aschmann, W. P. L. Carter, and A. M. Winer, *Int. J. Chem. Kinet.* **14**, 919 (1982).
- ³K. H. Becker and K. Wirtz, *J. Atmos. Chem.* **9**, 419 (1989).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH₃CO₃NO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 9.5 \times 10^{-13} \exp(-650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The 298 preferred value is the average of the room temperature rate coefficients of Wallington *et al.*¹ and Tsalkani *et al.*,² both of which are consistent with the upper limit to the rate coefficient previously determined by Winer *et al.*³

The temperature dependence is that reported by Wallington *et al.*¹ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴ The reaction is expected to proceed via H-atom abstraction from the C-H bonds to yield H₂O + CH₂CO₃NO₂.

References

- ¹T. J. Wallington, R. Atkinson, and A. M. Winer, *Geophys. Res. Lett.* **11**, 861 (1984).
- ²N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, *J. Atmos. Chem.* **7**, 409 (1988).
- ³A. M. Winer, A. C. Lloyd, K. R. Darnall, R. Atkinson, and J. N. Pitts, Jr., *Chem. Phys. Lett.* **51**, 221 (1977).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH₃COCH₂ONO₂ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Relative Rate Coefficients $< 4.4 \times 10^{-13}$	298 ± 2	Zhu, Barnes, and Becker, 1991 ¹	(a)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of CH₃ONO-NO-N₂-O₂ mixtures at 1 bar pressure. Concentrations of CH₃COCH₂ONO₂ and *n*-butane were measured during the experiments by GC, and the rate constant ratio of $k(\text{CH}_3\text{COCH}_2\text{ONO}_2)/k(n\text{-butane}) < 0.17$ was placed on an absolute basis by use of a rate coefficient of $k(n\text{-butane}) = 2.54 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²

Preferred Values

$k < 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

Based on the sole study of Zhu *et al.*,¹ but with a higher upper limit to reflect additional uncertainties.

References

- ¹T. Zhu, I. Barnes, and K. H. Becker, *J. Atmos. Chem.* **13**, 301 (1991).
- ²R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

HO + HCN → products

No new data have been published since our last evaluation.

Preferred Values

$k = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar.
 $k = 1.2 \times 10^{-13} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–440 K at 1 bar.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are those of Fritz *et al.*¹ with wider error limits. The rate coefficient increases with increasing pressure over this temperature range, and the rate coefficients

cited are those extrapolated by Fritz *et al.*¹ to the high-pressure limit. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

The reaction proceeds by HO radical addition over this temperature range. At higher temperatures the available rate coefficient data indicate a direct abstraction reaction.³

References

- ¹B. Fritz, K. Lorenz, W. Steinert, and R. Zellner, *Oxid. Comm.* **6**, 363 (1984).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 1**, 1 (1989).

HO + CH₃CN → products

No new data have been published since our last evaluation.

Preferred Values

$k = 2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (1 bar).
 $k = 8.1 \times 10^{-13} \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–390 K (1 bar).

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is a unit-weighted average of the rate coefficients of Poulet *et al.*,¹ Kurylo and Knable,² and Hynes and Wine.³ The temperature dependence is the mean of those determined by Kurylo and Knable² and Hynes and Wine.³ The mechanism and products of this reaction are not understood at present. Hynes and Wine³ observed no definitive evidence for a pressure dependence of the rate coefficient for the HO + CH₃CN reaction in N₂ or He diluent over the pressure range 46–700 Torr (N₂ diluent) or 30–630 Torr (He diluent). In the presence of O₂, the HO radical decays were nonexponential,³ indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD₃CN (for which the rate coef-

ficient was pressure dependent over the pressure range 40–692 Torr of N₂ diluent)³ and of DO radicals with CH₃CN and CD₃CN,³ these data suggest that the initial HO radical reaction proceeds by H-atom abstraction from the -CH₃ group and HO radical addition to the -CN group.³

Subsequent reactions of the addition adduct in the presence of O₂ then lead to the regeneration of HO radicals. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures³ (≤ 0.1 bar), the preferred values, which are identical to our previous evaluation, IUPAC, 1992,⁴ are applicable to atmospheric conditions.

References

- ¹G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, *J. Phys. Chem.* **88**, 6259 (1984).
- ²M. J. Kurylo and G. L. Knable, *J. Phys. Chem.* **88**, 3305 (1984).
- ³A. J. Hynes and P. H. Wine, *J. Phys. Chem.* **95**, 1232 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -156 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.9 \times 10^{-13} \exp(862/T)$	248–700	Lightfoot <i>et al.</i> , 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
$3.8 \times 10^{-13} \exp(780/T)$	225–580	IUPAC, 1992 ²	(b)
$5.6 \times 10^{-13} \exp(640/T)$	228–573	Wallington, Dagaut, and Kurylo, 1992 ³	(c)
$4.1 \times 10^{-13} \exp(790/T)$	230–680	Lightfoot <i>et al.</i> , 1992 ⁴	(d)
$3.8 \times 10^{-13} \exp(800/T)$	200–300	NASA, 1994 ⁵	(e)

Comments

- (a) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-CH}_3\text{OH-CH}_4\text{-O}_2\text{-N}_2$ mixtures at 760 Torr and over the temperature range 600 to 719 K. The temperature dependent rate coefficient listed above was derived by the authors from a reanalysis of all of their data, including previous studies from flash photolysis experiments.
- (b) k_{298} is the averaged value of Cox and Tyndall,⁶ Jenkin *et al.*,⁷ Dagaut *et al.*,⁸ Moortgat *et al.*,⁹ and Lightfoot *et al.*¹⁰ and the temperature coefficient is that reported by Lightfoot *et al.*¹⁰
- (c) Derived from an analysis of the data of Cox and Tyndall,⁶ McAdam *et al.*,¹¹ Kurylo *et al.*,¹² Jenkin *et al.*,⁷ Dagaut *et al.*,⁸ Moortgat *et al.*,⁹ and Lightfoot *et al.*¹⁰
- (d) k_{298} is an average value of the data of Cox and Tyndall,⁶ McAdam *et al.*,¹¹ Jenkin *et al.*,⁷ Dagaut *et al.*,⁸ Moortgat *et al.*,⁹ and Lightfoot *et al.*¹⁰
- (e) k_{298} is the averaged value of data from Cox and Tyndall,⁶ McAdam *et al.*,¹¹ Kurylo *et al.*,¹² Jenkin *et al.*,⁷ Moortgat *et al.*,⁹ and Lightfoot *et al.*¹⁰ E/R derived from the data of Cox and Tyndall,⁶ Dagaut *et al.*,⁸ and Lightfoot *et al.*¹⁰

Preferred Values

$$k = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.8 \times 10^{-13} \exp(780/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 225\text{--}580 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

There have been no new data at or around room temperature and our previous recommendation,² which is in accord with other subsequent recommendations,^{3–5} still stands. Wallington¹³ has extended the previous FTIR study¹⁴ of the products of the reaction at 760 Torr to a wider range of pressures (15–700 Torr) and confirmed that $92 \pm 5\%$ of the $\text{HO}_2 + \text{CH}_3\text{O}_2$ reaction produces $\text{O}_2 + \text{CH}_3\text{O}_2\text{H}$. Wallington and Hurley¹⁵ have shown from an FTIR study of the reaction between HO_2 and CD_3O_2 radicals that the sole product is CD_3OOH .

References

- P. D. Lightfoot, P. Roussel, F. Caralp, and R. Lesclaux, *J. Chem. Soc. Faraday Trans. 2*, **87**, 3213 (1991).
- IUPAC, Supplement IV, 1992 (see references in Introduction).
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- P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
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- R. A. Cox and G. S. Tyndall, *J. Chem. Soc. Faraday Trans. 2*, **76**, 153 (1980).
- M. E. Jenkin, R. A. Cox, G. D. Hayman, and L. J. Whyte, *J. Chem. Soc. Faraday Trans. 2*, **84**, 913 (1988).
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- T. J. Wallington and S. M. Japar, *Chem. Phys. Lett.* **167**, 513 (1990).
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$$\Delta H^\circ(2) = -473.1 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.6 \times 10^{-15} \exp(2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 275–335 K.

$k_2/k = 0.4$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 1500 \text{ K}$.

$\Delta(k_1/k) = \pm 0.4$ at 298 K.

Comments on Preferred Values

The two studies^{1,2} of the rate coefficient at 298 K are in good agreement and confirm that this reaction is fast compared with the HO_2 radical reactions with CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals. The product channel yielding HCOOH is

presumed to proceed via a six-membered cyclic intermediate, analogous to that proposed for the formation of HCHO , CH_3OH , and O_2 from the interaction of CH_3O_2 radicals.³ Both the temperature dependence and the branching ratio require independent confirmation. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, *J. Phys. Chem.* **93**, 2368 (1989).
- ²J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G.D. Hayman, and B. Veyret, *J. Phys. Chem.* **93**, 2375 (1989).
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- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$1.6 \times 10^{-13} \exp[(1260 \pm 130)/T]$	248–480	Fenter <i>et al.</i> , 1993 ¹	(a)
$(1.10 \pm 0.21) \times 10^{-11}$	298		
$6.9 \times 10^{-13} \exp[(702 \pm 69)/T]$	210–363	Maricq and Szenté, 1994 ²	(b)
$(8.3 \pm 1.5) \times 10^{-12}$	295		
Reviews and Evaluations			
$5.6 \times 10^{-13} \exp(650/T)$	250–380	Wallington, Dagaut, and Kurylo, 1992 ³	(c)
$6.5 \times 10^{-13} \exp(650/T)$	250–380	Lightfoot <i>et al.</i> , 1992 ⁴	(d)
$6.5 \times 10^{-13} \exp(650/T)$	240–380	IUPAC, 1992 ⁵	(d)
$7.5 \times 10^{-13} \exp(700/T)$	200–300	NASA, 1994 ⁶	(e)

Comments

- (a) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at 760 Torr total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths.
- (b) Flash photolysis-UV absorption study of $\text{F}_2\text{-H}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at a total pressure of ~ 200 Torr. Rate coefficients were derived from computer simulation of time-resolved decay curves.
- (c) Based on the data of Dagaut *et al.*⁷
- (d) The rate coefficient of $k = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K was derived from the data of Cattell *et al.*⁸ and Dagaut *et al.*,⁷ together with $E/R = -650 \text{ K}$ from Dagaut *et al.*⁷
- (e) Based on the rate coefficients of Cattell *et al.*,⁸ Dagaut *et al.*,⁷ Fenter *et al.*,¹ and Maricq and Szenté.²

Preferred Values

$k = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-13} \exp(1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The room temperature rate coefficients of Fenter *et al.*¹ and Maricq and Szenté² are in reasonable agreement with the previous direct studies of Cattell *et al.*⁸ and Dagaut *et al.*⁷ We have based our recommendations on the average value of k_{298} from these four studies.^{1,2,7,8} However, the temperature coefficients of Fenter *et al.*¹ and Maricq and Szenté² differ by almost a factor of two, indicating a systematic error in one or both studies. We have recommended an E/R value corresponding to the rounded-off mean of these two studies,^{1,2} but clearly more work is needed to resolve the difference.

As discussed in our previous evaluation,⁵ the FTIR spectroscopic product study of Wallington and Japar⁹ has shown

that this reaction has only one channel, to yield $\text{C}_2\text{H}_5\text{OOH} + \text{O}_2$.

References

- ¹F. F. Fenter, V. Catoire, R. Lesclaux, and P. D. Lightfoot, *J. Phys. Chem.* **97**, 3530 (1993).
²M. M. Maricq and J. J. Szente, *J. Phys. Chem.* **98**, 2078 (1994).
³T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).

- ⁴P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
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⁶NASA Evaluation No. 11, 1994 (see references in Introduction).
⁷P. Dagaut, T. J. Wallington, and M. J. Kurylo, *J. Phys. Chem.* **92**, 3836 (1988).
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⁹T. J. Wallington and S. M. Japar, *Chem. Phys. Lett.* **166**, 495 (1990).

$$\Delta H^\circ(2) = -132 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.3 \times 10^{-13} \exp[(1040 \pm 100)/T]$ $(1.3 \pm 0.3) \times 10^{-11}$	253–368 298	Moortgat, Veyret, and Lesclaux, 1989 ¹	(a)
<i>Branching Ratios</i>			
$k_2/k=0.23$	298	Niki <i>et al.</i> , 1985 ²	(b)
$k_2/k=0.33 \pm 0.07$	253–368	Moortgat, Veyret, and Lesclaux, 1989 ¹	(c)
$k_2/k=8.5 \times 10^{-3} \exp(1020/T)$	263–333	Horie and Moortgat, 1992 ²	(d)
$k_2k=0.26$	298		
<i>Reviews and Evaluations</i>			
$4.3 \times 10^{-13} \exp(1040/T)$	250–370	IUPAC, 1992 ⁴	(e)
$k_2/k=0.3$	250–370		(f)
$4.3 \times 10^{-13} \exp(1040/T)$	253–368	Wallington, Dagaut, and Kurylo, 1992 ²	(e)
$k_2/k=0.33$	253–300		(e)
$4.3 \times 10^{-13} \exp(1040/T)$	253–368	Lightfoot <i>et al.</i> , 1992 ⁶	(e)
$k_2/k=0.33$	253–368		(e)
$4.5 \times 10^{-13} \exp(1000/T)$	200–300	NASA, 1994 ⁷	(e)

Comments

- (a) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$ mixtures at total pressures of 600–650 Torr. $[\text{CH}_3\text{CO}_3]$ was monitored by UV absorption over the wavelength range 195–280 nm and the absorption cross section measured relative to $\sigma(\text{HO}_2)=5.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of CH_3CO_3 .
- (b) FTIR study of irradiated $\text{Cl}_2-\text{HCHO}-\text{CH}_3\text{CHO}-\text{O}_2$ mixtures. The branching ratio was based on the analysis of the products $\text{CH}_3\text{CO}_3\text{H}$, $\text{CH}_3\text{CO}_2\text{H}$, and O_3 .
- (c) Derived from the same experiments as in Comment (a) by making allowance for absorption by O_3 product.
- (d) FTIR study of irradiated $\text{CH}_3\text{COCOCH}_3$ in the presence of $\text{Ar}-\text{O}_2$ mixtures at total pressures of 730–770 Torr. The reaction products CO_2 , CO , HCHO ,

HCOOH , $\text{CH}_3\text{CO}_2\text{H}$, $\text{CH}_3\text{CO}_3\text{H}$, CH_3OH , H_2O_2 , and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio obtained was $\ln(k_1/k_2)=\{(5.8 \pm 1.7)-(1430 \pm 480)/T\}$, derived from the yields of $\text{CH}_3\text{CO}_3\text{H}$ and O_3 .

- (e) Based on the data of Moortgat *et al.*¹
 (f) Based on the data of Moortgat *et al.*¹ and Niki *et al.*²

Preferred Values

$k=1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k=4.3 \times 10^{-13} \exp(1040/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.
 $k_2/k=0.26$ at 298 K.
 $k_2/k=8.5 \times 10^{-3} \exp(1020/T)$ over the temperature range 260–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$$\Delta(E/R) = \pm 500 \text{ K.}$$

$$\Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E_2/R - E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended value of k together with its temperature dependence are unaltered since our last evaluation,⁴ and are based on the data of Moortgat *et al.*¹ Independent confirmation is required to lower the error limits. The study of the products of the reaction by Horie and Moortgat,³ leading to the measurement of the branching ratio, is much more direct than the previous study of Moortgat *et al.*¹ and, in contrast to the results of Moortgat *et al.*,¹ show a marked temperature dependence. The newer data³ are in reasonable agreement with the room temperature measurements of the branching ratio made by Niki *et al.*²

References

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- ²H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **89**, 588 (1985).
- ³O. Horie and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **88**, 3305 (1992).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).
- ⁶P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ⁷NASA Evaluation No. 11, 1994 (see references in Introduction).

HO₂ + HOCH₂CH₂O₂ → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The studies of Murrells *et al.*¹ by laser flash photolysis and by molecular modulation of the absorption spectrum of the HOCH₂CH₂O₂ radical have shown that the absorption cross-sections reported earlier by Jenkin and Cox² from molecular modulation studies of the photolysis of HOCH₂CH₂I are low by a factor of approximately 2. Jenkin and Cox² made the assumption that the photolysis of HOCH₂CH₂I in their system yielded entirely HOCH₂CH₂O₂ radicals, which was apparently not the case. Increasing $\sigma_{230}(\text{HOCH}_2\text{CH}_2\text{O}_2)$ by a factor of two in the interpretation¹ of the data of Jenkin and Cox² yields the revised value of $k = (8.4 \pm 3.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

The recommended rate coefficient is the mean of this revised value together with the value of Murrells *et al.*¹ The approximate value derived by Anastasi *et al.*³ in the pulsed radiolysis experiments is a factor of two higher than our recommended value, and we have not taken this value of Anastasi *et al.*³ into account, owing to the differences in the absorption spectrum of the radical observed by Anastasi *et al.*³ compared with the consistent spectra reported by Jenkin and Cox² and Murrells *et al.*¹ (see data for the reaction 2 HOCH₂CH₂O₂ → products). The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, *J. Chem. Soc. Faraday Trans.* **87**, 2351 (1991).
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- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Branching Ratios</i>			
$k_1/k = 0.53 \pm 0.08$	295	Wallington <i>et al.</i> , 1993 ¹	(a)
$k_2/k = 0.40 \pm 0.04$	295		

Comments

- (a) HO₂ and CH₃OCH₂O₂ radicals were generated from the steady-state photolysis of Cl₂ in the presence of CH₃OH-CH₃OCH₃-O₂ mixtures at a total pressure of 900 Torr. Branching ratios were derived from FTIR analyses of CH₃OCHO and CH₃OCH₂O₂H products, which accounted for 93±12% of the CH₃OCH₃ loss.

Preferred Values

$$k_1/k = 0.60 \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.40 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta(k_1/k) = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(k_2/k) = \pm 0.10 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The reaction between HO₂ radicals and CH₃OCH₂O₂ radicals is analogous to that between HO₂ radicals and HOCH₂O₂ radicals in that there are two channels of nearly equal importance at room temperature, producing (i) the hydroperoxide plus O₂ and (ii) a carbonyl product, H₂O and O₂. In contrast, the HO₂ reactions with unsubstituted alkyl peroxy radicals, RO₂, appear to have only a single channel, producing the alkyl hydroperoxide.

It has been proposed¹ that the reaction between HO₂ and substituted RO₂ radicals yielding the carbonyl compounds proceeds through a six-member transition state identical to that suggested by Russell² to explain the molecular products from the interactions of RO₂ radicals.

References

¹T. J. Wallington, M. D. Hurley, J. C. Ball, and M. E. Jenkin, Chem. Phys. Lett. **211**, 41 (1993).

²G. Russell, J. Am. Chem. Soc. **79**, 3871 (1957).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> (9.0±1.3)×10 ⁻¹²	298	Bridier <i>et al.</i> , 1993 ¹	(a)

Comments

- (a) Flash photolysis of Cl₂ in the presence of CH₃COCH₃-CH₃OH-N₂ mixtures at a total pressure of 760 Torr. The rate coefficient *k* was derived from a kinetic analysis of absorption-time profiles measured at 210 and 230 nm.

Preferred Values

$$k = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been obtained from the kinetic analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. No evidence was obtained by Bridier *et al.*¹ for products other than O₂ and CH₃COCH₂O₂H.

References

¹I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).

$$\Delta H^\circ = -68.1 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 7.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 9.7 \times 10^{-15} \exp(625/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 275–333 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 600 \text{ K}$.

Comments on Preferred Values

This data sheet is based on our previous evaluation, IUPAC, 1989.¹ The most recent studies of Barnes *et al.*² and Veyret *et al.*³ are in excellent agreement regarding this rate coefficient, and both are in good agreement with the earlier data of Veyret *et al.*⁴ The preferred rate equation is derived by taking an average value of the rate coefficients of Barnes *et al.*² [$k(273 \text{ K}) = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] and of

Veyret *et al.*³ [$k(275 \text{ K}) = 8.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] together with the value of E/R determined by Veyret *et al.*³ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

This reaction is believed to proceed via the initial formation of the adduct radical, $\text{HO}_2\text{CH}_2\text{O}$, which rapidly isomerizes to the product radical, HOCH_2OO via H-atom transfer.

References

- ¹IUPAC, Supplement III, 1989 (see references in Introduction).
- ²I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, *Chem. Phys. Lett.* **115**, 1 (1985).
- ³B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, *J. Phys. Chem.* **93**, 2368 (1989).
- ⁴B. Veyret, J.-C. Rayez, and R. Lesclaux, *J. Phys. Chem.* **86**, 3424 (1982).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = 68.1 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.5 \times 10^2 \text{ s}^{-1}$ at 298 K.

$k = 2.4 \times 10^{12} \exp(-7000/T) \text{ s}^{-1}$ over the temperature range 275–333 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 2000 \text{ K}$.

Comments on Preferred Values

This data sheet is based on our previous evaluation, IUPAC, 1989.¹ The studies of Barnes *et al.*² and Veyret *et al.*³ are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K from these studies together with the E/R determined by Veyret *et al.*³ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

It should be pointed out that the equilibrium constant, K_1 , for the reactions $\text{HO}_2 + \text{HCHO} \rightleftharpoons \text{HOCH}_2\text{O}_2$ (1,–1), $K_1 = 5.2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K, derived from the

kinetic study of Veyret *et al.*³ (which is identical to the value obtained from our recommended data for k_1 and k_{-1}), is in excellent agreement with the value of $K_1 = 4.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K obtained independently by Burrows *et al.*⁵ from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $K_1 = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K reported by Zabel *et al.*⁶ from EPR spectroscopic measurements of the ratio of concentrations of HO_2 and HOCH_2OO radicals in the photolysis of HCHO-O_2 mixtures.

References

- ¹IUPAC, Supplement III, 1989 (see references in Introduction).
- ²I. Barnes, K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, *Chem. Phys. Lett.* **115**, 1 (1985).
- ³B. Veyret, R. Lesclaux, M.-T. Rayez, J.-C. Rayez, R. A. Cox, and G. K. Moortgat, *J. Phys. Chem.* **93**, 2368 (1989).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G.D. Hayman, and B. Veyret, *J. Phys. Chem.* **93**, 2375 (1989).
- ⁶F. Zabel, K. A. Sahetchian, and C. Chachaty, *Chem. Phys. Lett.* **134**, 433 (1987).

$$\Delta H^\circ = 12.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-16}$	298	Burrows, Tyndall, and Moortgat, 1985 ¹	(a)
$\leq 2 \times 10^{-17}$	298 $\pm$ 2	Wallington <i>et al.</i> , 1986 ²	(b)
$\leq 8 \times 10^{-19}$	302	Boyd <i>et al.</i> , 1991 ³	(c)
<i>Relative Rate Coefficients</i>			
$<6 \times 10^{-21}$	~ 298	Cantrell <i>et al.</i> , 1987 ⁴	(d)
<i>Reviews and Evaluations</i>			
$<1 \times 10^{-18}$	298	Atkinson, 1991 ⁵	(e)

Comments

- (a) NO_3 radicals were generated by the modulated photolysis of $\text{Cl}_2\text{-ClONO}_2\text{-N}_2$ or $\text{F}_2\text{-HNO}_3\text{-N}_2$ mixtures and monitored by optical absorption at 662 nm.
- (b) NO_3 radicals were generated by the flash photolysis of $\text{ClONO}_2\text{-He}$ mixtures and detected by optical absorption at 662 nm.
- (c) Stopped-flow system with optical absorption detection of NO_3 radicals at 662 nm. Occurrence of secondary reactions were expected to lead to a stoichiometry factor of ≥ 2 , resulting in the upper limit to the rate coefficient cited in the table.
- (d) Relative rate method. Upper limit to the rate coefficient was derived from the absence of CO and CO_2 formation after addition of CH_4 to $\text{N}_2\text{O}_5\text{-NO}_3\text{-NO}_2\text{-N}_2$ mixtures. An equilibrium constant for the $\text{NO}_2 + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_5$ reactions of $3.41 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K⁵ has been used to derive the rate coefficient cited.
- (e) Based on the upper limits derived by Burrows *et al.*,¹ Wallington *et al.*,² and Cantrell *et al.*⁴

Preferred Values

$$k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the upper limits to the rate coefficients obtained by Cantrell *et al.*⁴ and Boyd *et al.*,³ and is consistent with the higher upper limits reported by Burrows *et al.*¹ and Wallington *et al.*²

References

- ¹J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, *J. Phys. Chem.* **89**, 4848 (1985).
- ²T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 4640 (1986).
- ³A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).
- ⁴C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, *J. Phys. Chem.* **91**, 6017 (1987).
- ⁵R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).

No new data have been published since our last evaluation.

Preferred Values

$$k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements of Atkinson *et al.*¹ show

C_2H_2 to be significantly less reactive than C_2H_4 . The preferred value of the upper limit to the rate coefficient is sufficiently high to be consistent with the data of Canosa-Mas *et al.*² Until there are confirmatory data for the reported temperature dependence³ of this rate coefficient, no temperature dependence is recommended. The preferred value is identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹R. Atkinson, S. M. Aschmann, and M. A. Goodman, *Int. J. Chem. Kinet.* **19**, 299 (1987).
²C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **84**, 247 (1988).
³C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **84**, 263 (1988).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

NO₃ + C₂H₄ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.7 \pm 0.5) \times 10^{-16}$	300	Biggs <i>et al.</i> , 1991; ¹ Boyd <i>et al.</i> , 1991 ²	(a)
<i>Reviews and Evaluations</i>			
$3.3 \times 10^{-12} \exp(-2880/T)$	270–340	IUPAC, 1992 ³	(b)
$4.88 \times 10^{-18} T^2 \exp(-2282/T)$	295–523	Atkinson, 1994 ⁴	(c)

Comments

- (a) Stopped-flow technique with optical absorption of the NO₃ radical at 662 nm. The influence of the reaction NO₂ + NO₃ + He → N₂O₅ + He was taken into account by numerical modeling, leading to a stoichiometry factor for NO₃ radical decays of ~1.9 and the cited rate coefficient for the elementary NO₃ + ethene reaction.
- (b) Based on the absolute rate coefficients of Canosa-Mas *et al.*^{5,6} and the relative rate coefficient of Atkinson *et al.*⁷ These data^{5–7} were fitted to the three-parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.88 \times 10^{-18} T^2 \exp(-2282/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 295–523 K. The Arrhenius expression, $k = A \exp(-B/T)$, was centered at 300 K and was derived from the three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.
- (c) Derived from the absolute rate coefficients of Canosa-Mas *et al.*^{5,6} and the relative rate coefficient of Atkinson *et al.*,⁷ using the three parameter expression $k = CT^2 \exp(-D/T)$.

Preferred Values

$k = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.3 \times 10^{-12} \exp(-2880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas *et al.*^{5,6} and the relative rate coefficient of Atkinson *et al.*⁷ These data were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.88 \times 10^{-18} T^2 \exp(-2282/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 295–523 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.

The preferred rate coefficient is in agreement with the 300 K rate coefficient of Biggs *et al.*¹ and Boyd *et al.*,² and the preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹P. Biggs, A. A. Boyd, C. E. Canosa-Mas, D. M. Joseph, and R. P. Wayne, *Meas. Sci. Technol.* **2**, 675 (1991).
²A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).
³IUPAC, Supplement IV, 1992 (see reference in Introduction).
⁴R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
⁵C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **84**, 247 (1988).
⁶C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **84**, 263 (1988).
⁷R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., *J. Phys. Chem.* **92**, 3454 (1988).

$$\Delta H^\circ = -3.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 4 \times 10^{-18}$	298 $\pm$ 2	Wallington <i>et al.</i> , 1986 ¹	(a)
$5.7 \times 10^{-12} \exp[-(4426 \pm 337)/T]$	453–553	Bagley <i>et al.</i> , 1990 ²	(b)
$\leq (2.7 \pm 0.2) \times 10^{-17}$	302	Boyd <i>et al.</i> , 1991 ³	(c)

Comments

- (a) NO_3 radicals were generated by the flash photolysis of ClONO_2 -He mixtures and detected by optical absorption at 662 nm.
- (b) Discharge flow system with detection of NO_3 radicals by optical absorption at 662 nm.
- (c) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. Secondary reactions were expected to lead to a stoichiometry factor of ≥ 2 , leading to the cited upper limit to the rate coefficient.

Comments on Preferred Values

Extrapolation of the absolute rate coefficients obtained by Bagley *et al.*² over the temperature range 453–553 K to 298 K leads to a 298 K rate coefficient of $2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, probably uncertain to at least a factor of 2 due to the long extrapolation and possible non-Arrhenius behavior of the rate coefficient for this reaction. The preferred upper limit is based on the upper limit of Wallington *et al.*¹ and extrapolation to 298 K of the elevated temperature rate coefficients of Bagley *et al.*²

References

- ¹T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 4640 (1986).
- ²J. A. Bagley, C. Canosa-Mas, M. R. Little, A. D. Parr, S. J. Smith, S. J. Waygood, and R. P. Wayne, *J. Chem. Soc. Faraday Trans.* **86**, 2109 (1990).
- ³A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).

Preferred Values

$$k < 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.74 \times 10^{-13} \exp[-(1171 \pm 66)/T]$ $(9.3 \pm 1.2) \times 10^{-15}$	298–423 298	Canosa-Mas <i>et al.</i> , 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
9.4×10^{-15}	298	IUPAC, 1992 ²	(b)
$4.59 \times 10^{-13} \exp(-1156/T)$	296–423	Atkinson, 1994 ³	(c)

Comments

- (a) Discharge flow system with optical absorption detection of the NO_3 radical at 662 nm. Rate coefficients were measured over the temperature range 298–523 K, and the Arrhenius plot exhibited curvature above 423 K.
- (b) Based on the relative rate coefficient study of Atkinson *et al.*⁴
- (c) Derived using the room temperature relative rate coefficient of Atkinson *et al.*⁴ and the absolute rate coefficients of Canosa-Mas *et al.*¹ over the temperature range 298–423 K. These rate coefficients^{1,4} were fitted to an Arrhenius expression.

Preferred Values
 $k = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

 $k = 4.6 \times 10^{-13} \exp(-1155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 296–423 K.
Reliability
 $\Delta \log k = \pm 0.2$ at 298 K.

 $\Delta(E/R) = \pm 300 \text{ K}$.
Comments on Preferred Values

The preferred values are derived using the room temperature relative rate coefficient of Atkinson *et al.*⁴ and the 298–423 K absolute rate coefficients of Canosa-Mas *et al.*¹ The preferred 298 K rate coefficient is in agreement with the previous relative rate measurements of Morris and Niki,⁵ Japar and Niki,⁶ and Atkinson *et al.*⁷ when the differing values of the equilibrium constant used for the $\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_3 + \text{NO}_2$ reactions are taken into account.

The NO_3 radical reaction with propene proceeds by initial

addition, leading to the formation under simulated tropospheric conditions of HCHO , CH_3CHO , and $\text{CH}_3\text{COCH}_2\text{ONO}_2$.^{3,8–11}

References

- ¹C. E. Canosa-Mas, S. J. Smith, S. J. Waygood, and R. P. Wayne, *J. Chem. Soc. Faraday Trans.* **87**, 3473 (1991).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁴R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., *J. Phys. Chem.* **92**, 3454 (1988).
- ⁵E. D. Morris, Jr. and H. Niki, *J. Phys. Chem.* **78**, 1337 (1974).
- ⁶S. M. Japar and H. Niki, *J. Phys. Chem.* **79**, 1629 (1975).
- ⁷R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **88**, 1210 (1984).
- ⁸H. Bandow, M. Okuda, and H. Akimoto, *J. Phys. Chem.* **84**, 3604 (1980).
- ⁹P. B. Shepson, E. O. Edney, T. E. Kleindienst, J. H. Pittman, G. R. Namié, and L. T. Cupitt, *Environ. Sci. Technol.* **19**, 849 (1985).
- ¹⁰I. Barnes, V. Bastian, K. H. Becker, and Z. Tong, *J. Phys. Chem.* **94**, 2413 (1990).
- ¹¹J. Hjorth, C. Lohse, C. J. Nielsen, H. Skov, and G. Restelli, *J. Phys. Chem.* **94**, 7494 (1990).

 $\Delta H^\circ(1) = -6.8 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H^\circ(2) = -14.3 \text{ kJ} \cdot \text{mol}^{-1}$
Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $\leq (4.8 \pm 1.7) \times 10^{-17}$	298	Boyd <i>et al.</i> , 1991 ¹	(a)

Comments

- (a) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. The occurrence of secondary reactions is expected to lead to a stoichiometry factor of ≥ 2 , resulting in the upper limit to the rate coefficient cited in the table.

Preferred Values
 $k < 7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
Comments on Preferred Values

Based on the upper limit derived by Boyd *et al.*¹

References

- ¹A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).

 $\Delta H^\circ = -58.4 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The data of Atkinson *et al.*,¹ Cantrell *et al.*,² and Hjorth *et al.*³ disagree by a factor of ~ 1.5 when the same equilibrium constant for the reactions $\text{NO}_2 + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_5$ is used to place the rate coefficients on an absolute basis. However, the rate coefficient obtained by Cantrell *et al.*² from experiments which were independent of this equilibrium constant agree well with that derived from the Atkinson *et al.*¹ data.

Accordingly, a rate coefficient of $5.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is recommended, with the uncertainty limits reflecting the need for an absolute measurement. The preferred

value is identical to our previous evaluation, IUPAC, 1992.⁴ While no temperature dependence of the rate coefficient has been measured to date, by analogy with the NO_3 radical reaction with CH_3CHO , a preexponential factor of $\sim 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is expected, and hence $k(\text{NO}_3 + \text{HCHO}) \sim 2 \times 10^{-12} \exp(-2430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

This reaction proceeds by H-atom abstraction.

References

- ¹R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **88**, 1210 (1984).
- ²C. A. Cantrell, W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltkopf, J. G. Calvert, and H. S. Johnston, *J. Phys. Chem.* **89**, 139 (1985).
- ³J. Hjorth, G. Ottobri, and G. Restelli, *J. Phys. Chem.* **92**, 2669 (1988).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -67.3 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.4 \times 10^{-12} \exp(-1860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}370 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred values are based upon the sole absolute rate coefficient study of Dlugokencky and Howard.¹ The rate coefficients reported by Morris and Niki,² Atkinson *et al.*,³ and Cantrell *et al.*⁴ (when reevaluated⁵ to be consistent with recent values of the equilibrium constant for the NO_2

+ $\text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_5$ reactions) are in good agreement with this preferred value. However, because of the significant uncertainties in this equilibrium constant,⁵ these relative rate coefficient data were not used in the evaluation of the preferred rate coefficient. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

References

- ¹E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **93**, 1091 (1989).
- ²E. D. Morris, Jr. and H. Niki, *J. Phys. Chem.* **78**, 1337 (1974).
- ³R. Atkinson, C. N. Plum, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **88**, 1210 (1984).
- ⁴C. A. Cantrell, J. A. Davidson, K. L. Busarow, and J. G. Calvert, *J. Geophys. Res.* **91**, 5347 (1986).
- ⁵R. Atkinson, *J. Phys. Chem. Ref. Data* **20**, 459 (1991).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -15.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $\leq (8.5 \pm 2.5) \times 10^{-18}$	302	Boyd <i>et al.</i> , 1991 ¹	(a)

Comments

- (a) Stopped flow system with detection of the NO_3 radical by optical absorption at 662 nm. Secondary reactions

were believed to be important and a stoichiometry factor of ≥ 2 has been used to obtain the cited upper limit to the rate coefficient.

Preferred Values

$$k < 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The upper limit to the preferred value is derived from the measured overall rate coefficient of $(1.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with no account taken of the expected greater than unity stoichiometry.

References

- ¹A. A. Boyd, C. E. Canosa-Mas, A. D. King, R. P. Wayne, and M. R. Wilson, *J. Chem. Soc. Faraday Trans.* **87**, 2913 (1991).

NO₃ + CH₃OH → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.3 \times 10^{-12} \exp(-2560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}480 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 700 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the absolute rate coefficient study of Canosa-Mas *et al.*,¹ and are identical to our

previous evaluation, IUPAC, 1992.² The 298 K preferred rate coefficient is consistent with the upper limit to the rate coefficient determined by Wallington *et al.*³

References

- ¹C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **85**, 709 (1989).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **19**, 243 (1987).

NO₃ + C₂H₅OH → products

No new data have been published since our last evaluation.

Preferred Values

$$k < 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the only study carried out to date,¹ and is identical to our previous evaluation, IUPAC,

1992.² A somewhat higher upper limit is recommended than cited by Wallington *et al.*¹

References

- ¹T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **19**, 243 (1987).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

NO₃ + *i*-C₃H₇OH → products

No new data have been published since our last evaluation.

Preferred Values

$$k < 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the only study carried out to date,¹ and is identical to our previous evaluation, IUPAC,

1992.² A somewhat higher upper limit is recommended than cited by Wallington *et al.*¹

References

- ¹T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **19**, 243 (1987).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -135.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$7.56 \times 10^{-31} (T/300)^{-3.64 \pm 1.0} [\text{N}_2]$	264–370	Kaiser, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.0 \times 10^{-30} (T/300)^{-3.3} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$4.5 \times 10^{-31} (T/300)^{-3.0} [\text{Air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Irradiation of $\text{CH}_4\text{-Cl}_2\text{-O}_2\text{-N}_2$ mixtures with a fluorescence lamp. CH_4 and CH_3Cl were analyzed by GC. Rate constants were measured relative to the reaction $\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}$ [$k = 3.95 \times 10^{-12} \times \exp(-267/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]^{4,5}. Falloff extrapolations were carried out with F_c values of 0.48, 0.46, and 0.42 at 264, 297, and 370 K, respectively.
- (b) Based on the results of Ref. 6 which were in good agreement with the previous preferred values of Ref. 7.
- (c) This value was based on a previous compilation,⁸ and mainly on the data from Keiffer *et al.*⁶

Preferred Values

$$k_0 = 1.0 \times 10^{-30} (T/300)^{-3.3} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The recent values of Kaiser¹ agree very well with our previous evaluation, IUPAC, 1992,² which remains unchanged.

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(1.31 \pm 0.1) \times 10^{-12} (T/300)^{1.2 \pm 0.8}$	264–370	Kaiser, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.2 \times 10^{-12} (T/300)^{1.0}$	200–400	IUPAC, 1992 ²	(b)
$1.8 \times 10^{-12} (T/300)^{-1.7}$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 .
- (b) Values based on Refs. 7 and 9 which have been extrapolated to high pressures with $F_c = 0.27$ at 300 K.
- (c) This value fits the data from Refs. 6 and 9. The temperature dependence was estimated. Extrapolation with $F_c = 0.6$.

Preferred Values

$$k_\infty = 1.8 \times 10^{-12} (T/300)^{1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3.$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The preferred value is an average of earlier results from Refs. 6 and 9 and the more recent determination by Kaiser.¹

References

- ¹E. W. Kaiser, *J. Phys. Chem.* **97**, 11681 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴L. J. Kovalenko and S. R. Leone, *J. Chem. Phys.* **80**, 3656 (1984).
- ⁵R. S. Timonen and D. Gutman, *J. Phys. Chem.* **90**, 2987 (1986).
- ⁶M. Keiffer, M. J. Pilling, and M. J. C. Smith, *J. Phys. Chem.* **91**, 6028 (1987).
- ⁷IUPAC, Supplement III, 1989 (see references in Introduction).
- ⁸NASA Evaluation No. 9, 1990 (see references in Introduction).
- ⁹C. J. Cobos, H. Hippler, K. Luther, A. R. Ravishankara, and J. Troe, *J. Phys. Chem.* **89**, 4332 (1985).

$$\Delta H^\circ = -54.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K and 1 bar.}$$

$$k = 1.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K and 0.133 bar.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at 298 K.}$$

Comments on Preferred Values

The recommended pressure-dependent values of k_{298} are from the product study of Kaiser *et al.*,¹ and are identical to our previous evaluation, IUPAC, 1992.² The temperature dependence of the rate coefficient has yet to be established, but

at a given pressure, increasing the temperature leads to an increased yield of C_2H_4 .

For a full discussion on the mechanism of the $\text{C}_2\text{H}_5 + \text{O}_2$ reaction see the paper of Wagner *et al.*³ It is clear that for atmospheric conditions the interaction of C_2H_5 with O_2 to form $\text{C}_2\text{H}_5\text{O}_2$ radicals is by far the dominant pathway.

References

¹E. W. Kaiser, I. M. Lorkovic, and T. J. Wallington, *J. Phys. Chem.* **94**, 3352 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, *J. Phys. Chem.* **94**, 1853 (1990).

$$\Delta H^\circ = -150.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 5.9 \times 10^{-29} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

Experiments so far have mainly been conducted in the bath gas He, the previously recommended rate coefficients¹

for $\text{M} = \text{N}_2$ and O_2 being estimated relative to the He data. The new study of Ref. 2 reports identical rate coefficients for $\text{M} = \text{He}$ and N_2 in the upper-half of the falloff curve. For this reason we revised the preferred values by using identical k_0 values for $\text{M} = \text{He}$ and N_2 . We prefer the most extensive results from Ref. 3 because the long falloff extrapolation to k_0 was done with a careful theoretical analysis. However, we retain the temperature coefficient from Ref. 4 which was determined theoretically. Falloff extrapolations were made with theoretically derived³ values of $F_c = 0.64$ at 200 K and 0.54 at 300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 7.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.2 \text{ over the temperature range 200–300 K.}$$

Comments on Preferred Values

As for k_0 , we prefer the most extensive data from Ref. 3 because of their combination with a careful theoretical analysis. We assume a temperature independent rate coefficient k_∞ below 300 K. Falloff curves were fitted³ with an expression $F_c = \{0.58 \exp(-T/1250) + 0.42 \exp(-T/183)\}$ which leads to $F_c = 0.64$ at 200 K and 0.54 at 300 K. Within the stated error

limits, the available data all agree with the preferred values based on Ref. 3. QRRK calculations⁴ of the reaction are less realistic than the RRKM calculations of Ref. 3. The analysis of the reaction system is complicated because there is a coupling of the addition reaction with the reaction forming C₂H₄, i.e., C₂H₅ + O₂ → C₂H₄ + HO₂, see the analysis in Ref. 3. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

- ¹IUPAC, Supplement III, 1989 (see references in Introduction).
- ²E. W. Kaiser, T. J. Wallington, and J. M. Andino, *Chem. Phys. Lett.* **168**, 309 (1990).
- ³A. F. Wagner, I. R. Slagle, D. Sarzynski, and D. Gutman, *J. Phys. Chem.* **94**, 1853 (1990).
- ⁴J. W. Bozzelli and A. M. Dean, *J. Phys. Chem.* **94**, 3313 (1990).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k = 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1–10 Torr and 298 K.
 $k_\infty = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ over the range 200–300 K.

Comments on Preferred Values

The available experimental data are consistent with each other.^{1,2} Because they were obtained at total pressures below 100 Torr, we estimate that some falloff corrections have to be applied and these are taken into account in the preferred

values. These values are consistent with experiments for the reactions C₂H₅ + O₂ + M → C₂H₅O₂ + M and *i*-C₃H₇ + O₂ + M → *i*-C₃H₇O₂ + M (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹R. P. Ruiz and K. D. Bayes, *J. Phys. Chem.* **88**, 2592 (1984).
- ²I. R. Slagle, J.-Y. Park, and D. Gutman, *20th International Symposium on Combustion, 1984* (Combustion Institute, Pittsburgh, PA, 1985), pp. 733–741.
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -158.9 \text{ kJ} \cdot \text{mol}^{-1}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are the average of the results from Refs. 1 and 2. Falloff corrections are probably within the uncertainties of the average. The rate coefficient k_∞ for this

reaction appears consistent with those for the reactions C₂H₅ + O₂ + M → C₂H₅O₂ + M and *n*-C₃H₇ + O₂ + M → *n*-C₃H₇O₂ + M (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹R. P. Ruiz and K. D. Bayes, *J. Phys. Chem.* **88**, 2592 (1984).
- ²J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, *Chem. Phys. Lett.* **132**, 417 (1986).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ at } 300 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the study of Cox *et al.*¹ Because this is the only study of this reaction, we indicate

large error limits. Near atmospheric pressure this reaction should be close to the high pressure limit. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

- ¹R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, *Chem. Phys. Lett.* **173**, 206 (1990).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -137.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

Comments on Preferred Values

The most recent measurements of the room temperature rate coefficient^{1,2} are in good agreement with our previous recommendation.³ The preferred temperature-independent rate coefficient is the average of the room-temperature rate coefficients of Washida *et al.*,⁴ Shibuya *et al.*,⁵ Veyret and Lesclaux,⁶ Timonen *et al.*,¹ and Stief *et al.*,² and is identical to our previous evaluation, IUPAC, 1992.⁷ Taken together, the temperature-dependent studies of Veyret and Lesclaux,⁶

Timonen *et al.*,¹ and Stief *et al.*² show that the rate coefficient of this reaction is essentially independent of temperature over the temperature range 200–400 K, within the error limits of the measurements.

References

- ¹R. S. Timonen, E. Ratajczak, and D. Gutman, *J. Phys. Chem.* **92**, 651 (1988).
²L. J. Stief, F. L. Nesbitt, and J. F. Gleason, abstracts of papers presented at the International Symposium of Gas Kinetics, Assisi, Italy, September 1990.
³CODATA, Supplement II, 1984; IUPAC, Supplement III, 1989 (see references in Introduction).
⁴N. Washida, R. I. Martinez, and K. D. Bayes, *Z. Naturforsch. Teil A* **29**, 251 (1974).
⁵K. Shibuya, T. Ebata, K. Obi, and I. Tanaka, *J. Phys. Chem.* **81**, 2292 (1977).
⁶B. Veyret and R. Lesclaux, *J. Phys. Chem.* **85**, 1918 (1981).
⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -148 \text{ kJ} \cdot \text{mol}^{-1}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1–4 Torr.

$k_{\infty} = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.5$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are based on Ref. 1 with some falloff correction estimated by comparison with the reaction C_2H_5

+ $\text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$ (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

¹C. E. McDade, T. M. Lenhardt, and K. D. Bayes, *J. Photochem.* **20**, 1 (1982).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -85.0 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 9.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction, and our recommendation is the average of the results of Grotheer *et al.*,¹ Nesbitt *et al.*,² Pagsberg *et al.*,³ Miyoshi *et al.*,⁴ Grotheer *et al.*,⁵ Dóbé *et al.*,⁶ and Payne *et al.*,⁷ and is identical to our previous evaluation, IUPAC, 1992.⁸ The earlier data of Wang *et al.*⁹ and Radford *et al.*¹⁰ are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications.¹¹ The two recent studies^{1,2} of the temperature dependence of this reaction indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200–700 K. The existing data are difficult to explain and more work is needed to confirm the observed temperature dependence of this reaction before a recommendation can be made.

Grotheer *et al.*¹ have carried out experiments replacing CH_3OH by CH_3OD and have observed no kinetic effect for the $\text{CH}_2\text{OH}/\text{CH}_2\text{OD} + \text{O}_2$ reactions.

References

¹H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, *J. Phys. Chem.* **92**, 4028 (1988); *22nd International Symposium on Combustion, 1988* (Combustion Institute, Pittsburgh, PA, 1989), pp. 963–972.

²F. L. Nesbitt, W. A. Payne, and L. J. Stief, *J. Phys. Chem.* **92**, 4030 (1988).

³P. Pagsberg, J. Munk, C. Anastasi, and V. J. Simpson, *J. Phys. Chem.* **93**, 5162 (1989).

⁴A. Miyoshi, H. Matsui, and N. Washida, *J. Phys. Chem.* **94**, 3016 (1990).

⁵H.-H. Grotheer, G. Riekert, U. Meier, and Th. Just, *Ber. Bunsenges. Phys. Chem.* **89**, 187 (1985).

⁶S. Dóbé, F. Temps, T. Böhland, and H. Gg. Wagner, *Z. Naturforsch. Teil A* **40**, 1289 (1985).

⁷W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, *Int. J. Chem. Kinet.* **20**, 63 (1988).

⁸IUPAC, Supplement IV, 1992 (see references in Introduction).

⁹W. C. Wang, M. Suto, and L. C. Lee, *J. Chem. Phys.* **81**, 3122 (1984).

¹⁰H. E. Radford, *Chem. Phys. Lett.* **71**, 195 (1980).

¹¹IUPAC, Supplement III, 1989 (see references in Introduction).

$\Delta H^\circ = -87.6 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is the mean of the results of Grotheer *et al.*,¹ Anastasi *et al.*,² and Miyoshi *et al.*,³ and is identical to our previous evaluation, IUPAC, 1992.⁴ The rather large discrepancy between the data of Miyoshi *et al.*³ and the other two studies^{1,2} could be due to the different

sources of generation of the CH_3CHOH radical. CH_3CHOH radical generation^{1,2} involving Cl attack on $\text{C}_2\text{H}_5\text{OH}$ may not be as clean a source as is the photolysis³ of $\text{CH}_3\text{COCHOHCH}_3$.

The temperature dependence of the rate coefficient determined by Grotheer *et al.*¹ shows a marked non-Arrhenius behavior, but this needs to be confirmed before a recommendation can be made.

Evidence for the reaction between CH_3CHOH and O_2 yielding CH_3CHO as a major product comes from the product study of the photooxidation of ethanol by Carter *et al.*⁵

References

- ¹H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, *22nd International Symposium on Combustion, 1988* (Combustion Institute, Pittsburgh, PA, 1989), pp. 963–972.
- ²C. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, *Chem. Phys. Lett.* **164**, 18 (1989).
- ³A. Miyoshi, H. Matsui, and N. Washida, *Chem. Phys. Lett.* **160**, 291 (1989).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵W. P. L. Carter, K. R. Darnall, R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **83**, 2305 (1979).

$\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The direct measurements¹ of this rate coefficient, from the pulsed laser photolysis of either $\text{ClCH}_2\text{CH}_2\text{OH}$ or $\text{BrCH}_2\text{CH}_2\text{OH}$ as the radical source, showed a good level of consistency. By analogy with the reactions $\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$ and $\text{CH}_3\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{CO}_3 + \text{M}$ (this evaluation), the rate coefficient for this reaction is expected to be close to the high-pressure limit under the experimental conditions employed. The UV absorption spectrum of the $\text{HOCH}_2\text{CH}_2\text{O}_2$ radical has recently been

observed^{2,3} by pulsed radiolysis of $\text{SF}_6\text{-H}_2\text{O}$ mixtures² and laser flash photolysis of H_2O_2 (Ref. 3) in the presence of C_2H_4 and O_2 . These observations indicate that the reaction between $\text{CH}_2\text{CH}_2\text{OH}$ radicals and O_2 leads significantly to the adduct peroxy radical. The preferred value is identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹A. Miyoshi, H. Matsui, and N. Washida, *Chem. Phys. Lett.* **160**, 291 (1989).
- ²C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, *J. Phys. Chem.* **95**, 5791 (1991).
- ³T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, *J. Chem. Soc. Faraday Trans.* **87**, 2351 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$

$$\Delta H^\circ = -111.6 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.2 \times 10^{-14} \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 298\text{--}610 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The direct measurements of the rate coefficients by Lorenz *et al.*¹ (298–450 K) and Wantuck *et al.*² (298–973 K) are in

good agreement with the similar measurements of Gutman *et al.*³ (413–608 K), where the temperature ranges overlap. The preferred values are derived from a least-mean-squares analysis of these three sets of data^{1–3} over the temperature range 298–608 K and are identical to our previous evaluation, IUPAC, 1992.⁴ The higher temperature measurements of Wantuck *et al.*² give a clear indication of non-Arrhenius behavior over the extended temperature range. The anomalously low A-factor for a simple H-atom transfer reaction and the possibility of a more complicated mechanism have both been noted.⁵

References

¹K. Lorenz, D. Rhäsa, R. Zellner, and B. Fritz, Ber. Bunsenges. Phys. Chem. **89**, 341 (1985).

²P. J. Wantuck, R. C. Oldenberg, S. L. Baughcum, and K. R. Winn, J. Phys. Chem. **91**, 4653 (1987).

³D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

⁵NASA Evaluation No. 9, 1990 (see references in Introduction).

$$\Delta H^\circ = -134.0 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.0 \times 10^{-14} \exp(-550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 295\text{--}425 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient and the temperature dependence are obtained from the mean of the room temperature rate coefficients of Gutman *et al.*¹ (296 K) and of Hartmann *et al.*² (295 K) and by taking the rounded-off value of E/R of Hartmann *et al.*² The rate coefficients of Gutman *et al.*¹ and of Hartmann *et al.*² differ by 30–50% which, although within the range of the individual error limits, is somewhat higher than might be expected from two direct studies.

The relative rate measurements of Zabarnick and Heicklen³ are within the error limits which we recommend for our preferred values. We have not taken these results into account, however, owing to the uncertainty concerned with the rate coefficient of the reference reaction of $\text{CH}_3\text{O} + \text{NO} \rightarrow$ products.

It should be noted that the A -factor for the above reaction is very low, but in keeping with that for the analogous reaction $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

¹D. Gutman, N. Sanders, and J. E. Butler, J. Phys. Chem. **86**, 66 (1982).

²D. Hartmann, J. Karthäuser, J. P. Sawersyn, and R. Zellner, Ber. Bunsenges. Phys. Chem. **94**, 639 (1990).

³S. Zabarnick and J. Heicklen, Int. J. Chem. Kinet. **17**, 455 (1985).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -131.4 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is identical to our previous evaluation, IUPAC, 1992.¹ The rate coefficient at 298 K is derived from the study of Zabarnick and Heicklen² which, though heavily dependent upon the choice of data for the reference reaction, $n\text{-C}_3\text{H}_7\text{O} + \text{NO} \rightarrow$ products, is consistent with data for other $\text{RO} + \text{O}_2$ reactions obtained from direct studies. Here

we have selected k_{298} to be equal to that for the $\text{C}_2\text{H}_5\text{O} + \text{O}_2$ reaction.

The temperature coefficient determined by Zabarnick and Heicklen² from their relative rate system is considerably greater than those for the $\text{C}_2\text{H}_5\text{O} + \text{O}_2$ ($E/R=550 \text{ K}$) or the $i\text{-C}_3\text{H}_7\text{O} + \text{O}_2$ ($E/R=200 \text{ K}$) reactions, both of which were obtained from direct studies. This aspect of the reaction requires further experimental work.

References

¹IUPAC, Supplement IV, 1992 (see references in Introduction).

²S. Zabarnick and J. Heicklen, Int. J. Chem Kinet. **17**, 477 (1985).

$$\Delta H^\circ = -150.3 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.5 \times 10^{-14} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}390 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.¹ The results of Balla *et al.*² on the rate coefficient of this reaction appear reasonable in relation to data for other reactions of this type. Both the rate coefficient and temperature coefficient require confirmation.

References

¹IUPAC, Supplement IV, 1992 (see references in Introduction).

²R. J. Balla, H. H. Nelson, and J. R. McDonald, *Chem. Phys.* **99**, 323 (1985).

(R=H, alkyl or substituted alkyl)

Rate coefficient data

Reactions	$k_1 \cdot k_2^{-1} / \text{cm}^3 \text{ molecule}^{-1}$	Temp./K	Reference	Comments
$\text{CH}_3\text{OCH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{OCHO} + \text{HO}_2$ (1)	$k_1[\text{O}_2] \sim k_2$ (1 atm, air)	295	Jenkin <i>et al.</i> , 1993 ¹	(a)
$\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$ (2)				
$\text{CH}_3\text{COCH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{COCHO} + \text{HO}_2$ (1)	$k_1[\text{O}_2] \ll k_2$ (1 atm, air)	298	Jenkin <i>et al.</i> , 1993 ²	(b)
$\text{CH}_3\text{COCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{CO} + \text{HCHO} + \text{M}$ (2)	$k_1[\text{O}_2] \ll k_2$ (1 atm, air)	298	Bridier <i>et al.</i> , 1993 ³	(c)

Comments

- Steady-state photolyses of $\text{Cl}_2\text{-CH}_3\text{OCH}_3\text{-O}_2\text{-N}_2$ mixtures (10–760 Torr) with long-path FTIR analyses, and molecular modulation studies of similar reactant mixtures with UV absorption monitoring of $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals. In both systems, kinetic treatments indicate that reactions (1) and (2) were competing under the conditions of the experiments.
- Steady-state photolyses of $\text{Cl}_2\text{-CH}_3\text{COCH}_3\text{-O}_2\text{-N}_2$ mixtures (700 Torr) with long-path FTIR and long-path UV visible diode array spectroscopy analyses of products. Data indicate that reaction (2) predominated over reaction (1) under the conditions of the experiments.
- Flash photolyses of $\text{Cl}_2\text{-CH}_3\text{COCH}_3\text{-air}$ mixtures (1 atm) with UV absorption monitoring of $\text{CH}_3\text{COCH}_2\text{O}_2$ radicals. Data indicate that reaction (2) predominated over reaction (1) under the conditions of the experiments.

Preferred Values

No quantitative recommendations.

Comments on Preferred Values

Although the results listed above for the reactions of the $\text{CH}_3\text{OCH}_2\text{O}$ and $\text{CH}_3\text{COCH}_2\text{O}$ radicals are not quantitative, for the purposes of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered.

References

¹M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, *J. Phys. Chem.* **97**, 11712 (1993).

²M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **89**, 2983 (1993).

³I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, *J. Chem. Soc. Faraday Trans.* **89**, 2993 (1993).

No new data have been published since our last evaluation.

Preferred Values

$k = 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.1 \times 10^{-12} \exp(-210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the revised calculations by Paltenghi *et al.*¹ of the earlier data of Ogryzlo *et al.*,²

which result from a correction for the pressure drop along the flow tube between the reaction vessel and the manometer, and are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹R. Paltenghi, E. A. Ogryzlo, and K. D. Bayes, J. Phys. Chem. **88**, 2595 (1984).
²E. A. Ogryzlo, R. Paltenghi, and K. D. Bayes, Int. J. Chem. Kinet. **13**, 667 (1981).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -173.2 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -116.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_{01}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(8.6 \pm 1.3) \times 10^{-30} [\text{He}]$	296	Ohmori, Yamasaki, and Matsui, 1993 ¹	(a)
$(4.3 \pm 1.0) \times 10^{-30} [\text{N}_2]$	296		
$(1.01 \pm 0.45) \times 10^{-29} [\text{CF}_4]$	296		
$(1.55 \pm 0.40) \times 10^{-29} [\text{SF}_6]$	296		
<i>Reviews and Evaluations</i>			
$1.6 \times 10^{-29} (T/300)^{-3.5} [\text{N}_2]$	200–400	IUPAC, 1992 ²	(b)
$1.4 \times 10^{-29} (T/300)^{-3.8} [\text{Air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) CH_3O radicals were generated by photolysis of CH_3ONO at 266 and 355 nm and detected by LIF. Bath gas pressures were varied between 7–100 Torr (He), 10–70 Torr (N_2), 15–50 Torr (CF_4), and 10–50 Torr (SF_6).
 (b) Based on the data of Refs. 4 and 5 using $F_c = 0.6$. A branching ratio of $k_2/(k_1 + k_2) = 0.45$ is reported in Ref. 6.
 (c) Taken from the results of Frost and Smith⁴ for $\text{M} = \text{Ar}$.

Preferred Values

$k_{01} = 1.6 \times 10^{-29} (T/300)^{-3.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

$k_2 = 4 \times 10^{-12} (T/300)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm 0.1$ at 298 K.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred rate coefficient values are based on the data of Frost and Smith⁴ and McCaulley *et al.*,⁵ and are identical to our previous evaluation, IUPAC, 1992.² The branching ratio is also from Ref. 2. The recently reported k_{01} values by Ohmori *et al.*¹ for $\text{M} = \text{N}_2$ at 296 K are a factor of 3.7 lower than previously recommended. The cause of this difference is not clear but it may be in the separation of k_1 and k_2 .

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(4.5 \pm 1.5) \times 10^{-11}$	298	Ohmori, Yamasaki, and Matsui, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$3.6 \times 10^{-11} (T/300)^{-0.6}$	200–400	IUPAC, 1992 ²	(b)
$3.6 \times 10^{-11} (T/300)^{-0.6}$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_{01} . $k_{\infty 1}$ evaluated using Lindemann-Hinshelwood theory, i.e., using $F_c=1$.
- (b) The recommended values are from Ref. 4. Because they have been evaluated with $F_c=1$, an increase of $k_{\infty 1}$ is expected when an analysis with a smaller, more realistic value of F_c is done.
- (c) See comment (c) for k_{01} .

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992,² and are consistent with the results from Ohmori *et al.*¹ at 296 K.

References

- ¹K. Ohmori, K. Yamasaki, and H. Matsui, Bull. Chem. Soc. Jpn. **66**, 51 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).
- ⁵J. A. McCaulley, A. M. Moyle, M. F. Golde, S. M. Anderson, and F. Kaufman, J. Chem. Soc. Faraday Trans. **86**, 4001 (1990).
- ⁶M. E. Jenkin, G. D. Hayman, and R. A. Cox, J. Photochem. A **42**, 187 (1988).

Preferred Values

$k_{\infty 1} = 3.6 \times 10^{-11} (T/300)^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$$\Delta \log k_{\infty 1} = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta H^\circ(1) = -176.9 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -139.3 \text{ kJ} \cdot \text{mol}^{-1}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

$$k_2 = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty 1} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The recommended value of $k_{\infty 1}$ is based on the data of Frost and Smith,¹ and is consistent with values for related reactions such as $\text{CH}_3\text{O} + \text{NO} + \text{M} \rightarrow \text{CH}_3\text{ONO} + \text{M}$ and $i\text{-C}_3\text{H}_7\text{O} + \text{NO} + \text{M} \rightarrow i\text{-C}_3\text{H}_7\text{ONO} + \text{M}$ (see this evaluation).

The value of k_2 is estimated via the preferred value of $k_{\infty 1}$ and the ratio $k_2/k_{\infty 1}=0.3$ such as measured in Ref. 2. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1757 (1990).
- ²G. Baker and R. Shaw, J. Chem. Soc. A, 6965 (1965).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(2) = -155.6 \text{ kJ}\cdot\text{mol}^{-1}$$

High-pressure rate coefficients

Rate coefficient data

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

$k_2 = 6.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

$\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value of $k_{\infty 1}$ is based on the study of Balla *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.² The value of k_2 is obtained from the preferred $k_{\infty 1}$ and the rate coefficient ratio $k_2/k_1 = 0.19 \pm 0.03$, independent of temperature, measured in Ref. 3.

References

¹R. J. Balla, H. H. Nelson, and J. R. McDonald, *Chem. Phys.* **99**, 323 (1985).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³L. Batt and R. T. Milne, *Int. J. Chem. Kinet.* **9**, 141 (1977).

$$\Delta H^\circ(1) = -170.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -238.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{01} = 2.8 \times 10^{-29} (T/300)^{-4.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_{01} = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The agreement between the studies of Refs. 1 and 2 appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_0 for $\text{M} = \text{Ar}$ and N_2 . Falloff curves are constructed with $F_c = 0.44$ at 300 K such as chosen in Ref. 2. Reaction (2) appears to play only a minor role at pressures above 10 Torr.¹

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred $k_{\infty 1}$ value based on Ref. 2 appears consistent with the values for related reactions $\text{RO} + \text{NO} + \text{M}$

→ RONO + M (with R = CH₃, C₂H₅, *i*-C₃H₇, see this evaluation). Falloff curves are constructed with $F_c=0.44$ from Ref. 2. Reaction (2) appears to be only of minor importance.¹ These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹J. A. McCaulley, S. M. Anderson, J. B. Jeffries, and F. Kaufman, Chem. Phys. Lett. **115**, 180 (1985).
²M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -170.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -261.3 \text{ kJ}\cdot\text{mol}^{-1}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$$\Delta \log k_{\infty 1} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

The value of $k_{\infty 1}$ is based on the data of Frost and Smith,¹ and appears consistent with values for related reactions² such as RO + NO + M → RONO + M (with M = CH₃,

C₂H₅, and *i*-C₃H₇) or CH₃O + NO₂ + M → CH₃ONO₂ + M (see this evaluation). Reaction (2) appears to be of minor importance ($k_2/k_{\infty 1} < 0.2$) in the high-pressure range of the reaction² (see also the CH₃O + NO₂ reaction system; this evaluation). The preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹M. J. Frost and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **86**, 1751 (1990).
²R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -171.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -277.6 \text{ kJ}\cdot\text{mol}^{-1}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$$\Delta \log k_{\infty 1} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

Comments on Preferred Values

This recommendation is based on Ref. 1. The values of $k_{\infty 1}$ are consistent with other related reactions such as RO + NO + M → RONO + M and RO + NO₂ + M

→ RONO₂ + M (with R = CH₃, C₂H₅, *i*-C₃H₇, see this evaluation and Ref. 2). It is estimated that $k_2/k_{\infty 1} < 0.2$. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹R. J. Balla, H. H. Nelson, and J. R. McDonald, Chem. Phys. **99**, 323 (1985).
²R. Atkinson and A. C. Lloyd, J. Phys. Chem. Ref. Data **13**, 315 (1984).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -49.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(8.8 \pm 1.4) \times 10^{-12}$	298	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$3.9 \times 10^{-12} \exp(200/T)$	240–370	Wallington, Dagaut, and Kurylo, 1992 ²	(b)
$4.1 \times 10^{-12} \exp(180/T)$	218–365	Lightfoot <i>et al.</i> , 1992 ³	(c)
$4.2 \times 10^{-12} \exp(180/T)$	240–360	IUPAC, 1992 ⁴	(c)
$4.2 \times 10^{-12} \exp(180/T)$	200–300	NASA, 1994 ⁵	(c)

Comments

- (a) Pulse radiolysis of $\text{SF}_6\text{-CH}_4\text{-O}_2\text{-NO}$ mixtures at a total pressure of 760 Torr, with UV absorption determination of $[\text{CH}_3\text{O}_2]$.
- (b) Least-squares analysis of selected data of Plumb *et al.*,^{6,7} Cox and Tyndall,⁸ Sander and Watson,⁹ Ravishankara *et al.*,¹⁰ Simonaitis and Heicklen,¹¹ and Zellner *et al.*¹²
- (c) k_{298} was the mean of the data of Plumb *et al.*,⁷ Cox and Tyndall,⁸ Sander and Watson,⁹ Ravishankara *et al.*,¹⁰ Simonaitis and Heicklen,¹¹ and Zellner *et al.*,¹² and E/R was from the data of Ravishankara *et al.*¹⁰ and Simonaitis and Heicklen.¹¹

Preferred Values

$$k = 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.2 \times 10^{-12} \exp(180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}360 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 180 \text{ K.}$$

Comments on Preferred Values

The data of Sehested *et al.*¹ are in good agreement with the earlier results,^{6–12} and the preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹J. Sehested, O. J. Nielsen, and T. J. Wallington, *Chem. Phys. Lett.* **213**, 457 (1993).
- ²T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).
- ³P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, *Chem. Phys. Lett.* **63**, 255 (1979).
- ⁷I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, *J. Phys. Chem.* **85**, 3136 (1981).
- ⁸R. A. Cox and G. Tyndall, *Chem. Phys. Lett.* **65**, 357 (1979); *J. Chem. Soc. Faraday Trans. 2*, **76**, 153 (1980).
- ⁹S. P. Sander and R. T. Watson, *J. Phys. Chem.* **84**, 1664 (1980).
- ¹⁰A. R. Ravishankara, F. L. Eisele, N. M. Kreutter, and P. H. Wine, *J. Chem. Phys.* **74**, 2267 (1981).
- ¹¹R. Simonaitis and J. Heicklen, *J. Phys. Chem.* **85**, 2946 (1981).
- ¹²R. Zellner, B. Fritz, and K. Lorenz, *J. Atmos. Chem.* **4**, 241 (1986).

$$\Delta H^\circ(1) = -45.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -215.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
9×10^{-12}	298	Wallington, Dagaut, and Kurylo, 1992 ²	(b)
8.9×10^{-12}	298	Lightfoot <i>et al.</i> , 1992 ³	(b)
8.9×10^{-12}	298	IUPAC, 1992 ⁴	(b)
$k_2/k \leq 0.014$ (1 bar)	298		(c)
8.7×10^{-12}	200–300	NASA, 1994 ⁵	(d)

Comments

- (a) Pulse radiolysis study of $\text{SF}_6\text{-C}_2\text{H}_6\text{-O}_2\text{-NO}$ mixtures at a total pressure of 760 Torr, with UV absorption kinetic spectroscopy of $\text{C}_2\text{H}_5\text{O}_2$ radicals.
- (b) Based on the data of Plumb *et al.*⁶
- (c) Based on the data of Atkinson *et al.*⁷
- (d) Based on the room temperature rate coefficients of Plumb *et al.*⁶ and Sehested *et al.*¹ The zero temperature dependence of the rate coefficient was estimated.

Preferred Values

$$k = 8.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2/k \leq 0.014 \text{ at } 298 \text{ K and } 1 \text{ bar pressure.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value of k_{298} is the mean of the data of Plumb *et al.*⁶ and Sehested *et al.*,¹ which are in excellent agreement. A measurement of the temperature dependence of k is still lacking but it appears likely that E/R will be close to zero by analogy with the $\text{CH}_3\text{O}_2 + \text{NO}$ reaction.

References

- ¹J. Sehested, O. J. Nielsen, and T. J. Wallington, *Chem. Phys. Lett.* **213**, 457 (1993).
- ²T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).
- ³P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶I. C. Plumb, K. R. Ryan, J. R. Steven, and M. F. R. Mulcahy, *Int. J. Chem. Kinet.* **14**, 183 (1982).
- ⁷R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **86**, 4563 (1982).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(9 \pm 4) \times 10^{-12}$	298	Becker, Geiger, and Wiesen, 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
9×10^{-12}	298	Lightfoot <i>et al.</i> , 1992 ²	(b)

Comments

- (a) Pulsed excimer laser photolysis of H_2O_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-NO}$ mixtures at total pressures of 760 ± 5 Torr. Relative HO radical concentrations were determined as a function of time using LIF, and simulated

- by a mechanism consisting of 11 reactions, of which k of above reaction was the most sensitive.
- (b) Based on the data of Becker *et al.*¹

Preferred Values

$k = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The rate coefficient reported by Becker *et al.*,¹ which is recommended, is consistent with the rate coefficients of the

reactions of CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals with NO. Independent confirmation is needed to reduce the recommended error limits.

References

- ¹K. H. Becker, H. Geiger, and P. Wiesen, Chem. Phys. Lett. **184**, 256 (1991).
²P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, Atmos. Environ. **26A**, 1805 (1992).

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 0.020$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_2/k) = \pm 0.01$ at 298 K (1 bar).

Comments on Preferred Values

In our previous evaluations,¹⁻³ in the absence of any experimental data we recommended the value $k = 8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K by analogy with the reaction $\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{products}$ and in line with our recommendations for the reaction $i\text{-C}_3\text{H}_7\text{O}_2 + \text{NO} \rightarrow \text{products}$. Now

that we have changed the recommendation for the latter reaction, we have also changed the above recommendation, but note that it is still in line with the value for the reaction, $\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{products}$.

The preferred branching ratio is that measured by Atkinson *et al.*⁴ and subsequently revised by Carter and Atkinson.⁵

References

- ¹CODATA, Supplement II, 1984 (see references in Introduction).
²IUPAC, Supplement III, 1989 (see references in Introduction).
³IUPAC, Supplement IV, 1992 (see references in Introduction).
⁴R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **86**, 4563 (1982).
⁵W. P. L. Carter and R. Atkinson, J. Atmos. Chem. **8**, 165 (1989).

$\Delta H^\circ(1) = -40.5 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(2) = -212.2 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.0 \pm 1.2) \times 10^{-12}$	290	Peeters, Vertommen, and Langhans, 1992 ¹	(a)
Branching Ratios			
$k_2/k = 0.042 \pm 0.003$ (735 Torr air)	299	Atkinson <i>et al.</i> , 1982 ² ; Carter and Atkinson, 1989 ³	(b)
Reviews and Evaluations			
8.9×10^{-12}	298	IUPAC, 1992 ⁴	(c)
$k_2/k = 0.043$	298		
4.3×10^{-12}	294	Lightfoot <i>et al.</i> , 1992 ⁵	(d)

Comments

- (a) Fast-flow system with molecular beam sampling mass spectrometry at a total pressure of 2 Torr. The rate coefficient k was derived from the rate of formation of NO_2 .
- (b) Photolysis of $\text{CH}_3\text{ONO-NO-C}_3\text{H}_8$ or $\text{Cl}_2\text{-NO-C}_3\text{H}_8$ mixtures at total pressures of 735 Torr of air. The branching ratio was determined² from the measured yields of $i\text{-C}_3\text{H}_7\text{ONO}_2$ and the consumption of C_3H_8 . Carter and Atkinson³ have recalculated the branching ratio, cited above, from the original data² on the basis of revised data for the rate coefficients of the $\text{HO} + \text{alkane}$ reactions.
- (c) The value of k was assumed to be equal to that of the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{products}$, and the branching ratio was taken from Atkinson *et al.*²
- (d) Average of the data of Adachi and Basco⁶ and Peeters *et al.*¹

Preferred Values

$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 0.042$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_2/k) = \pm 0.01$ at 298 K (1 bar).

Comments on Preferred Values

The recent study of Peeters *et al.*¹ appears to be reliable and their rate coefficient is recommended. The earlier result of Adachi and Basco⁶ ($k = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K), although now reasonably close to our recommended value, was discounted in our previous evaluation.⁴

References

- ¹J. Peeters, J. Vertommen, and I. Langhans, *Ber. Bunsenges. Phys. Chem.* **96**, 431 (1992).
- ²R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **86**, 4563 (1982).
- ³W. P. L. Carter and R. Atkinson, *J. Atmos. Chem.* **8**, 165 (1989).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ⁶H. Adachi and N. Basco, *Int. J. Chem. Kinet.* **14**, 1243 (1982).

$\Delta H^\circ = -133 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 280–325 K.

Reliability

$\Delta \log k = \pm 0.2$ over the temperature range 280–325 K.

$\Delta(E/R) = \pm 600 \text{ K}$.

Comments on Preferred Values

The two studies^{1,2} of the rate coefficient ratio $k/k(\text{CH}_3\text{CO}_3 + \text{NO}_2)$ are in good agreement. The preferred value is obtained from the mean value of $k/k(\text{CH}_3\text{CO}_3 + \text{NO}_2) = 2.1 \pm 0.3$ obtained from the data of Kirchner *et al.*¹ and Tuazon *et al.*² at total pressures of 740 and 750 Torr of air. Over the temperature range 283–321 K these two sets of data indicate that this ratio is essentially temperature-independent, within the error limits of the measurements

($E/R = 646 \pm 564 \text{ K}$). The rate coefficient k was then obtained by taking $k(\text{CH}_3\text{CO}_3 + \text{NO}_2) = 9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 atm pressure (see data sheets for the reaction $\text{CH}_3\text{CO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{CO}_3 + \text{NO}_2 + \text{M}$, this evaluation). The preferred values are identical to our previous evaluation, IUPAC, 1992.³

The experiments of Kirchner *et al.*¹ also show that the rate coefficient k shows no pressure dependence over the pressure range 22–750 Torr, as expected.

References

- ¹F. Kirchner, F. Zabel, and K. H. Becker, *Ber. Bunsenges. Phys. Chem.* **94**, 1379 (1990).
- ²E. C. Tuazon, W. P. L. Carter, and R. Atkinson, *J. Phys. Chem.* **95**, 2434 (1991).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i> 1.9×10^{-11}	302	Kerr and Stocker, 1985 ¹	(a)

Comments

- (a) Photolysis of dilute mixtures of synthetic air containing NO, NO₂, and C₂H₅CHO at a total pressure of 1 atm. The rate coefficient ratio $k/k(\text{C}_2\text{H}_5\text{CO}_3 + \text{NO}_2) = 1.9$ was determined from the effect of the $[\text{NO}]/[\text{NO}_2]$ ratio on the yield of peroxypropionyl nitrate, CH₃CH₂C(O)OONO₂. The rate coefficient k is calculated here using a rate coefficient of $k(\text{C}_2\text{H}_5\text{CO}_3 + \text{NO}_2) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atm pressure, by analogy with the reaction $\text{CH}_3\text{CO}_3 + \text{NO}_2 + \text{M}$ (this evaluation).

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This reaction requires to be studied by a more direct technique to lower the recommended error limits, although the above value is in agreement with the value of $k(\text{CH}_3\text{CO}_3 + \text{NO}) = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 280–325 K (this evaluation).

Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

References

¹J. A. Kerr and D. W. Stocker, J. Photochem. **28**, 475 (1985).

$\Delta H^\circ = -88 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 2.5 \times 10^{-30} (T/300)^{-5.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the theoretical analysis of Ref. 1, which used the previous experimental determinations. These values are based on a theoretically determined value of $F_c = 0.36$ at 300 K. The difference between Refs. 2 and 3 is due to the different values of F_c used, with the analysis of Ref. 3 being based on a standard value of $F_c = 0.6$. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–350 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

See comments on k_0 .

Intermediate falloff range

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
$(4.4 \pm 0.4) \times 10^{-12}$	760	air	298	Bridier, Lesclaux, and Veyret, 1992 ⁵	(a)
$(2.84 \pm 0.15) \times 10^{-12}$	760	air	333		
$(2.25 \pm 0.32) \times 10^{-12}$	760	air	353		
$(2.09 \pm 0.9) \times 10^{-12}$	760	air	368		
$(1.4 \pm 0.4) \times 10^{-12}$	760	air	373		

Comments

- (a) Flash photolysis study of the $\text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightleftharpoons \text{CH}_3\text{O}_2\text{NO}_2 + \text{M}$ reaction system. CH_3 radicals were generated by photolysis of $\text{Cl}_2\text{-CH}_4\text{-O}_2$ mixtures and monitored at 245 nm. The spectrum of $\text{CH}_3\text{O}_2\text{NO}_2$ was monitored between 200–280 nm. From the temperature dependence of the determined equilibrium constant, $\Delta H_{298}^\circ = -(92.7 \pm 0.5) \text{ kJ mol}^{-1}$ was derived.

References

- ¹M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).
²CODATA, Supplement I, 1982 (see references in Introduction).
³NASA Evaluation No. 11, 1994 (see references in Introduction).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
⁵I. Bridier, R. Lesclaux, and B. Veyret, *Chem. Phys. Lett.* **191**, 259 (1992).

$$\Delta H^\circ = 88 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 6.8 \times 10^{-19} [\text{N}_2] \text{ s}^{-1}$ at 298 K.
 $k_0 = 9 \times 10^{-5} \exp(-9690/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred values correspond to the data and analysis of Ref. 1. A theoretical analysis of these data and those of the reverse reaction in Ref. 2 gives an internally consistent picture (with $\Delta H^\circ = 88.5 \text{ kJ mol}^{-1}$). Slightly lower limiting rate coefficients were obtained in Ref. 3, where a value of $F_c = 0.6$ was used. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_{\infty} = 4.5 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 1.1 \times 10^{16} \exp(-10560/T) \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

See comments on preferred values of k_0 .

Intermediate falloff range

Rate coefficient data

k/s^{-1}	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
52.3 ± 13.2	760	air	333	Bridier, Lesclaux, and Veyret, 1992 ⁵	(a)
297 ± 34	760	air	353		
977 ± 76	760	air	368		
1328 ± 283	760	air	373		

Comments

- (a) Flash photolysis study of the $\text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightleftharpoons \text{CH}_3\text{O}_2\text{NO}_2 + \text{M}$ reaction system. CH_3O_2 radicals were generated by photolysis of $\text{Cl}_2\text{-CH}_4\text{-O}_2$ mixtures and monitored at 245 nm. The spectrum of $\text{CH}_3\text{O}_2\text{NO}_2$ was observed between 200–280 nm. From the temperature dependence of the determined equilibrium constant $\Delta H_{298}^\circ = -(92.7 \pm 0.5) \text{ kJ mol}^{-1}$ was derived.

References

- ¹F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, J. Phys. Chem. **93**, 5500 (1989).
²M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
³A. Bahta, R. Simonaitis, and J. Heicklen, J. Phys. Chem. **86**, 1849 (1982).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
⁵I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).

$$\Delta H^\circ = -67.7 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.3 \times 10^{-29} (T/300)^{-6.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The preferred values are an average of the data from Refs. 1 and 2. The temperature dependence is from the theoretical analysis of Ref. 2. Falloff extrapolations were made with $F_c = 0.31$ at 250–300 K such as given from the theoretical analysis of Ref. 2.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Comments on Preferred Values

See comments on k_0 . The preferred values of k_0 and k_{∞} are identical to those in our previous evaluation, IUPAC, 1992.³

References

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 200–300 K.

¹G. Elfers, F. Zabel, and K. H. Becker, Chem. Phys. Lett. **168**, 14 (1990).

²M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^{\circ} = 67.7 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.4 \times 10^{-17} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

$k_0 = 4.8 \times 10^{-4} \exp(-9285/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 300 K.

$\Delta(E/R) = \pm 1000 \text{ K}$.

Comments on Preferred Values

The dissociation data are consistent with experimental recombination data (see this evaluation) and the theoretical analysis from Ref. 1. Falloff curves are constructed with $F_c = 0.31$ (over the range 250–300 K).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 5.4 \text{ s}^{-1}$ at 298 K.

$k_{\infty} = 8.8 \times 10^{15} \exp(-10440/T) \text{ s}^{-1}$ over the temperature range 250–300 K.

Comments on Preferred Values

See comment on k_0 . The preferred values of k_0 and k_{∞} are identical to those in our previous evaluation, IUPAC, 1992.²

References

Reliability

$\Delta \log k_{\infty} = \pm 0.5$ at 300 K.

$\Delta(E/R) = \pm 1000 \text{ K}$.

¹M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^{\circ} = -119 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 2.7 \times 10^{-28} (T/300)^{-7.1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The extensive and internally consistent study of $\text{CH}_3\text{CO}_3\text{NO}_2$ (PAN) formation and dissociation in Ref. 1 is preferred. Falloff extrapolations were performed with a modeled value of $F_c = 0.3$.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 1.2 \times 10^{-11} (T/300)^{-0.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0 . The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.²

References

¹I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, *J. Phys. Chem.* **95**, 3594 (1991).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = 119 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.1 \times 10^{-20} [\text{N}_2] \text{ s}^{-1}$ at 298 K.
 $k_0 = 4.9 \times 10^{-3} \exp(-12100/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 300–330 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 1000 \text{ K}$.

Comments on Preferred Values

The data base of Ref. 1 is large enough to allow for a falloff extrapolation to k_0 , in part because falloff curves for PAN dissociation and recombination were measured independently. Falloff extrapolations were made with a modeled value of $F_c = 0.3$. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

High-pressure rate coefficients**Rate coefficient data**

k_∞/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.5 \times 10^{17} \exp[-(14340 \pm 250)/T]$	302–323	Roberts and Bertman, 1992 ³	(a)
3.1×10^{-4}	298	Rouwelis and Glavas, 1992 ⁴	(b)
$1.6 \times 10^{16} \exp[-(13539 \pm 1060)/T]$	288–298	Grosjean, Grosjean, and Williams, 1992 ⁵	(c)
<i>Reviews and Evaluations</i>			
$4.0 \times 10^{16} \exp(-13600/T)$	298–330	IUPAC, 1992 ²	(d)

Comments

- (a) Thermal decomposition of PAN at 760 Torr total pressure. PAN concentrations were measured by packed column GC with electron capture detection.
- (b) Thermal decomposition of PAN in N₂ as well in the presence of O₂, NO₂, and NO at 1 atm total pressure. The products methyl nitrate and NO₂ in pure PAN-N₂ mixtures were measured by GC. In the presence of large amounts of O₂, no methyl nitrate was formed at 333 K, indicating that the decomposition of PAN to methyl nitrate and CO₂ does not occur. The data obtained were simulated with 23 reactions.
- (c) Thermal decomposition of PAN in 1 atm of air. PAN was measured by GC with electron capture detection.
- (d) Based on the rate data of Refs. 1 and 6 at 1 atm total pressure.

Preferred Values

$$k_{\infty} = 3.8 \times 10^{-4} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 5.4 \times 10^{16} \exp(-13830/T) \text{ s}^{-1} \text{ over the temperature range } 300\text{--}330 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The recently reported values from Refs. 3–5 are in very good agreement at 298 K but are a factor of two smaller than our previous recommendation.² The preferred values attempt to reconcile all measurements. The direct PAN decompositions to methyl nitrate and CO₂^{4,7} or to CH₃CO₂ and NO₃⁷ are very slow compared to the decomposition to CH₃CO₃ + NO₂.

References

- ¹I. Bridier, F. Caralp, H. Loirat, R. Lesclaux, B. Veyret, K. H. Becker, A. Reimer, and F. Zabel, *J. Phys. Chem.* **95**, 3594 (1991).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³J. M. Roberts and S. B. Bertman, *Int. J. Chem. Kinet.* **24**, 297 (1992).
- ⁴N. Roumelis and S. Glavas, *Monatsch. Chem.* **123**, 63 (1992).
- ⁵D. Grosjean, E. Grosjean, and E. L. Williams II, *Air & Waste* **44**, 391 (1994).
- ⁶E. C. Tuazon, W. P. L. Carter, and R. Atkinson, *J. Phys. Chem.* **95**, 2434 (1991).
- ⁷J. J. Orlando, G. S. Tyndall, and J. G. Calvert, *Atmos. Environ.* **26A**, 3111 (1992).

High-pressure rate coefficients

Rate coefficient data

k_{∞}/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2 \times 10^{15} \exp(-12800/T)$	298–315	Mineshos and Glavas, 1991 ¹	(a)

Comments

- (a) Thermal decomposition of peroxypropionyl nitrate (PPN) in a 4.5 liter glass flask in the presence of 1 atm N₂. PPN and the products, ethyl nitrate, NO₂, and methyl nitrate, were analyzed by GC at 323 K. In the presence of NO, ethyl nitrate was the major product observed.¹

Preferred Values

$$k_{\infty} = 4.4 \times 10^{-4} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 2 \times 10^{15} \exp(-12800/T) \text{ s}^{-1} \text{ over the temperature range } 300\text{--}315 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.4 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The values from the only reported study of this reaction by Mineshos and Glavas¹ are recommended here.

References

- ¹G. Mineshos and S. Glavas, *React. Kinet. Catal. Lett.* **45**, 305 (1991).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(2.3 \pm 0.7) \times 10^{-12}$	298	Crowley <i>et al.</i> , 1990 ¹	(a)

Comments

- (a) Molecular modulation study involving the 253.7 nm photolysis of $\text{HNO}_3\text{-CH}_4\text{-O}_2$ mixtures in a flow system. The rate coefficient k was derived from a computer fit of the NO_3 radical absorption profiles (at 623 nm) based on a mechanism of 33 reactions.

coefficient. Until more work is carried out on this reaction, we make no recommendation.

A further study by Crowley *et al.*,² using HNO_3 as a source of NO_3 radicals, has shown that an additional “dark” source of NO_3 radicals arises from the thermal decomposition of N_2O_5 , present in the initial HNO_3 . Taking this into account² may reduce the rate coefficient reported above¹ by as much as a factor of 3.

Preferred Values

No recommendation.

References

Comments on Preferred Values

The only reported study of this reaction by Crowley *et al.*¹ involves a complex system of chemical reactions and consequently leads to a very indirect determination of the rate

¹J. N. Crowley, J. P. Burrows, G. K. Moortgat, G. Poulet, and G. Le Bras, *Int. J. Chem. Kinet.* **22**, 673 (1990).

²J. N. Crowley, J. P. Burrows, G. K. Moortgat, G. Poulet, and G. Le Bras, *Int. J. Chem. Kinet.* **25**, 795 (1993).

$$\Delta H^\circ(1) = -331.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = 14.4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -146.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $1.0 \times 10^{-13} \exp(416/T)$	248–700	Lightfoot <i>et al.</i> , 1991 ¹	(a,b)
<i>Reviews and Evaluations</i> $1.1 \times 10^{-13} \exp(365/T)$	200–400	IUPAC, 1992 ²	(c)
$9.2 \times 10^{-14} \exp(390/T)$	250–600	Wallington, Dagaut, and Kurylo, 1992 ³	(d)
$9.1 \times 10^{-14} \exp(416/T)$	248–650	Lightfoot <i>et al.</i> , 1992 ⁴	(e)
$2.5 \times 10^{-13} \exp(190/T)$	200–300	NASA, 1994 ⁵	(f)

Comments

- (a) k is defined by $-\text{d}[\text{CH}_3\text{O}_2]/\text{d}t = 2k[\text{CH}_3\text{O}_2]^2$ and was derived from the measured overall second-order decay of CH_3O_2 radicals (k_{obs}) by correcting for secondary removal of CH_3O_2 radicals.
- (b) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-CH}_3\text{OH-CH}_4\text{-O}_2\text{-N}_2$ mixtures at 760 Torr over the temperature range 600–719 K. The temperature-dependent value of k listed above was derived by the

authors from a re-analysis of all of their data, including previous studies, from flash photolysis experiments.

- (c) See Comments on Preferred Values.

- (d) $k_{\text{obs}} = 2.5 \times 10^{-13} \exp(180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived from a least-squares analysis of the data of Anastasi *et al.*,⁶ Sander and Watson,⁷ Kurylo and Wallington,⁸ Lightfoot *et al.*,⁹ and Jenkin and Cox.¹⁰ The value of k cited in the table was then calculated using $k_2/k = \{1.24 - (280/T)\}$.

- (e) Based on the same approach as for Comment (c), with E/R being taken from the data of Lightfoot *et al.*¹
- (f) k_{298} was based on the data of Cox and Tyndall,¹¹ Sander and Watson,⁷ McAdam *et al.*,¹² Kurylo and Wallington,⁸ Jenkin *et al.*,¹³ Lightfoot *et al.*,⁹ and Simon *et al.*¹⁴ E/R was derived from the data of Sander and Watson,⁷ Kurylo and Wallington,⁸ Lightfoot *et al.*,⁹ and Jenkin and Cox.¹⁰

Preferred Values

$k = 3.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.1 \times 10^{-13} \exp(365/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.
 $k_2 = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2 = 5.9 \times 10^{-13} \exp(-509/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–330 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.
 $\Delta \log k_2 = \pm 0.15$ at 298 K.
 $\Delta(E_2/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

There have been no new data at or around room temperature and our previous recommendation,² which is in substantial agreement with other subsequent recommendations,^{3–5} still stands. Here we repeat the comments of our last evaluation.

The most recent room temperature measurements^{9,10,14} of k_{obs}/σ are in excellent agreement with our previously recommended value of $k_{\text{obs}}/\sigma(250 \text{ nm}) = 1.24 \times 10^5 \text{ cm s}^{-1}$, which is unaltered. In addition, the measurements of the absorption cross-section by Simon *et al.*¹⁴ are also in agreement with our previous recommendation of $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ which is also unaltered. Thus, our earlier recommendation of $k_{\text{obs}} = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K¹⁵ is confirmed.

Taking the revised branching ratio of $k_2/k = 0.30$ at 298 K (see below) yields the slightly revised value of k at 298 K listed above.

The temperature dependence of k reported by Lightfoot *et al.*⁹ is in excellent agreement with the previous studies of Sander and Watson⁷ and Kurylo and Wallington.⁸ Here we have recommended the E/R value of Lightfoot *et al.*⁹ on the basis of their more extensive temperature range. The recommended Arrhenius equation follows from the recommended values of k_{298} and E/R .

The two studies^{9,16} of the temperature dependence of the branching ratio involve different temperature ranges. Here we have selected the results of Horie *et al.*¹⁶ over the more atmospherically relevant temperature range of 200–330 K in calculating the recommended value of k_2 . This is derived from the temperature-dependent value of k_2/k (see below)¹⁶ and our recommended Arrhenius equation for k .

It should be noted that, from an analysis of their own data¹⁶ together with the results of Lightfoot *et al.*,⁹ Anastasi *et al.*,⁶ Kan *et al.*,¹⁷ Parkes,¹⁸ Niki *et al.*,¹⁹ and Weaver *et al.*,²⁰ the equation $k_2/k = 1/\{1 + [\exp(1330/T)]/33\}$ was obtained by Horie *et al.*¹⁶ for the more extensive temperature range 223–573 K. This equation shows slight non-Arrhenius behavior.

Lightfoot *et al.*⁹ observed no pressure dependence of the branching ratio, k_2/k , over the range 210–760 Torr.

References

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$$\Delta H^\circ(1) = -28 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -379 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Branching Ratios</i>			
$k_2/k=6.1 \times 10^{-6} \exp(2990/T)$	263–333	Horie and Moortgat, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
$k_1=5.5 \times 10^{-12}$	298	IUPAC, 1992 ²	(b)
$k_2=5.5 \times 10^{-12}$	298		
$k_1=1.8 \times 10^{-9} \exp(-1800/T)$	298–368	Wallington, Dagaut, and Kurylo, 1992 ³	(b)
$k_2=4.1 \times 10^{-15} \exp(2100/T)$	298–368		
$5.1 \times 10^{-12} \exp(272/T)$	253–368	Lightfoot <i>et al.</i> , 1992 ⁴	(c)
$k_1/k_2=4.4 \times 10^5 \exp(-3910/T)$	253–368		
1.4×10^{-11}	200–300	NASA, 1994 ⁵	(b)

Comments

- (a) FTIR spectroscopic study of irradiated $\text{CH}_3\text{COCOCH}_3$ in the presence of Ar- O_2 mixtures at total pressures of 730–770 Torr. The reaction products CO_2 , CO , HCHO , HCOOH , $\text{CH}_3\text{CO}_2\text{H}$, $\text{CH}_3\text{CO}_3\text{H}$, CH_3OH , H_2O_2 , and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio, $k_1/k_2=2.2 \times 10^6 \exp(-3870/T)$, was derived from the yields of HCHO , $\text{CH}_3\text{CO}_2\text{H}$, HCO_2H , CH_3OH , and O_3 .
- (b) Based on the data of Moortgat *et al.*⁶
- (c) Re-analysis of the data of Moortgat *et al.*⁶

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

$$\Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta[(E_2-E)/R] = \pm 500 \text{ K.}$$

Comments on Preferred Values

We have amended our previous recommendation of k slightly, to take account of the re-analysis by Lightfoot *et al.*⁴ of the data of Moortgat *et al.*⁶ The recent study of the products of this reaction by Horie and Moortgat,¹ leading to the temperature dependence of the branching ratio listed above, is much more direct than the earlier study of Moortgat *et al.*,⁶ and is recommended.

References

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- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶G. K. Moortgat, B. Veyret, and R. Lesclaux, J. Phys. Chem. **93**, 2362 (1989).

Preferred Values

$$k=1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k=5.1 \times 10^{-12} \exp(272/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}370 \text{ K.}$$

$$k_2/k=0.14 \text{ at } 298 \text{ K.}$$

$$k_2/k=6.1 \times 10^{-6} \exp(2990/T) \text{ over the temperature range } 260\text{--}350 \text{ K.}$$

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 0.4) \times 10^{-12}$	298	Bridier <i>et al.</i> , 1993 ¹	(a)
<i>Branching Ratios</i>			
$k_1/k = (0.5 \pm 0.1)$	298	Jenkin <i>et al.</i> , 1992 ²	(b)
$k_2/k = (0.2 \pm 0.1)$	298		
$k_3/k = (0.3 \pm 0.1)$	298	Bridier <i>et al.</i> , 1993 ¹	(c)

Comments

- (a) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{COCH}_3\text{-CH}_4\text{-N}_2$ mixtures at a total pressure of 760 Torr. The overall rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 230 and 260 nm.
- (b) Steady-state photolysis of Cl_2 in the presence of $\text{CH}_3\text{COCH}_3\text{-N}_2$ mixtures at a total pressure of 700 Torr. Branching ratios were deduced from measurements of HCHO and CH_3COCHO products by long-path FTIR spectroscopy and long-path UV-VIS diode array spectroscopy.
- (c) Derived from a kinetic analysis of the time-profiles obtained in the experiments described in Comment (a).

$k_2/k = 0.2$ at 298 K.

$k_3/k = 0.3$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(k_1/k) = \Delta(k_2/k) = \Delta(k_3/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and branching ratios are based on the measurements of Bridier *et al.*¹ and Jenkin *et al.*,² and require independent confirmation to reduce the assigned error limits.

References

¹I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).

²M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).

Preferred Values

$k = 3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1/k = 0.5$ at 298 K.

No new data have been published since our last evaluation.

Preferred Values

$k_1 = 7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1 = 5.7 \times 10^{-14} \exp(750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 275–325 K.

$k_2 = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

$\Delta(E_1/R) = \pm 750 \text{ K}$.

$\Delta \log k_2 = \pm 0.3$ at 298 K.

Comments on Preferred Values

The parallel studies of Veyret *et al.*¹ and Burrows *et al.*² confirm that the interaction of HOCHO_2 radicals involves two channels. The two reports^{1,2} of the rate coefficient k_1 at room temperature are in good agreement, and indicate that this channel is a factor of $\sim 3\text{--}4$ faster than the analogous interaction of CH_3O_2 radicals. The rate coefficient k_2 is even higher than k_1 , with a value ~ 50 times that of the analogous reaction of CH_3O_2 radicals. The preferred values are identical to our previous evaluation, IUPAC, 1992.³ Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the temperature coefficient of k_2 .

References

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$$\Delta H^\circ(1) = -343.2 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = 23.0 \text{ kJ mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.7 \times 10^{-14} \exp[(60 \pm 40)/T]$	248–460	Fenter <i>et al.</i> , 1993 ¹	(a,b)
$(7.9 \pm 0.5) \times 10^{-14}$	298		
<i>Reviews and Evaluations</i>			
$9.8 \times 10^{-14} \exp(-110/T)$	250–450	IUPAC, 1992 ²	(a,c)
$8.5 \times 10^{-14} \exp(-125/T)$	260–380	Wallington, Dagaut, and Kurylo, 1992 ³	(a,d)
$9.8 \times 10^{-14} \exp(-100/T)$	228–457	Lightfoot <i>et al.</i> , 1992 ⁴	(a,e)
6.8×10^{-14}	200–300	NASA, 1994 ⁵	(a,f)

Comments

- (a) k is defined by $-d[\text{C}_2\text{H}_5\text{O}_2]/dt = 2k[\text{C}_2\text{H}_5\text{O}_2]^2$ and is derived from the observed overall second-order decay of $\text{C}_2\text{H}_5\text{O}_2$ radicals.
- (b) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at 760 Torr total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths. The value of $k_{\text{obs}} = (1.40 \pm 0.11) \times 10^{-13} \times \exp[(-20 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was corrected⁴ at each temperature by dividing by $(1 + \alpha)$, where $\alpha = \beta/(1 + \beta)$ and $\beta = 10.2 \exp(-533/T)$.
- (c) k_{298} was calculated from the mean k_{obs} value from the studies of Adachi *et al.*,⁶ Anastasi *et al.*,⁷ Cattell *et al.*,⁸ Wallington *et al.*,⁹ and Bauer *et al.*,¹⁰ and corrected for secondary removal of $\text{C}_2\text{H}_5\text{O}_2$ radicals by the use of $k_2/k = 0.62$. E/R was from the study of Wallington *et al.*⁹
- (d) k_{298} was calculated from $k_{\text{obs}} = 2.1 \times 10^{-13} \times \exp(-250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, derived from least-squares analysis of the data of Anastasi *et al.*¹¹ and Wallington *et al.*⁹ and corrected for secondary removal of $\text{C}_2\text{H}_5\text{O}_2$ radicals by the use of $k_2/k = \{1.33 - (209/T)\}$.
- (e) k_{298} was calculated from the mean value of k_{obs} from the data of Adachi *et al.*,⁶ Anastasi *et al.*,⁷ Cattell *et al.*,⁸ Wallington *et al.*,⁹ and Bauer *et al.*,¹⁰ and was corrected for secondary removal of $\text{C}_2\text{H}_5\text{O}_2$ radicals by

the use of $k_2/k = 0.63$. E/R was the average from the data of Anastasi *et al.*,⁷ Cattell *et al.*,⁸ Wallington *et al.*,⁹ and Bauer *et al.*¹⁰

- (f) k_{298} was calculated from the mean k_{obs} value from the studies of Cattell *et al.*,⁸ Wallington *et al.*,⁹ Bauer *et al.*,¹⁰ and Fenter *et al.*,¹ and corrected for secondary removal of $\text{C}_2\text{H}_5\text{O}_2$ radicals by the use of $k_2/k = 0.6$. E/R was from the studies of Anastasi *et al.*,^{7,11} Cattell *et al.*,⁸ Wallington *et al.*,⁹ Bauer *et al.*,¹⁰ and Fenter *et al.*¹

Preferred Values

$k = 6.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–450 K.

$k_2/k = 0.62$ at 298 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

$\Delta(E/R) = {}^{+300}_{-100} \text{ K}$.

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The rate coefficients reported by Fenter *et al.*¹ are in good agreement with previous data for this reaction.² The temperature coefficient reported in the same study¹ ($E/R = -60 \text{ K}$) agrees with the data of Cattell *et al.*⁸ ($E/R \approx 0 \text{ K}$) but less well with those of Anastasi *et al.*⁷ ($E/R = 470 \text{ K}$), Wallington *et al.*⁹ ($E/R = 110 \text{ K}$), or Bauer *et al.*¹⁰ ($E/R = -230 \text{ K}$). In view of the small temperature coefficients reported in most

of these studies, together with the relatively large associated error limits, we have selected a temperature-independent rate coefficient k based on k_{298} . Thus, from the data of Adachi *et al.*,⁶ Anastasi *et al.*,⁷ Cattell *et al.*,⁸ Wallington *et al.*,⁹ and Fenter *et al.*,¹ the average value of $k_{\text{obs}} = 1.03 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Taking $k_2/k = 0.62$ at 298 K (the mean of the data of Niki *et al.*,¹² Anastasi *et al.*,⁷ and Wallington *et al.*¹³) yields the recommended value of $k_{298} = 6.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The temperature dependence of the branching ratio reported by Anastasi *et al.*⁷ still requires confirmation.

References

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- ¹³T. J. Wallington, C. A. Gierczak, J. C. Ball, and S. M. Japar, *Int. J. Chem. Kinet.* **21**, 1077 (1989).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.4) \times 10^{-12}$	300	Dagaut, Wallington, and Kurylo, 1989 ¹	(a,b)
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin <i>et al.</i> , 1993 ²	(c)
<i>Branching Ratios</i>			
$k_2/k = (0.67 \pm 0.11)$	295	Jenkin <i>et al.</i> , 1993 ²	(d)
$k_2/k = (0.67 \pm 0.13)$	298	Jenkin <i>et al.</i> , 1993 ²	(e)
<i>Reviews and Evaluations</i>			
2.7×10^{-12}	298	Lightfoot <i>et al.</i> , 1992 ³	(f)

Comments

- (a) k is defined by $-\text{d}[\text{CH}_3\text{OCH}_2\text{O}_2]/\text{dt} = 2k[\text{CH}_3\text{OCH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Flash photolysis of $\text{Cl}_2\text{-CH}_3\text{OCH}_3\text{-O}_2\text{-N}_2$ mixtures at total pressures of 25–800 Torr from 228 to 380 K. $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{240} = (3.65 \pm 0.35) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. k_{obs} showed a strong pressure dependence and when treated by the Troe theory as a simple association reaction in the fall-off region, with a fixed $F_c = 0.6$, the following expressions were derived for the low and high-pressure limiting rate coefficients: $k_0 = (2.5 \pm 0.4) \times 10^{-30} (T/300 \text{ K})^{-(5.0 \pm 0.5)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $k_\infty = (2.7 \pm 0.2) \times 10^{-12} (T/300)^{-(4.5 \pm 0.4)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (c) Molecular modulation study of $\text{Cl}_2\text{-CH}_3\text{OCH}_3\text{-O}_2\text{-N}_2$ mixtures together with a pulse radiolysis study of

$\text{SF}_6\text{-CH}_3\text{OCH}_3\text{-O}_2$ mixtures. k_{obs} was found to be dependent on the total pressure (17–760 Torr) and on the composition of the reaction mixture. On the basis of a mechanism involving the generation of H atoms via the reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$, it was possible to derive the above pressure-independent value of k .

- (d) FTIR spectroscopic study of the steady-state photolysis of Cl_2 in the presence of $\text{CH}_3\text{OCH}_3\text{-O}_2\text{-N}_2$ mixtures over the total pressure range 10–700 Torr. The branching ratio was determined from the yields of CH_3OCHO and $\text{CH}_3\text{OCH}_2\text{OOH}$. Minor amounts of $\text{CH}_3\text{OCH}_2\text{OH}$ were also observed.
- (e) Similar study to that described in Comment (c). The branching ratio and k were derived from a kinetic analysis of the effects of $[\text{O}_2]$ and $[\text{Cl}_2]$ on k_{obs} , based on a mechanism including the production of H atoms from the reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$.

(f) Based on the data of Dagaut *et al.*¹

Preferred Values

$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 0.67$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The apparent effect of total pressure on k , the first reported for this type of reaction,¹ has been shown to be an artifact by the more recent experiments of Jenkin *et al.*² This comprehensive study² has shown that the pressure effect was due to secondary chemistry involving H atoms which arise from the

reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$. A kinetic analysis of the molecular modulation system, allowing for secondary chemistry, yielded the preferred rate coefficient. At the same time the derived value of the branching ratio,² k_2/k , is in excellent agreement with that obtained from a steady-state photolysis system with FTIR spectroscopic analyses.²

References

- ¹P. Dagaut, T. J. Wallington, and M. J. Kurylo, *J. Photochem. Photobiol.* **48**, 187 (1989).
- ²M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, *J. Phys. Chem.* **97**, 11712 (1993).
- ³P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).

$\Delta H^\circ = -71 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.8 \times 10^{-12} \exp(530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The agreement among the three measurements^{1–3} of this rate coefficient at room temperature is rather poor. The most recent study of Moortgat *et al.*³ is selected as the basis for our recommendation, on the grounds that it is based upon a

more complete knowledge of the complicated chemistry involved than was available for the earlier studies.^{1,2} At the same time, until more experimental data are available we have assigned considerable error limits, particularly with regard to the temperature coefficient. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹M. C. Addison, J. P. Burrows, R. A. Cox, and R. Patrick, *Chem. Phys. Lett.* **73**, 283 (1980).
- ²N. Basco and S. S. Parmar, *Int. J. Chem. Kinet.* **17**, 891 (1985).
- ³G. K. Moortgat, B. Veyret, and R. Lesclaux, *J. Phys. Chem.* **93**, 2362 (1989).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(5.0 \pm 2.0) \times 10^{-12}$	298	Bridier <i>et al.</i> , 1993 ¹	(a)
$k_1 \leq 4 \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_2/k = (0.5 \pm 0.2)$	298	Jenkin <i>et al.</i> , 1993 ²	(b)

Comments

- (a) Flash photolysis of Cl_2 in the presence of CH_3COCH_3 - CH_3CHO - N_2 mixtures at a total pressure of 760 Torr. The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210, 220, 230, and 245 nm, using the value of $k_2/k=0.5$ determined by Jenkin *et al.*²
- (b) Steady-state photolysis of Cl_2 in the presence of CH_3COCH_3 - N_2 mixtures at a total pressure of 700 Torr. The branching ratio was deduced from measurements of HCHO and CH_3COCHO products by long-path FTIR spectroscopy and long-path UV-VIS diode array spectroscopy.

 $k_2/k=0.5$ at 298 K.

Reliability

 $\Delta \log k = \pm 0.3$ at 298 K.

 $\Delta(k_2/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred values of the rate coefficient and the branching ratio are from the studies of Bridier *et al.*¹ and Jenkin *et al.*,² and require independent confirmation.

References

- ¹I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, J. Chem. Soc. Faraday Trans. **89**, 2993 (1993).
²M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, J. Chem. Soc. Faraday Trans. **89**, 2983 (1993).

Preferred Values

 $k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

 $k_1 \leq 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Branching Ratios</i>			
$k_2/k = 0.5 \pm 0.1$	298	Barnes, Becker, and Ruppert, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
2.3×10^{-12}	298	IUPAC, 1992 ²	(b,c)
$k_2/k = 0.36$	298		

Comments

- (a) Steady-state photolysis at 254 nm of $\text{HOCH}_2\text{CH}_2\text{I}$ - N_2 - O_2 or H_2O_2 - C_2H_4 - N_2 - O_2 mixtures at pressures of 150–900 mbar with FTIR spectroscopic detection of the products HCHO, HOCH_2CHO , and

$\text{HOCH}_2\text{CH}_2\text{OH}$. Values of $k_2/k = 0.49 \pm 0.05$ and 0.51 ± 0.04 were derived from the two different reactant systems, independent of total pressure or O_2 partial pressure.

- (b) k is defined by $-\text{d}[\text{HOCH}_2\text{CH}_2\text{O}_2]/\text{d}t = 2k[\text{HOCH}_2\text{CH}_2\text{O}_2]^2$ and has been derived from the

measured overall second-order decay of $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals (k_{obs}) by correcting for secondary removal of $\text{HOCH}_2\text{CH}_2\text{O}_2$.

- (c) k_{298} was based on the data of Jenkin and Cox,³ Anastasi *et al.*,⁴ and Murrells *et al.*,⁵ and k_2/k was from the data of Murrells *et al.*⁵

Preferred Values

$k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 0.5$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k_{298} is identical to our previous evaluation, IUPAC, 1992.² The recent measurements of the branching ratio, k_2/k , by Barnes *et al.*¹ are based on direct measurements of the products of the reaction channels and are also independent of the source of the radicals. For these reasons their branching ratio¹ is preferred to the earlier, less direct determination of Murrells *et al.*⁵

References

- ¹I. Barnes, K. H. Becker, and L. Ruppert, Chem. Phys. Lett. **203**, 295 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³M. E. Jenkin and R. A. Cox, J. Phys. Chem. **95**, 3229 (1991).
- ⁴C. Anastasi, D. J. Muir, V. J. Simpson, and P. Pagsberg, J. Phys. Chem. **95**, 5791 (1991).
- ⁵T. P. Murrells, M. E. Jenkin, S. J. Shalliker, and G. D. Hayman, J. Chem. Soc. Faraday Trans. **87**, 2351 (1991).

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient is the rounded-off value from the study of Adachi and Basco,¹ and is identical to our previous evaluation, IUPAC, 1992.² The room temperature rate coefficient requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals. On the other hand, the recommended rate

coefficient for the self-reaction of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical is considerably lower ($k_{298} = 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and that reported³ for the $t\text{-C}_4\text{H}_9\text{O}_2$ radical is even lower still ($k_{298} = 2.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This trend is in keeping with that observed in the liquid phase for the RO_2 radical interactions,⁴ i.e., $k(\text{primary } \text{RO}_2) > k(\text{secondary } \text{RO}_2) > k(\text{tertiary } \text{RO}_2)$.

References

- ¹H. Adachi and N. Basco, Int. J. Chem. Kinet. **14**, 1125 (1982).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³C. Anastasi, I. W. M. Smith, and D. A. Parks, J. Chem. Soc. Faraday Trans. 1, **74**, 1693 (1978).
- ⁴J. E. Bennett, D. M. Brown, and B. Mile, Trans. Faraday Soc. **66**, 386 (1970).

$\Delta H^\circ(1) = -351.9 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H^\circ(2) = 33.2 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-12} \exp(-2200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–400 K.

$k_1/k = 0.44$ at 298 K.

$k_1/k = 3.7 \times 10^{-2} \exp(740/T)$ over the temperature range 300–400 K.

$k_2/k = 0.56$ at 298 K.

$k_2/k = 2.0 \exp(-380/T)$ over the temperature range 300–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient (k) at 298 K is the average of the rate coefficients from the data of Kirsch *et al.*^{1,2} and Adachi and Basco,³ which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk *et al.*,⁴ for which experimental details are lacking. The recommended temperature dependence of k is based on

the results of Kirsch *et al.*,¹ which have been rounded-off and adjusted to the recommended value of k_{298} .

The measurements of the branching ratio and its temperature dependence^{2,5} appear to be reliable and have been adopted here, but require further confirmation. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

The value of k_{298} is considerably lower than that for the analogous reaction of the $n\text{-C}_3\text{H}_7\text{O}_2$ radical, which is in keeping with the trend observed in studies of the interactions of alkylperoxy radicals in solution,⁷ i.e., $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$.

References

- ¹L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday Trans. 1*, **74**, 2293 (1978).
- ²L. J. Kirsch, D. A. Parkes, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday Trans. 1*, **75**, 2678 (1979).
- ³H. Adachi and N. Basco, *Int. J. Chem. Kinet.* **14**, 1125 (1982).
- ⁴J. Munk, P. Pagsberg, E. Ratajczak, and A. Sillesen, *Chem. Phys. Lett.* **132**, 417 (1986).
- ⁵L. T. Cowley, D. J. Waddington, and A. Woolley, *J. Chem. Soc. Faraday Trans. 1*, **78**, 2535 (1982).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁷J. E. Bennett, D. M. Brown, and B. Mile, *Trans Faraday Soc.* **66**, 386 (1970).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.0 \pm 0.2) \times 10^{-12}$	298	Bridier <i>et al.</i> , 1993 ¹	(a,b)
Branching Ratios			
$k_2/k = (0.75 \pm 0.1)$	298	Bridier <i>et al.</i> , 1993 ¹	(c)
Reviews and Evaluations			
$\leq 1 \times 10^{-11}$	298	IUPAC, 1992 ²	(d)
8.3×10^{-12}	298	Wallington, Dagaut, and Kurylo, 1992 ³	(d)
8.3×10^{-12}	298	Lightfoot <i>et al.</i> , 1992 ⁴	(d)

Comments

- (a) k is defined by $-\text{d}[\text{CH}_3\text{COCH}_2\text{O}_2]/\text{dt} = 2k[\text{CH}_3\text{COCH}_2\text{O}_2]$.²
- (b) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{COCH}_3\text{-N}_2$ mixtures at a total pressure of 760 Torr. The rate coefficient k was derived from a kinetic analysis of absorption-time profiles at 230 and 260 nm, taking account of the information on the mechanism of

the overall reaction obtained from the product study of Jenkin *et al.*⁵

- (c) Same experiments as for Comment (a). The branching ratio was obtained on the basis of absorption due to radicals formed in reaction (2) and subsequent reactions.
- (d) Based on the data of Cox *et al.*⁶

Preferred Values

$k = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 0.75$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The above recommendations on the overall rate coefficient and the branching ratio at 298 K require independent verification.

References

- ¹I. Bridier, B. Veyret, R. Lesclaux, and M. E. Jenkin, *J. Chem. Soc. Faraday Trans.* **89**, 2993 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).
- ⁴P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ⁵M. E. Jenkin, R. A. Cox, M. Emrich, and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **89**, 2983 (1993).
- ⁶R. A. Cox, J. Munk, O. J. Nielsen, P. Pagsberg, and E. Ratajczak, *Chem. Phys. Lett.* **173**, 206 (1990).

(R=H or CH₃)

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Biradical	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>				
$k_2/k_8 = (6.1 \pm 0.3) \times 10^{-5}$	CH ₃ CHOO	295	Calvert <i>et al.</i> , 1978 ¹	(a)
$k_1:k_3:k_4:k_5:k_8 = 2.5 \times 10^{-3}:1.8 \times 10^{-3}:2.5 \times 10^{-1}:2.5 \times 10^{-3}:1.0$	CH ₂ OO	296	Su, Calvert, and Shaw, 1980 ²	(b)
$k_2/k_8 = (2.3 \pm 1) \times 10^{-4}$	CH ₂ OO	298	Suto, Manzanares, and Lee, 1984 ³	(c)
$k_7/k_8 = (1.4 \pm 0.4) \times 10^{-2}$	CH ₂ OO	298	Manzanares, Suto, and Lee, 1987 ⁴	(d)
$k_2/k_8 = (8.3 \pm 3.6) \times 10^{-4}$	CH ₂ OO	298	Becker, Bechara, and Brockman, 1993 ⁵	(e)
$k_2/k_8 = (4.1 \pm 2.2) \times 10^{-4}$	(CH ₃) ₂ COO	298	Becker, Bechara, and Brockman, 1993 ⁵	(f)
<i>Reviews and Evaluations</i>				
$k_2 = 2 \times 10^{-19}$ to 1×10^{-15}	CH ₂ OO	298	Herron, Martinez, and Huie, 1982 ⁶	(g)
$k_4 = 2 \times 10^{-16}$ to 8×10^{-13}	CH ₂ OO	298		(h)
$k_7 = 1 \times 10^{-17}$ to 7×10^{-14}	CH ₂ OO/	298		(i)
	CH ₃ CHOO			
$k_8 = 3 \times 10^{-15}$ to 1.7×10^{-11}	CH ₂ OO/	298		(j)
	CH ₃ CHOO			
$k_2:k_3:k_4:k_6:k_7:k_8 = 5 \times 10^{-5}:2 \times 10^{-3}:0.25:10^2:10:1$	CH ₂ OO/	298	Atkinson, and Lloyd, 1984 ⁷	(k)
$k_2 \sim 4 \times 10^{-18}$	CH ₃ CHOO	298		(l)
	CH ₂ OO/			
$k_4 \sim 2 \times 10^{-14}$	CH ₃ CHOO	298		(l)
	CH ₂ OO/			
$k_6 = 7 \times 10^{-12}$	CH ₃ CHOO	298		(m)
	CH ₂ OO/			
$k_7 \sim 7 \times 10^{-13}$	CH ₃ CHOO	298		(l)
	CH ₂ OO/			
$k_8 \sim 7 \times 10^{-14}$	CH ₃ CHOO	298		(l)
	CH ₂ OO/			
$k_2 = 4 \times 10^{-16}$	CH ₂ OO	298	Kerr and Calvert, 1984 ⁸	(n)
$k_3 = 1.3 \times 10^{-14}$	CH ₂ OO	298		(n)
$k_4 = 2 \times 10^{-12}$	CH ₂ OO	298		(n)
$k_6 = 7 \times 10^{-12}$	CH ₂ OO/	298		(n)
	CH ₃ CHOO			
$k_7 = 1.0 \times 10^{-13}$	CH ₂ OO/	298		(n)
	CH ₃ CHOO			
$k_8 = 7 \times 10^{-12}$	CH ₂ OO	298		(n)

Comments

- (a) Derived from a reanalysis of the data of Cox and Penkett⁹ from a study of the aerosol formation from

SO₂ in the presence of O₃-O₂-*cis*-2-C₄H₈ mixtures at atmospheric pressure. In this system the biradical intermediate involved is believed to be CH₃CHOÖ.

- (b) FTIR study of the $\text{C}_2\text{H}_4\text{-O}_3$ reaction in the presence of $\text{O}_2\text{-N}_2$ mixtures at a total pressure of 700 Torr and with added CO, HCHO, or SO_2 . Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.
- (c) Flow system involving $\text{C}_2\text{H}_4\text{-O}_3\text{-SO}_2\text{-H}_2\text{O}$ mixtures in which H_2SO_4 aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O_3 , SO_2 , and H_2O .
- (d) Similar study to that of comment (c), with the inclusion of the effect of added NO_2 on the formation of the H_2SO_4 aerosol.
- (e) Study of the $\text{C}_2\text{H}_4\text{-O}_3$ reaction in the presence of 1 atm of synthetic air with and without added SO_2 ; H_2O_2 yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy.
- (f) Same study as for comment (e) with $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ as the reactant.
- (g) Based on the ratio $k_2/k_8 \approx 6 \times 10^{-5}$, as derived by Calvert *et al.*¹ from the data of Cox and Penkett,⁹ and taking $3 \times 10^{-15} < k_8 < 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [see comment (k)].
- (h) Based on a study of the ozonide formation in the system $\text{O}_3\text{-O}_2\text{-cis-2-C}_4\text{H}_8\text{-HCHO}$ by Niki *et al.*¹⁰ and on thermochemical kinetic estimates of Nangia and Benson.¹¹ Details were not provided. It has been assumed that the reactivities of the $\dot{\text{C}}\text{H}_2\text{OO}$ and $\text{CH}_3\dot{\text{C}}\text{HOO}$ biradicals are identical.
- (i) Derived from the ratio $k_4/k_7 \approx 14$, which has been estimated from the data of Martinez *et al.*¹² from a study of the reduction in secondary ozonide formation from the $\text{O}_3\text{-O}_2\text{-trans-2-C}_4\text{H}_8$ reaction in the presence of NO_2 . k_7 was calculated by taking $2 \times 10^{-16} < k_4 < 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [see comment (h)]. It has been assumed that the reactivities of the $\dot{\text{C}}\text{H}_2\text{OO}$ and $\text{CH}_3\dot{\text{C}}\text{HOO}$ biradicals are identical.
- (j) Based on the suppression of ozonide formation in the $\text{O}_3\text{-O}_2\text{-cis-2-C}_4\text{H}_8\text{-HCHO}$ system by SO_2 observed by Niki *et al.*¹⁰ and on thermochemical kinetic estimates of Nangia and Benson.¹¹ Details were not provided. It has been assumed that the reactivities of the $\dot{\text{C}}\text{H}_2\text{OO}$ and $\text{CH}_2\dot{\text{C}}\text{HOO}$ biradicals are identical.
- (k) The relative rate coefficients are proposed on the basis that the data on $\dot{\text{C}}\text{H}_2\text{OO}$ (Su *et al.*²) and on $\text{CH}_3\dot{\text{C}}\text{HOO}$ (Cox and Penkett⁹) can be amalgamated, i.e., $\dot{\text{C}}\text{H}_2\text{OO}$ and $\text{CH}_3\dot{\text{C}}\text{HOO}$ have the same reactivities. From the studies of Akimoto *et al.*^{13,14} on the $\text{O}_3\text{-C}_2\text{H}_4$ and C_3H_6 system, it was estimated that $k_6:k_7:k_8=10^2:10:1$.
- (l) Calculated from the above relative rate coefficients and assuming that $k_6=7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [see comment (m)].
- (m) This rate coefficient was assumed to have a value similar to that for the reaction of alkylperoxy radicals with NO ($\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$), and hence $k_6=7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (n) Calculated (i) on the assumption that $k_6=k_8$ and taking the estimated value of $k_6=7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ of Atkinson and Lloyd⁷ and (ii) from the relative rate data of Calvert *et al.*,¹ Su *et al.*,² and Suto *et al.*³

Preferred Values

No recommendation.

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1992.¹⁵ Vibrationally excited Criegee intermediates or biradicals, $[\text{RCHO}\ddot{\text{O}}]^\ddagger$, are produced from the reactions of O_3 with alkenes.¹⁶ These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated biradicals, $\text{RCHO}\ddot{\text{O}}$. Here we consider the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated biradicals.

Studies have been made of the reactions of $\text{RCHO}\ddot{\text{O}}$ with aldehydes,^{2,10,17-20} SO_2 ,^{1,2,9,10,21} and H_2O ,^{1,9,13,22} but detailed kinetic data are often lacking. Relative rate coefficients have been derived by Calvert *et al.*,¹ Su *et al.*,² and Suto *et al.*³ based on experimental measurements of the rates of consumption of molecular reactants relative to consumption of SO_2 in systems involving $\text{RCHO}\ddot{\text{O}}$ biradicals. The only compound, other than SO_2 , common to any of these studies is H_2O , for which the derived relative rate coefficients differ by a factor of ~ 4 . Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the biradicals $\text{CH}_3\dot{\text{C}}\text{HOO}$ with O_3 , CO and alkenes are not important under atmospheric conditions. The reactions with H_2O , RCHO, NO_2 , and SO_2 need to be considered, although for most tropospheric conditions the only effective reaction of the biradicals is likely to be that with H_2O .

Previous reviewers^{7,8} have made the reasonable assumption that the reaction of $\text{RCHO}\ddot{\text{O}}$ with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway $\text{RCHO}\ddot{\text{O}} + \text{NO} \rightarrow \text{RCHO} + \text{NO}_2$. Unfortunately, there is no direct experimental evidence for this reaction and very little information upon which to base an estimate of its rate coefficient. Atkinson and Lloyd⁷ have estimated the relative rate coefficients for $\text{RCHO}\ddot{\text{O}}$ reacting with NO and SO_3 , corresponding to $k_6/k_7=10^2$, whereas Kerr and Calvert⁸ propose $k_6/k_7=1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients of any of the $\text{RCHO}\ddot{\text{O}}$ bimolecular reactions, both Atkinson and Lloyd⁷ and Kerr and Calvert⁸ have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$, with $k_6=7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. While this seems a reasonable proposition, it is desirable to obtain experimental verification. At present it is difficult to see how any direct measurements could be made

with $\dot{\text{R}}\text{CHO}\dot{\text{O}}$ systems involving O_3 -alkene reactions owing to the complex chemistry involved. In this regard the recent studies of Hatakeyama *et al.*²² involving the generation of $\dot{\text{C}}\text{H}_2\text{OO}$ biradicals from the reaction of $\text{CH}_2(^3\text{B}_1)$ with O_2 are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary to compare data obtained from different O_2 -alkene systems and to assume that all the $\dot{\text{R}}\text{CHO}\dot{\text{O}}$ biradicals have equal reactivity, e.g., $\dot{\text{C}}\text{H}_2\text{OO}$ and $\text{CH}_3\dot{\text{C}}\text{HO}\dot{\text{O}}$. Again, while this seems to be a reasonable assumption, it requires experimental verification.

There is very little direct experimental evidence on the products of any of the reactions (1) to (8). Where the products are stated these have largely been suggested on the basis of analogy with related reactions.

In addition to the expected formation of carboxylic acids from the reactions of the biradicals with H_2O ,

recent studies of the reactions of O_3 with *trans*-2-butene,^{5,23,24} isoprene,^{23,24} and monoterpenes^{23,24} have reported varying amounts of H_2O_2 product. Since the yields of H_2O_2 were considerably enhanced by the presence of H_2O , it was proposed that H_2O_2 was formed in a direct reaction involving Criegee biradicals:

In some of these experiments,²³ as in previous O_3 -alkene studies,^{25,26} hydroperoxides were also detected as products. The hydroperoxides were suggested to arise also from a direct Criegee biradical- H_2O interaction:

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$\text{O}_3 + \text{C}_2\text{H}_2 \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 1.0 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The literature data¹⁻⁶ exhibit a large degree of scatter at room temperature. While the most recent and lowest rate

coefficient of Atkinson and Aschmann⁶ may be the most accurate (any impurities would lead to higher rate constants), the preferred value and its associated large uncertainty cover the available 298 K rate coefficients. No recommendation is made regarding the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC, 1992.⁷

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$5.1 \times 10^{-15} \exp[-(2446 \pm 91)/T]$	240–324	Treacy <i>et al.</i> , 1992 ¹	(a)
$(1.37 \pm 0.08) \times 10^{-18}$	298		
<i>Reviews and Evaluations</i>			
$1.2 \times 10^{-14} \exp(-2630/T)$	180–360	IUPAC, 1992 ²	(b)
$9.14 \times 10^{-15} \exp(-2580/T)$	178–362	Atkinson, 1994 ³	(c)
$1.2 \times 10^{-14} \exp(-2630/T)$	180–360	NASA, 1994 ⁴	(b)

Comments

- (a) Static system, with chemiluminescence detection of O₃.
 (b) Based on the rate coefficient data of DeMore,⁵ Stedman *et al.*,⁶ Herron and Huie,⁷ Japar *et al.*,^{8,9} Toby *et al.*,¹⁰ Su *et al.*,¹¹ Adeniji *et al.*,¹² Kan *et al.*,¹³ Atkinson *et al.*,¹⁴ and Bahta *et al.*¹⁵
 (c) Based on a least-squares analysis of the rate coefficients of DeMore,⁵ Stedman *et al.*,⁶ Herron and Huie,⁷ Japar *et al.*,^{8,9} Toby *et al.*,¹⁰ Atkinson *et al.*,¹⁴ Bahta *et al.*,¹⁵ and the 298 K rate coefficient of Treacy *et al.*¹

Preferred Values $k = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. $k = 9.1 \times 10^{-15} \exp(-2580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–360 K.**Reliability** $\Delta \log k = \pm 0.10$ at 298 K. $\Delta(E/R) = \pm 100 \text{ K}$.**Comments on Preferred Values**

The most recent kinetic studies of Bahta *et al.*¹⁵ and Treacy *et al.*¹ are in good agreement, and the rate coefficients from these studies^{1,15} are somewhat lower than many of the previous rate coefficient data, including those of Su *et al.*¹¹ and Kan *et al.*¹³ Since Treacy *et al.*¹ did not tabulate the individual rate coefficients at the various temperatures studied, only the 298 K rate constant can be used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares analysis of the rate coefficients of DeMore,⁵ Stedman *et al.*,⁶ Herron and Huie,⁷ Japar *et al.*,^{8,9} Toby *et al.*,¹⁰ Atkinson *et al.*,¹⁴ Bahta *et al.*,¹⁵ (averaging the rate coefficients at each of the four temperatures studied) and the 298 K rate coefficient of Treacy *et al.*¹

As discussed by Atkinson and Lloyd,¹⁶ Atkinson and Carter,¹⁷ and Atkinson,³ the initial reaction forms the energy-rich trioxane which rapidly decomposes:

to yield HCHO and the energy-rich biradical $[\dot{\text{C}}\text{H}_2\text{O}\dot{\text{O}}]^\ddagger$.

This energy-rich biradical can either decompose or be stabilized

At room temperature and atmospheric pressure, the fraction of stabilization is ~ 0.37 ,^{3,11,13,18–21} and is pressure dependent.²⁰ The fractions of the overall reactions proceeding via pathways (a) through (c) at room temperature and atmospheric pressure are then approximately 0.13, 0.31–0.58, and 0.06–0.10, respectively.³ However, Atkinson *et al.*²² have observed the formation of OH radicals at room temperature and atmospheric pressure of air, with a yield of ~ 0.12 . The observed formation of OH radicals,²² presumably via pathway (d), probably indicates that pathway (c) does not occur, since the study of Herron and Huie²³ could not differentiate between formation of H atoms and OH radicals (any H atoms formed would rapidly react with O₃ in the

reaction system used by Herron and Huie²³ to produce OH radicals). Hence a possible reaction sequence is

The relative importance of these decomposition/stabilization reactions of the $[\dot{\text{C}}\text{H}_2\text{O}\ddot{\text{O}}]^\ddagger$ radical are, however, pressure dependent,²⁰ with no quantitative data being available other than at ~ 1 bar of air.

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O₃ + C₃H₆ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.9 \times 10^{-15} \exp[-(1858 \pm 70)/T]$	240–324	Treacy <i>et al.</i> , 1992 ¹	(a)
$(9.4 \pm 0.4) \times 10^{-18}$	298		
<i>Reviews and Evaluations</i>			
$6.5 \times 10^{-15} \exp(-1880/T)$	230–370	IUPAC, 1992 ²	(b)
$5.51 \times 10^{-15} \exp(-1878/T)$	235–362	Atkinson, 1994 ³	(c)
$6.5 \times 10^{-15} \exp(-1900/T)$	235–360	NASA, 1994 ⁴	(d)

Comments

- (a) Static system, with chemiluminescence detection of O₃.
- (b) Derived from a least-squares analysis of the absolute rate coefficient data of Cox and Penkett,⁵ Stedman *et al.*,⁶ Herron and Huie,⁷ Japar *et al.*,^{8,9} Adeniji *et al.*,¹⁰ and Atkinson *et al.*¹¹
- (c) Derived from the absolute rate coefficient data of Herron and Huie⁷ and Treacy *et al.*¹
- (d) Based mainly on the absolute rate coefficient data of Herron and Huie.⁷

Preferred Values

$k = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–370 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Herron and Huie⁷ (note that the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie⁷) and Treacy *et al.*¹ are in excellent agreement for propene, 1-butene, *cis*- and *trans*-2-butene, 2-methylpropene, and 2-methyl-2-butene over the temperature ranges common to both studies.³ Accordingly, the 298 K rate coefficients and temperature dependencies of Herron and Huie⁷ and Treacy *et al.*¹ have been averaged to yield the preferred Arrhenius expression (note that the individual rate coefficients at the various temperatures studied by Treacy *et al.*¹ were not tabulated).

The reaction proceeds via the initial formation of a trioxane, which rapidly decomposes:

The rate coefficient ratio k_a/k_b has not been experimentally determined, and is assumed to be approximately unity although this is probably not the case.^{12,13} It is generally assumed^{14,15} that the reactions of the energy-rich biradical $[\dot{\text{C}}\text{H}_2\text{OO}]^\ddagger$ formed from propene are similar to those for $[\dot{\text{C}}\text{H}_2\text{OO}]^\ddagger$ formed from ethene. Hence, as for the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction at room temperature and 1 bar of air

Less data are available concerning the stabilization and decomposition reactions of the $[\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}]^\ddagger$ biradical. Based upon the SO_2 to H_2SO_4 conversion yield in an O_3 + propene reaction system, Hatakeyama *et al.*¹⁶ determined an overall stabilized biradical ($\dot{\text{C}}\text{H}_2\text{OO} + \text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}$) yield of 0.254 ± 0.023 at room temperature and atmospheric pressure, while Horie and Moortgat¹² obtained a stabilized biradical yield of 0.44. Using the data of Hatakeyama *et al.*¹⁶ and assuming that $k_a = k_b$ and that the $[\dot{\text{C}}\text{H}_2\text{OO}]^\ddagger$ stabilization yield is 0.37, then the fraction of $[\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}]^\ddagger$ biradicals which are stabilized at ~ 298 K and 1 bar of air is 0.14. While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}]^\ddagger$ biradicals which are stabilized at 298 K and 1 bar of air is similar to the measured yields of stabilized $\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}$ from *trans*-2-butene (0.185¹⁶) and *cis*-2-butene (0.18¹⁷). A yield of stabilized $\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}$ from $[\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}]^\ddagger$ of 0.15 at 298 K and 1 bar of air is recommended, consistent with the product data of Hatakeyama *et al.*¹⁶:

The decomposition pathways are less well understood,^{12,14,15} but are expected to involve formation of $\text{CH}_3 + \text{CO} + \text{OH}$,

Recent studies and evaluations^{2,12} conclude that these channels have approximate fractional overall yields at ~ 1 bar of air of: channel (a) 0.15–0.42; channel (b), 0.16–0.30; channel (c), 0.17–0.34; channel (d), 0–0.07; channel (e), 0.14–0.17; and channel (f), 0–0.07. However, Atkinson and Aschmann¹³ have observed the formation of OH radicals from the ozone reaction with propene at room temperature and atmospheric pressure of air, with a yield of 0.33 (uncertain to a factor of ~ 1.5). A possible reaction sequence for the $[\text{CH}_3\dot{\text{C}}\text{HO}\ddot{\text{O}}]^\ddagger$ biradical at 298 K and 1 bar air is

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HCHO + *hν* → products

Primary photochemical transitions

Reaction	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HCHO + <i>hν</i> → H + HCO (1)	363.8	329
→ H ₂ + CO (2)	−1.9	−

Preferred Values

Absorption cross-sections for HCHO photolysis over the wavelength region 240–360 nm, T = 285 K^a

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
240	0.064	271	1.789	302	1.064	333	0.215
241	0.056	272	1.227	303	3.201	334	0.171
242	0.105	273	0.645	304	6.902	335	0.143
243	0.115	274	0.656	305	4.914	336	0.194
244	0.082	275	2.232	306	4.632	337	0.417
245	0.103	276	2.416	307	2.100	338	2.360
246	0.098	277	1.402	308	1.494	339	4.712
247	0.135	278	1.050	309	3.407	340	2.481
248	0.191	279	2.548	310	1.950	341	0.759
249	0.282	280	2.083	311	0.521	342	0.681
250	0.205	281	1.475	312	1.120	343	1.953
251	0.170	282	0.881	313	1.116	344	1.137
252	0.288	283	1.066	314	4.747	345	0.323
253	0.255	284	4.492	315	5.247	346	0.113
254	0.255	285	3.592	316	2.899	347	0.066
255	0.360	286	1.962	317	5.373	348	0.122
256	0.509	287	1.295	318	2.975	349	0.032
257	0.339	288	3.356	319	0.918	350	0.038
258	0.226	289	2.838	320	1.262	351	0.104
259	0.504	290	1.304	321	1.529	352	0.713
260	0.505	291	1.746	322	0.669	353	2.212
261	0.549	292	0.832	323	0.345	354	1.536
262	0.520	293	3.727	324	0.816	355	0.676
263	0.933	294	6.535	325	1.850	356	0.135
264	0.823	295	3.950	326	5.950	357	0.036
265	0.430	296	2.333	327	3.485	358	0.0057
266	0.495	297	1.513	328	1.087	359	0.058
267	1.239	298	4.037	329	3.353	360	0.082
268	1.110	299	2.871	330	3.321		
269	0.878	300	0.871	331	1.073		
270	0.936	301	1.715	332	0.289		

^aAveraged over 0.5 nm wavelength intervals centered at the cited wavelength [G. K. Moortgat and W. Schneider (unpublished data)].

Absorption cross-sections for HCHO photolysis over the wavelength region 301.25–356.25 nm^a as a function of temperature (223–293 K)^b

λ/nm	σ/cm^2		Intercept (273 K)	Temp. gradient
	223 K	293 K		
301.25	1.38E-20	1.36E-20	1.37E-20	−2.10E-24
303.75	4.67E-20	4.33E-20	4.43E-20	−4.73E-23
306.25	3.32E-20	3.25E-20	3.27E-20	−1.06E-23
308.75	2.27E-20	2.22E-20	2.24E-20	−7.24E-24
311.25	7.58E-21	9.31E-21	8.82E-21	2.48E-23
313.75	3.65E-20	3.40E-20	3.47E-20	−3.64E-23
316.25	4.05E-20	3.89E-20	3.94E-20	−2.30E-23
318.75	1.66E-20	1.70E-20	1.69E-20	6.59E-24
321.25	1.24E-20	1.13E-20	1.16E-20	−1.52E-23
323.75	4.65E-21	4.73E-21	4.71E-21	1.18E-24
326.25	5.06E-20	4.44E-20	4.61E-20	−8.86E-23
328.75	2.44E-20	2.29E-20	2.43E-20	−2.15E-23
331.25	1.39E-20	1.28E-20	1.31E-20	−1.53E-23
333.75	9.26E-22	1.23E-21	1.14E-21	4.32E-24
336.25	1.27E-21	1.13E-21	1.30E-21	5.03E-25
338.75	3.98E-20	3.36E-20	3.45E-20	−8.96E-23
341.25	8.05E-21	9.36E-21	8.98E-21	1.86E-23
343.75	1.44E-20	1.26E-20	1.31E-20	−2.64E-23
346.25	3.39E-23	7.10E-22	5.18E-22	9.57E-24
348.75	9.05E-23	3.97E-22	3.10E-22	4.38E-24
351.25	1.69E-21	2.35E-21	2.16E-21	9.48E-24
353.75	1.83E-20	1.55E-20	1.63E-20	−4.05E-23
356.25	3.54E-22	1.25E-21	9.19E-22	1.27E-23

^a2.5 nm interval centered at given λ .
^bAt any temperature within the range 223–293 K, σ can be calculated from the listed gradient (slope) and intercept fit parameters, with $\sigma = (\text{slope} \times T(^{\circ}\text{C}) + \text{intercept})$ [C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, *J. Phys. Chem.* **94**, 3902 (1990)].

Quantum Yields for HCHO photolysis

λ/nm	ϕ_1	ϕ_2
240	0.27	0.49
250	0.29	0.49
260	0.30	0.49
270	0.38	0.43
280	0.57	0.32
290	0.73	0.24
300	0.78	0.21
310	0.78	0.22
320	0.62	0.38
330	0.27	0.66
340	0.00	0.56
350	0.00	0.21
360	0.00	0.03

Comments on Preferred Values

The preferred values are identical to our previous evaluation, 1992.¹ The recommended absorption cross-sections are those of Moortgat and Schneider² for $\lambda \leq 300$ nm and of Cantrell *et al.*³ for $\lambda = 301\text{--}356$ nm, the latter providing a temperature dependence over the range 223–293 K.

The problem of understanding the measured quantum yields and branching ratios, $Y_2 = \phi_2/(\phi_1 + \phi_2)$, remains unresolved. If the photochemistry were governed by a sequence of light absorption into the first excited electronic state, internal conversion to the electronic ground state, and subsequent competition of the reactions $\text{HCHO}^* \rightarrow \text{H} + \text{HCO}$ and $\text{HCHO}^* \rightarrow \text{H}_2 + \text{CO}$, then the measured values of Y_2 for $\lambda \leq 300$ nm would be difficult to interpret. Simulations⁴ of the rates of the competing processes of HCHO^* and measurements of the product yields in molecular beams⁵ in-

dicates that the radical channel (1), $\text{HCHO}^* \rightarrow \text{H} + \text{HCO}$ dominates for $\lambda \leq 300$ nm, with $Y_2 < 0.1$ at 284 nm.⁵ An analysis of the details of the photophysical processes⁶ has failed to resolve this discrepancy with the macroscopic photochemical observations. The branching ratios for ≤ 300 nm should therefore be treated with caution.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
- ²G. K. Moortgat and W. Schneider, unpublished data.
- ³C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, *J. Phys. Chem.* **94**, 3902 (1990).
- ⁴J. Troe, *J. Phys. Chem.* **88**, 4375 (1984).
- ⁵P. Ho, D. J. Bamford, R. J. Buss, Y. T. Lee, and C. B. Moore, *J. Chem. Phys.* **76**, 3630 (1982).
- ⁶C. B. Moore and J. C. Weisshaar, *Annu. Rev. Phys. Chem.* **34**, 325 (1983).

 $\text{CH}_3\text{CHO} + h\nu \rightarrow \text{products}$ **Primary photochemical transitions**

Reaction	$\Delta H_{298}^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_4 + \text{CO}$ (1)	−19.5	
$\rightarrow \text{CH}_3 + \text{HCO}$ (2)	349.0	343
$\rightarrow \text{CH}_3\text{CO} + \text{H}$ (3)	359.5	333

Absorption cross-sections

Wavelength range/nm	Reference	Comments
202–365	Martinez <i>et al.</i> , 1992 ¹	(a)

Comments

- (a) Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

Preferred Values

Absorption cross-sections for acetaldehyde					
λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
202	0.056	297	4.38	334	0.363
206	0.053	298	4.41	335	0.350
210	0.049	299	4.26	336	0.238
214	0.048	300	4.16	337	0.222
218	0.052	301	3.99	338	0.205
222	0.065	302	3.86	339	0.219
226	0.096	303	3.72	340	0.150
230	0.151	304	3.48	341	0.074
234	0.241	305	3.42	342	0.042
238	0.375	306	3.42	343	0.031
242	0.564	307	3.36	344	0.026
246	0.818	308	3.33	345	0.021
250	1.128	309	3.14	346	0.019
254	1.524	310	2.93	347	0.015
258	1.994	311	2.76	348	0.016
262	2.44	312	2.53	349	0.010
266	3.05	313	2.47	350	0.008
270	3.42	314	2.44	351	0.007
274	4.03	315	2.20	352	0.006
278	4.19	316	2.04	353	0.005
280	4.50	317	2.07	354	0.005
281	4.69	318	1.979	355	0.004
282	4.72	319	1.874	356	0.005
283	4.75	320	1.723	357	0.003
284	4.61	321	1.484	358	0.004
285	4.49	322	1.402	359	0.002
286	4.44	323	1.244	360	0.003
287	4.59	324	1.091	361	0.002
288	4.72	325	1.136	362	0.001
289	4.77	326	1.074	363	0.000
290	4.89	327	0.858	364	0.000
291	4.78	328	0.747	365	0.000
292	4.68	329	0.707		
293	4.53	330	0.688		
294	4.33	331	0.588		
295	4.27	332	0.530		
296	4.24	333	0.398		

Quantum Yields for 1 atm air

λ/nm	ϕ_1	ϕ_2
260	0.46	0.31
270	0.31	0.39
280	0.05	0.58
290	0.01	0.53
295	0.00	0.48
300		0.43
305		0.37
315		0.17
320		0.10
325		0.04
330		0.00

Comments on Preferred Values

The preferred absorption cross-sections are from the recent more extensive measurements of Martinez *et al.*¹ Over the wavelength region 260–320 nm these cross-sections are within 5% of our previous recommendations based on the data of Calvert and Pitts² and Weaver *et al.*³

Our previous recommendations⁴ for the quantum yields remain unaltered.

References

- ¹R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, *Atmos. Environ.* **26A**, 785 (1992).
- ²J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
- ³J. Weaver, J. Meagher, and J. Heicklen, *J. Photochem.* **6**, 111 (1976).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

 $\text{C}_2\text{H}_5\text{CHO} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_5 + \text{HCO}$ (1)	343.1	349
$\rightarrow \text{C}_2\text{H}_6 + \text{CO}$ (2)	−7.1	
$\rightarrow \text{C}_2\text{H}_4 + \text{HCHO}$ (3)	131.0	913
$\rightarrow \text{CH}_3 + \text{CH}_2\text{CHO}$ (4)	336.4	356

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez <i>et al.</i> , 1992 ¹	(a)

Comments

- (a) Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

Preferred Values

Absorption cross-sections for propanal

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
202	0.049	295	5.57	330	0.575
206	0.049	296	5.37	331	0.494
210	0.057	297	5.16	332	0.466
214	0.069	298	5.02	333	0.430
218	0.080	299	5.02	334	0.373
222	0.091	300	5.04	335	0.325
226	0.115	301	5.09	336	0.280
230	0.163	302	5.07	337	0.230
234	0.257	303	4.94	338	0.185
238	0.407	304	4.69	339	0.166
242	0.622	305	4.32	340	0.155
246	0.909	306	4.04	341	0.119
250	1.287	307	3.81	342	0.076
254	1.745	308	3.65	343	0.045
258	2.25	309	3.62	344	0.031
262	2.88	310	3.60	345	0.025
266	3.43	311	3.53	346	0.019
270	4.12	312	3.50	347	0.016
274	4.59	313	3.32	348	0.014
278	5.17	314	3.06	349	0.013
280	5.16	315	2.77	350	0.010
281	5.21	316	2.43	351	0.008
282	5.35	317	2.18	352	0.007
283	5.57	318	2.00	353	0.005
284	5.78	319	1.864	354	0.004
285	5.86	320	1.831	355	0.002
286	5.82	321	1.777	356	0.001
287	5.72	322	1.662	357	0.001
288	5.59	323	1.577	358	0.000
289	5.52	324	1.488	359	0.000
290	5.56	325	1.300	360	0.000
291	5.68	326	1.129	361	0.000
292	5.81	327	0.996	362	0.000
293	5.88	328	0.828	363	0.000
294	5.80	329	0.685	364	0.000
				365	0.000

Quantum Yields for 1 atm air

λ/nm	ϕ_1
294	0.89
302	0.85
313	0.50
325	0.26
334	0.15

Comments on Preferred Values

The preferred absorption cross-sections are from the recent more extensive measurements of Martinez *et al.*¹ Over the wavelength region 260–320 nm these cross-sections are within 5% of our previous recommendations based on the data of Calvert and Pitts.²

The preferred values of the quantum yields for the photodissociation yielding C_2H_5 radicals are taken from the study of Hecklen *et al.*,³ and refer to photolysis in air at a total pressure of 1 atm. No explanation has been put forward to account for the large differences in the reported values of ϕ_1 as a function of wavelength.^{3–5}

References

- ¹R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, *Atmos. Environ.* **26A**, 785 (1992).
- ²J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
- ³J. Hecklen, J. Desai, A. Bahta, C. Harper, and R. Simonaitis, *J. Photochem.* **34**, 117 (1986).
- ⁴P. B. Shepson and J. Hecklen, *J. Photochem.* **18**, 169 (1982).
- ⁵P. B. Shepson and J. Hecklen, *J. Photochem.* **19**, 215 (1982).

 $(\text{CHO})_2 + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$(\text{CHO})_2 + h\nu \rightarrow \text{H}_2 + 2\text{CO}$ (1)	−9.1	
$\rightarrow 2\text{HCO}$ (2)	286.3	418
$\rightarrow \text{HCHO} + \text{CO}$ (3)	−7.2	

Preferred Values

Absorption cross-sections for glyoxal

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
230.5	0.30	390	3.14	427	10.76
235	0.30	391	3.45	428	16.65
240	0.42	392	3.25	429	4.06
245	0.57	393	2.23	430	5.07
250	0.84	394	2.64	431	4.87
255	1.15	395	3.04	432	4.06
260	1.45	396	2.64	433	3.65
265	1.88	397	2.44	434	4.06
270	2.30	398	3.25	435	5.07
275	2.60	399	3.04	436	8.12
280	2.87	400	2.84	437	5.28
285	3.33	401	3.25	438	10.15
290	3.18	402	4.46	439	7.71
295	3.33	403	5.28	440	24.76
300	3.60	404	4.26	441	8.12
305	2.76	405	3.05	442	6.09
310	2.76	406	3.05	443	7.51
312.5	2.88	407	2.84	444	9.34
315	2.30	408	2.44	445	11.37
320	1.46	409	2.84	446	5.28
325	1.15	410	6.09	447	2.44
327.5	0.30	411	5.27	448	2.84
330	0.00	412	4.87	449	3.86
335	0.00	413	8.32	450	6.09
340	0.00	414	7.51	451	10.96
345	0.00	415	8.12	452	12.18
350	0.00	416	4.26	453	23.95
355	0.00	417	4.87	454	17.05
360	0.23	418	5.89	455	40.60
365	0.30	419	6.70	456	10.14
370	0.80	420	3.86	457	1.63
375	1.03	421	5.68	458	1.22
380	1.72	422	5.28	459	0.41
382	1.57	423	10.55	460	0.41
384	1.49	424	6.09	461	0.20
386	1.49	425	7.31	462	0.00
388	2.87	426	11.77		

Comments on Preferred Values

This data sheet is largely reproduced from our previous evaluation, IUPAC, 1992.¹ The preferred values listed above are taken from the results of Plum *et al.*² and are in good agreement with the earlier published data summarized by Calvert and Pitts.³

The selection of preferred quantum yields for the photolysis of glyoxal as a function of wavelength under atmospheric conditions must await further investigations. The “effective” quantum yield of $\phi=0.029$ reported by Plum *et al.*² is valid only for the particular spectral distribution used in their study. This value of ϕ may be used to calculate the rates of photolyses of glyoxal under tropospheric conditions within the spectral region 325–470 nm. For the lower wavelength band in the troposphere it is recommended that the value $\phi=0.4$, reported by Langford and Moore⁴ at 308 nm, be used in such calculations.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
- ²C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., *Environ. Sci. Technol.* **17**, 479 (1983).
- ³J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
- ⁴A. O. Langford and C. B. Moore, *J. Chem. Phys.* **80**, 4211 (1984).

CH₃COCHO + $h\nu$ → products

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ COCHO + $h\nu$ → CH ₄ + 2CO (1)	−24.7	
→ CH ₃ CO + HCO (2)	284.0	421
→ CH ₃ CHO + CO (3)	−5.2	

Preferred Values

Absorption cross-sections for methylglyoxal between 225 and 410 nm, at 5 nm intervals

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
225	1.268	320	1.511
230	1.477	325	0.938
235	1.803	330	0.652
240	2.071	335	0.482
245	2.304	340	0.323
250	2.612	345	0.300
255	2.859	350	0.394
260	3.280	355	0.560
265	3.618	360	0.695
270	4.159	365	1.077
275	4.413	370	1.475
280	4.877	375	1.911
285	4.719	380	2.429
290	4.838	385	3.221
295	4.362	390	4.029
300	3.754	395	4.732
305	3.361	400	5.664
310	2.365	405	6.923
315	1.891	410	8.459

Preferred Values

Absorption cross-sections for methylglyoxal between 401 and 475 nm, at 1 nm intervals

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
401	5.90	439	11.01
402	6.07	440	9.94
403	6.35	441	10.39
404	6.54	442	10.20
405	6.91	443	10.17
406	7.20	444	11.17
407	7.58	445	9.61
408	7.94	446	8.90
409	8.12	447	9.84
410	8.52	448	9.18
411	8.63	449	10.13
412	9.07	450	8.67
413	9.37	451	6.34
414	9.62	452	6.33
415	9.68	453	6.08
416	9.71	454	4.46
417	10.04	455	3.69
418	10.07	456	3.08
419	10.12	457	2.46
420	10.21	458	1.81
421	10.34	459	1.28
422	10.51	460	0.914
423	10.45	461	0.795
424	10.15	462	0.642
425	10.34	463	0.479
426	10.24	464	0.332
427	9.84	465	0.268
428	10.01	466	0.227
429	9.94	467	0.187
430	10.41	468	0.160
431	10.53	469	0.133
432	9.79	470	0.108
433	10.64	471	0.099
434	10.54	472	0.089
435	10.81	473	0.077
436	11.13	474	0.067
437	9.99	475	0.062
438	10.59		

Comments on Preferred Values

The preferred values of the absorption cross-sections are identical to our previous evaluation, IUPAC, 1992.¹ The measurements of the cross-sections reported by Meller *et al.*² are approximately a factor of two higher than the previous measurements of Plum *et al.*³ The data of Meller *et al.*² are preferred because of the agreement between the cross-sections measured by conventional spectroscopy and from *in situ* generation of methylglyoxal.² In addition, Meller *et al.*² found evidence of problems in the handling of methylglyoxal which were minimized by the *in situ* generation technique and which seem likely to have been present in the study of Plum *et al.*³

No further work has been reported on the quantum yields for the photolysis of methylglyoxal as a function of wavelength under atmospheric conditions. Plum *et al.*³ measured the rate of photolysis of methylglyoxal, equal to $\int \sigma_{\lambda} \phi_{\lambda} J_{\lambda} \times d\lambda$. Hence the “effective value of ϕ measured by Plum *et al.*³ for the spectral range (325–475 nm) and distribution used³ must be reduced by a factor of ~ 2 to be consistent with the increased values of σ now being recommended.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
- ²R. Meller, W. Raber, J. N. Crowley, M. E. Jenkin, and G. K. Moortgat, J. Photochem. Photobiol., A: Chemistry **62**, 163 (1991).
- ³C. N. Plum, E. Sanhueza, R. Atkinson, W. P. L. Carter, and J. N. Pitts, Jr., Environ. Sci. Technol. **17**, 479 (1983).

CH₃COCH₃ + *hν* → products**Primary photochemical transitions**

Reaction	$\Delta H_{298}^{\circ}/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ COCH ₃ + <i>hν</i> → CH ₃ CO + CH ₃ (1)	338.9	353
→ 2CH ₃ + CO (2)	398.7	300

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez <i>et al.</i> , 1992 ¹	(a)
260–360	Hynes <i>et al.</i> , 1992 ²	(b)

Comments

- (a) Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).
- (b) Cross-sections measured as a function of temperature over the range 260–360 K. Data were presented in graphical form and show a marked decrease in cross-section with decreasing temperature.

Preferred Values**Absorption cross-sections for acetone**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
202	0.533	295	3.52	330	0.067
206	0.125	296	3.35	331	0.051
210	0.104	297	3.20	332	0.040
214	0.120	298	2.07	333	0.031
218	0.163	299	2.91	334	0.026
222	0.242	300	2.77	335	0.017
226	0.361	301	2.66	336	0.014
230	0.533	302	2.53	337	0.011
234	0.774	303	2.37	338	0.009
238	1.086	304	2.24	339	0.006
242	1.479	305	2.11	340	0.005
246	1.944	306	1.952	341	0.005
250	2.47	307	1.801	342	0.003
254	3.04	308	1.663	343	0.004
258	3.61	309	1.537	344	0.002
262	4.15	310	1.408	345	0.002
266	4.58	311	1.276	346	0.001
270	4.91	312	1.173	347	0.002
274	5.06	313	1.081	348	0.001
278	5.07	314	0.967	349	0.001
280	5.05	315	0.858	350	0.001
281	5.01	316	0.777	351	0.000
282	4.94	317	0.699	352	0.001
283	4.86	318	0.608	353	0.000
284	4.76	319	0.530	354	0.001
285	4.68	320	0.467	355	0.000
286	4.58	321	0.407		
287	4.50	322	0.344		
288	4.41	323	0.287		
289	4.29	324	0.243		
290	4.19	325	0.205		
291	4.08	326	0.168		
292	3.94	327	0.135		
293	3.81	328	0.108		
294	3.67	329	0.086		

Quantum Yields for 1 atm air

λ/nm	ϕ_1
250	0.76
260	0.80
270	0.64
280	0.55
290	0.30
300	0.15
310	0.05
320	0.028
330	0.033

Comments on Preferred Values

The preferred absorption cross-sections are from the recent extensive measurements of Martinez *et al.*¹ Over the wavelength region 260–320 nm these cross-sections are within 5% of our previous recommendations based on the data of Calvert and Pitts³ and Meyrahn *et al.*⁴ The cross-sections reported by Hynes *et al.*² at room temperature contain large error limits at 320 and 340 nm but are in reasonable agreement with those recommended here.

This latter study² has also shown that the cross-sections are temperature dependent. Since no easily presentable formulation of the effect of temperature on the cross-sections was given, the original paper² should be consulted for de-

tails. It was noted, however, that neglecting the temperature-dependence of the cross-sections results in significant over-estimation of the photodissociation rates at lower temperature, by, for example, ~50% at 220 K in the upper troposphere.²

The two studies^{4,5} of the photodissociation of acetone in air are not in agreement regarding the quantum yield measurements. As pointed out by Meyrahn *et al.*,⁴ further work on this system is needed to elucidate more quantitative details such as the collisional deactivation of photoexcited acetone. In the meantime, we have recommended the quantum yield data of Meyrahn *et al.*,⁴ on the basis that the trend in ϕ_1 with wavelength observed by these authors appears to be reasonable.

References

- ¹R. D. Martinez, A. A. Buitrago, N. W. Howell, C. H. Hearn, and J. A. Joens, *Atmos. Environ.* **26A**, 785 (1992).
- ²A. J. Hynes, E. A. Kenyon, A. J. Pounds, and P. H. Wine, *Spectrochim. Acta* **48A**, 1235 (1992).
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- ⁴H. Meyrahn, J. Pauly, W. Schneider, and P. Warneck, *J. Atmos. Chem.* **4**, 277 (1986).
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CH₃OOH + $h\nu$ → products

Primary photochemical transitions

Reaction	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$ ^a	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ OOH + $h\nu$ → CH ₃ O + HO (1)	188	637
→ CH ₃ + HO ₂ (2)	292	410
→ CH ₃ O ₂ + H (3)	359	333

^aCalculated assuming $\Delta H_0^{\circ} = \Delta H_{298}^{\circ}$, C_p data are not available for CH₃OOH.

Preferred Values

Absorption cross-sections

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.¹ The preferred absorption cross-section data are those of Vaghjiani and Ravishankara,² which are approximately 25% lower than the previously recommended data of Molina and Arguello.³ The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello³ used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara² showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara,⁴ who showed that $\phi_{\text{OH}} \sim 1.0$ at $\lambda = 248 \text{ nm}$, we recommend that for atmospheric photolysis of CH_3OOH , ϕ_1 be taken to be unity for wavelengths $> 290 \text{ nm}$.

References

¹IUPAC, Supplement IV, 1992 (see references in Introduction).

²G. L. Vaghjiani and A. R. Ravishankara, *J. Geophys. Res.* **94**, 3487 (1989).

³M. J. Molina and G. Arguello, *Geophys. Res. Lett.* **6**, 953 (1979).

⁴G. L. Vaghjiani and A. R. Ravishankara, *J. Chem. Phys.* **92**, 996 (1990).

 $\text{CH}_3\text{ONO}_2 + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{ONO}_2 + h\nu \rightarrow \text{CH}_3\text{O} + \text{NO}_2$ (1)	170.5	702
$\rightarrow \text{HCHO} + \text{HONO}$ (2)	-68.4	
$\rightarrow \text{CH}_3\text{ONO} + \text{O}$ (3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–335	Rattigan <i>et al.</i> , 1992 ¹	(a)

Comments

- (a) Cross-sections were measured with a dual-beam diode array spectrometer with a spectral resolution of 0.3 nm over the temperature range 238–294 K. The temperature dependence of σ was found to obey the equation, $\log_{10}\sigma = \log_{10}\sigma_0 + BT$ with the following values of the intercept and slope of this equation:

λ/nm	$10^{21} \sigma_0/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
270	8.91	1.41
280	4.92	1.70
290	2.18	2.00
300	0.62	2.58
310	0.129	3.23
320	0.0035	6.56
330	0.0004	7.38

Preferred Values at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$
270	2.37
275	1.99
280	1.57
285	1.17
290	0.836
295	0.559
300	0.356
305	0.211
310	0.139
315	0.0626
320	0.0312
325	0.0144
330	0.0066

Comments on Preferred Values

The preferred absorption cross-sections are the average values at room temperature from the data of Roberts and Fajer² and Rattigan *et al.*,¹ which are in reasonable agreement with the absorption spectrum reported by Calvert and Pitts³ and with the cross-sections reported by Maria *et al.*⁴ The results of Taylor *et al.*⁵ are consistently higher than the values of the other four studies,^{1–4} by as much as a factor of two in the region 290–330 nm. There is no apparent expla-

nation of this discrepancy.⁶ The effect of temperature on σ may be calculated from the expression reported by Rattigan *et al.*¹ and listed above.

The sole evidence on the primary processes comes from the study of Gray and Style,⁷ who concluded from the products of photolyses that reaction (1) occurred, but reported no quantum yield data. It has generally been assumed⁶ that the lack of structure in the absorption spectra of RONO_2 molecules indicates that the quantum yield for dissociation is unity. In the case of ethyl and propyl nitrates this conclusion is supported by experimental data on the rates of photolysis of the nitrates in sunlight (see comments on photolyses of other alkyl nitrates).

References

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- ²J. M. Roberts and R. W. Fajer, *Environ. Sci. Technol.* **23**, 945 (1989).
- ³J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966).
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- ⁶J. M. Roberts, *Atmos. Environ.* **24A**, 243 (1990).
- ⁷J. A. Gray and D. W. G. Style, *Trans. Faraday Soc.* **49**, 52 (1953).

 $\text{C}_2\text{H}_5\text{ONO}_2 + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{C}_2\text{H}_5\text{ONO}_2 + h\nu \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$ (1)	170.0	704
$\rightarrow \text{CH}_3\text{CHO} + \text{HONO}$ (2)	–91.2	
$\rightarrow \text{C}_2\text{H}_5\text{ONO} + \text{O}$ (3)		

Preferred Values

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
185	1710	260	4.1
188	1760	265	3.7
190	1710	270	3.2
195	1490	275	2.8
200	1140	280	2.3
205	738	285	1.8
210	400	290	1.3
215	195	295	0.85
220	91	300	0.54
225	45	305	0.32
230	24	310	0.18
235	13	315	0.091
240	8.0	320	0.045
245	5.6	325	0.023
250	4.7	330	0.011
255	4.3		

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.¹ The preferred absorption cross-sections are from the measurements of Turberg *et al.*² over the wavelength region 185–265 nm, and are the average of the measurements of Roberts and Fajer³ and of Turberg *et al.*² over the wavelength region 270–330 nm. These two studies^{2,3} are in good agreement over the wavelength region 270–315 nm, but show variations in the cross-sections of up to a factor of two over the region 320–330 nm. The data of Calvert and Pitts⁴ from 245 to 303 nm and of Kaya *et al.*⁵ from 185 to 225 nm yield somewhat higher cross-sections than the preferred data.

There are insufficient definitive data to recommend values of the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation are unity. Evidence for this conclusion comes from direct measurements of the rates of formation of NO_2 from the photolyses of ethyl nitrate in sunlight.^{6,7} These agreed well

with the calculated rates of photolysis based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1=1$ throughout the region 290–340 nm.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
²M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P.

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⁶W. T. Luke and R. R. Dickerson, *Geophys. Res. Lett.* **15**, 1181 (1988).
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$n\text{-C}_3\text{H}_7\text{ONO}_2 + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$n\text{-C}_3\text{H}_7\text{ONO}_2 + h\nu \rightarrow n\text{-C}_3\text{H}_7\text{O} + \text{NO}_2$ (1)	165.9	721
$\rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{HONO}$ (2)	−92.8	
$\rightarrow \text{C}_3\text{H}_7\text{ONO} + \text{O}$ (3)		

Preferred Values

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
185	1810	260	4.3
188	1830	265	4.0
190	1800	270	3.6
195	1600	275	3.0
200	1260	280	2.5
205	855	285	1.9
210	489	290	1.4
215	244	295	1.0
220	114	300	0.66
225	57	305	0.40
230	29	310	0.23
235	16	315	0.17
240	9.2	320	0.11
245	6.4	325	0.078
250	5.0	330	0.060
255	4.6		

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.¹ The preferred absorption cross-sections are from the measurements of Turberg *et al.*² over the wavelength region 185–265 nm and 315–330 nm, and are the average of the measurements of Roberts and Fajer³ and of

Turberg *et al.*² over the wavelength region 250–310 nm. These two studies^{2,3} are in agreement except at the longest wavelengths where the cross-sections become small, and consequently must involve large error limits.

There are no data on either the products of photodissociation or the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation will be unity. Evidence for this conclusion comes from direct measurements of the rate of formation of NO_2 from the photolyses of $n\text{-C}_3\text{H}_7\text{ONO}_2$ in sunlight.⁴ These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross-sections, solar irradiances and an assumed value of $\phi_1=1$ throughout the wavelength region 290–340 nm.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
²M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, *J. Photochem. Photobiol.* **A51**, 281 (1990).
³J. M. Roberts and R. W. Fajer, *Environ. Sci. Technol.* **23**, 945 (1989).
⁴W. T. Luke, R. R. Dickerson, and L. J. Nunermacker, *J. Geophys. Res.* **94**, 14905 (1989).

$i\text{-C}_3\text{H}_7\text{ONO}_2 + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$i\text{-C}_3\text{H}_7\text{ONO}_2 + h\nu \rightarrow \text{C}_3\text{H}_7\text{O} + \text{NO}_2$ (1)	171.7	697
$\rightarrow \text{CH}_3\text{COCH}_3 + \text{HONO}$ (2)	−105.9	
$\rightarrow i\text{-C}_3\text{H}_7\text{ONO} + \text{O}$ (3)		

Preferred Values

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
185	1790	260	4.9
188	1810	265	4.6
190	1790	270	4.1
195	1610	275	3.6
200	1260	280	2.9
205	867	285	2.3
210	498	290	1.7
215	247	295	1.2
220	117	300	0.81
225	58	305	0.52
230	31	310	0.32
235	18	315	0.19
240	11	320	0.11
245	7.0	325	0.061
250	5.7	330	0.037
255	5.2		

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.¹ The preferred absorption cross-sections are from the measurements of Turberg *et al.*² over the wavelength region 185–265 nm, and are the average of the measurements of Roberts and Fajer³ and of Turberg *et al.*² over the wavelength region 270–330 nm. These two studies^{2,3} are

in good agreement except at the longest wavelengths where the cross-sections become small, and consequently must involve large error limits.

There are no data on either the products of photodissociation or the quantum yields. It seems likely, however, since the absorption spectra of organic nitrates are structureless continua, that the total primary quantum yields for dissociation will be unity. Evidence from measurements of the rate of formation of NO₂ from the photolyses of alkyl nitrates in sunlight supports this conclusion.⁴ Thus the measured rates of formation of NO₂ matched well with calculated rates of photolyses of the RONO₂ based on measurements of the absorption cross-sections, solar irradiances and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290–330 nm.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
- ²M. P. Turberg, D. M. Giolando, C. Tilt, T. Soper, S. Mason, M. Davies, P. Klingensmith, and G. A. Takacs, *J. Photochem. Photobiol.* **A51**, 281 (1990).
- ³J. M. Roberts and R. W. Fajer, *Environ. Sci. Technol.* **23**, 945 (1989).
- ⁴W. T. Luke, R. R. Dickerson, and L. J. Nunnermacker, *J. Geophys. Res.* **94**, 14905 (1989).

CH₃O₂NO₂ + $h\nu$ → products

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ} \cdot \text{mol}^{-1}$ ^a	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ O ₂ NO ₂ + $h\nu$ → CH ₃ O ₂ + NO ₂ (1)	88	1359
→ CH ₃ O + NO ₃ (2)	126	949

^aOnly approximate values of ΔH_{298}° values are given since the heat of formation of CH₃O₂NO₂ is not well known.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–280	Bridier, Lesclaux, and Veyret, 1992 ¹	(a)

Comments

- (a) Flash photolysis of Cl₂ in the presence of CH₄-O₂-NO₂ mixtures at a total pressure of 760 Torr, with UV absorption to monitor the concentrations of CH₃O₂ radicals and CH₃O₂NO₂.

Preferred Values

Absorption cross-sections for $\text{CH}_3\text{O}_2\text{NO}_2$

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

In view of the thermal instability of $\text{CH}_3\text{O}_2\text{NO}_2$, the measurement of the cross-sections for $\text{CH}_3\text{O}_2\text{NO}_2$ presents considerable experimental problems. Nevertheless the recent measurements of Bridier *et al.*¹ are in moderately good

agreement with previous data²⁻⁴ at wavelengths <255 nm. At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall,² which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \geq 290$ nm), show large scatter. The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO_2NO_2 (this evaluation).

There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the $-\text{NO}_2$ chromophore (for example, HNO_3), it is likely that absorption around 270 nm is associated with an orbitally forbidden $n-\pi^*$ transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1 + \phi_2 = 1$.

References

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- ³O. Morel, R. Simonaitis, and J. Heicklen, Chem. Phys. Lett. **73**, 38 (1980).
- ⁴S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).

 $\text{CH}_3\text{CO}_3\text{NO}_2 + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CO}_3\text{NO}_2 + h\nu \rightarrow \text{CH}_3\text{CO}_3 + \text{NO}_2$ (1)	119	1005
$\rightarrow \text{CH}_3\text{CO}_2 + \text{NO}_3$ (2)	115	1040

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(\text{NO}_2)$	248	Mazely, Friedl, and Sander, 1995 ¹	(a)

Comments

- (a) Pulsed laser photolysis of PAN with LIF detection of NO_2 . The quantum yield for NO_2 formation was measured relative to that from the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(\text{NO}_2)$ from

HNO_3 of unity at this wavelength (see data sheet for HNO_3 photolysis, this evaluation). A value of $\phi(\text{NO}_2) = 0.83 \pm 0.09$ from the photolysis of PAN at 248 nm was obtained.

Preferred Values

Absorption cross-sections

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	317	255	7.9
205	237	260	5.7
210	165	265	4.04
215	115	270	2.79
220	77	275	1.82
225	55	280	1.14
230	39.9	285	0.716
235	29.0	290	0.414
240	20.9	295	0.221
245	15.9	300	0.105
250	10.9		

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Senum *et al.*,² which are in substantial

agreement with the previously recommended provisional data,³ and with the less direct measurements of Basco and Parmar.⁴

Measurements are still needed on the quantum yields and relative importance of the proposed primary processes as a function of wavelength. The NO_2 formation quantum yield measured by Mazely *et al.*¹ at 248 nm suggests that pathway (1) dominates. It is therefore suggested that $(\phi_1 + \phi_2) = 1$ for absorption in the UV region and that channel (1) forming CH_3CO_3 and NO_2 is the dominant photochemical primary process.

References

- ¹T. L. Mazely, R. R. Friedl, and S. P. Sander, *J. Phys. Chem.* **99**, 8162 (1995).
- ²G. I. Senum, Y.-N. Lee, and J. S. Gaffney, *J. Phys. Chem.* **88**, 1269 (1984).
- ³CODATA, Supplement I, 1982 (see references in Introduction).
- ⁴N. Basco and S. S. Parmar, *Int. J. Chem. Kinet.* **19**, 115 (1987).

4.5 Sulfur Species

$$\Delta H^\circ = -355 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.7 \times 10^{-10} \exp(-760/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 150\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

Because of its significance in the CO chemical laser, this reaction has been the subject of a number of studies.^{1–4} The values of k obtained at 298 K fall within a range of about 20%. The preferred value is the mean of these measure-

ments, all of which seem reliable. To obtain the preferred expression for k , the only available value of E/R is accepted³ and the pre-exponential factor is adjusted to fit the preferred value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

- ¹I. R. Slagle, R. E. Graham, J. R. Gilbert, and D. Gutman, *Chem. Phys. Lett.* **32**, 184 (1975).
- ²G. T. Bida, W. H. Breckenridge, and W. S. Kolln, *J. Chem. Phys.* **64**, 3296 (1976).
- ³H. V. Lilenfeld and R. J. Richardson, *J. Chem. Phys.* **67**, 3991 (1977).
- ⁴G. Hancock and I. W. M. Smith, *Trans. Faraday Soc.* **67**, 2586 (1971).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -133 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.3 \times 10^{-11} \exp(409/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 270\text{--}560 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The data of Nip *et al.*¹ are in excellent agreement, over the whole temperature range, with both of the studies of Lee *et al.*^{2,3} The preferred values of k at 298 K and (E/R) are obtained from a least-squares fit of the data from those three

studies and are identical to those in our previous evaluation, IUPAC, 1992.⁴ The product study of Cvetanovic *et al.*⁵ suggests that at high pressures (0.39–1.58 bar) the reaction proceeds almost entirely by addition followed by rapid fragmentation to $\text{CH}_3 + \text{CH}_3\text{SO}$.

References

- ¹W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, *J. Am. Chem. Soc.* **103**, 3526 (1981).
- ²J. H. Lee, R. B. Timmons, and L. J. Stief, *J. Chem. Phys.* **64**, 300 (1976).
- ³J. H. Lee, I. N. Tang, and R. B. Klemm, *J. Chem. Phys.* **72**, 1793 (1980).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, *J. Am. Chem. Soc.* **103**, 3530 (1981).

$$\Delta H^\circ(1) = -89 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -348 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -231 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Branching Ratios</i>			
$k_2/k=0.030\pm0.010$	296	Cooper and Herschberger, 1992 ¹	(a)
$k_3/k=0.085\pm0.010$	296		
<i>Reviews and Evaluations</i>			
$3.2\times10^{-11}\exp(-650/T)$	200–500	IUPAC, 1992 ²	(b)
$3.2\times10^{-11}\exp(-650/T)$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Pulsed laser photolysis at 355 nm of $\text{NO}_2\text{-CS}_2\text{-SF}_6$ mixtures. CO and OCS were monitored by an infra-red diode laser absorption system, and concentrations were calculated using literature values of absorption line-strengths. Total O(³P) produced was obtained from the NO_2 absorption coefficient and dissociation quantum yield.
- (b) See Comments on Preferred Values.
- (c) Based on the work of Westenberg and deHaas,⁴ Callear and Hedges,⁵ Slagle *et al.*,⁶ Wei and Timmons,⁷ Graham and Gutman,⁸ Callear and Smith,⁹ and Homann *et al.*¹⁰

Timmons,⁷ Graham and Gutman,⁸ Callear and Smith,⁹ and Homann *et al.*¹⁰ The preferred temperature coefficient is that of Wei and Timmons.⁷ There is evidence to suggest that the Arrhenius plot is not linear over a wide temperature range but over the range for which our preferred values apply the other studies of the temperature dependence of k ^{8,10} are in good agreement with the value of Wei and Timmons.⁷

The reported values for the branching ratios show considerable scatter. For k_3/k values of 0.085,¹ 0.015,¹² 0.30,¹³ 0.006,¹⁴ and 0.093⁶ have been reported and for k_2/k_1 values of 0.03,¹ 0.006,¹⁴ 0.014,¹¹ and 0.05–0.20.⁶ Channel 1 is clearly the major channel but at this stage our only recommendation is that $k_1/k \geq 0.90$.

References

- ¹W. F. Cooper and J. F. Herschberger, *J. Phys. Chem.* **96**, 5405 (1992).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **50**, 707 (1969).
- ⁵A. B. Callear and R. E. M. Hedges, *Trans. Faraday Soc.* **66**, 605 (1970).
- ⁶I. R. Slagle, J. R. Gilbert, and D. Gutman, *J. Chem. Phys.* **61**, 704 (1974).
- ⁷C. N. Wei and R. B. Timmons, *J. Chem. Phys.* **62**, 3240 (1975).
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- ⁹A. B. Callear and I. W. M. Smith, *Nature* **213**, 382 (1967).
- ¹⁰K. H. Homann, G. Krome, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.* **72**, 998 (1968).
- ¹¹D. S. Y. Hsu, W. M. Shaub, T. L. Burks, and M. C. Lin, *Chem. Phys. Lett.* **44**, 143 (1979).
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- ¹³R. D. Stuart, P. H. Dawson, and G. H. Kimball, *J. Appl. Phys.* **81**, 207 (1977).
- ¹⁴V. L. Talrose, N. I. Butkovskaya, M. N. Larichev, I. O. Leipintskii, I. I. Morozov, A. F. Dodonov, B. V. Kudrov, V. V. Zelenov, and V. V. Raznikov, *Adv. Mass Spectrom.* **7**, 693 (1978).

Preferred Values

$$k = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.2 \times 10^{-11} \exp(-650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}500 \text{ K.}$$

$$k_1/k \geq 0.90 \text{ over the temperature range } 200\text{--}500 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

There are several determinations of k at 298 K using a variety of techniques, which are in good agreement. The preferred value is an average of the values of Westenberg and deHaas,⁴ Callear and Hedges,⁵ Slagle *et al.*,⁶ Wei and

$$\Delta H^\circ = -167 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 5.5 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}570 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The data of Nip *et al.*¹ using a modulated photolysis technique are about a factor of 2 lower than the data from the earlier discharge flow-resonance fluorescence study of Lee *et al.*,² who reported no temperature dependence over the rather limited range 270–329 K. The cause of the discrepancy between the two measurements is not clear. The pre-

ferred value at 298 K is an average of the values from the two studies.^{1,2} The temperature dependence is that from Nip *et al.*¹ with the *A* factor adjusted to yield the preferred value at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.³

The product study of Cvetanovic *et al.*⁴ suggests that at high pressures, 0.39–1.58 bar, the reaction proceeds mainly by addition followed by rapid fragmentation to $\text{CH}_3\text{S} + \text{CH}_3\text{SO}$.

References

- ¹W. S. Nip, D. L. Singleton, and R. J. Cvetanovic, *J. Am. Chem. Soc.* **103**, 3526 (1981).
- ²J. H. Lee, I. N. Tang, and R. B. Klemm, *J. Chem. Phys.* **72**, 5718 (1980).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴R. J. Cvetanovic, D. L. Singleton, and R. S. Irwin, *J. Am. Chem. Soc.* **103**, 3530 (1981).

$$\Delta H^\circ(1) = -213 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -224 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.6 \times 10^{-11} \exp(-2150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}500 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

Comments on Preferred Values

The values obtained for *k* by a variety of techniques^{1–9} are in excellent agreement over a wide range of temperatures, and pressures (≤ 340 mbar). The available evidence suggests that at low temperatures the reaction proceeds by channel (1) and that channel (2) may only become significant at temperatures above 600 K.

Because of the possible enhancement of the rate by channel 2 at high temperatures, the recommended value of *E/R* is the mean of the values obtained in studies by Wei and Timmons⁷ and Klemm and Stief⁶ which were limited to tem-

peratures below 502 K. The value of *k* at 298 K is the mean of the values in Refs. 1–9, and the pre-exponential factor is adjusted to fit this value of *k* and the recommended value of *E/R*. The preferred values are identical to our previous evaluation, IUPAC, 1992.¹⁰

Approximate values of k_2/k_1 measured are: 10^{-3} at 298 K¹¹ and 10^{-2} at 500 K.³

References

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- ²K. Hoyerman, H. Gg. Wagner, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.* **71**, 603 (1967).
- ³K. H. Homann, G. Krome, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.* **72**, 998 (1968).
- ⁴A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **50**, 707 (1969).
- ⁵W. H. Breckenridge and T. A. Miller, *J. Chem. Phys.* **56**, 465 (1972).
- ⁶R. B. Klemm and L. J. Stief, *J. Chem. Phys.* **61**, 4900 (1974).
- ⁷C. N. Wei and R. B. Timmons, *J. Chem. Phys.* **62**, 3240 (1975).
- ⁸R. G. Manning, W. Braun, and M. J. Kurylo, *J. Chem. Phys.* **65**, 2609 (1976).
- ⁹N. Yoshida and S. Saito, *Bull. Chem. Soc. Jpn.* **51**, 1635 (1978).
- ¹⁰IUPAC, Supplement IV, 1992 (see references in Introduction).
- ¹¹S. Dondes and P. Safrany, reported in Ref. 1.

$$\Delta H^\circ = -348.1 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.4 \times 10^{-33} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 4.0 \times 10^{-32} \exp(-1000/T) [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 200–400 K.

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 300 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K over the temperature range } 200\text{--}400 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the data from Ref. 1, the high temperature dissociation results from Ref. 2, and the

theoretical analysis from Ref. 3. Because the reaction has an activation barrier, the Arrhenius form is chosen. The falloff transition to the high pressure range is expected at pressures not too far above 1 bar. However, no experimental data are available in this pressure region. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹R. Atkinson and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **10**, 1081 (1978).
- ²D. C. Astholz, G. Glänzer, and J. Troe, *J. Chem. Phys.* **70**, 2409 (1979).
- ³J. Troe, *Ann. Rev. Phys. Chem.* **29**, 223 (1978).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -23.0 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 230\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

All of the available measurements of k are in good agreement. Clyne and Whitefield¹ found a small decrease in k with increase in temperature, but until more definitive measurements of E/R are made a temperature independent k is recommended with error limits encompassing the existing mea-

sured values. The preferred value at 298 K is the mean of values from Refs. 1–6, and is identical to our previous evaluation, IUPAC, 1992.⁷

References

- ¹M. A. A. Clyne and P. D. Whitefield, *J. Chem. Soc. Faraday Trans. 2*, **75**, 1327 (1979).
- ²R. W. Fair and B. A. Thrush, *Trans. Faraday Soc.* **65**, 1557 (1969).
- ³R. W. Fair, A. Van Roodselaar, and O. P. Strausz, *Can. J. Chem.* **49**, 1659 (1971).
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- ⁵R. J. Donovan and D. J. Little, *Chem. Phys. Lett.* **13**, 488 (1972).
- ⁶M. A. A. Clyne and L. W. Townsend, *Int. J. Chem. Kinet. Symp.* **1**, 73 (1975).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -414.9 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only available experimental determination¹ is accepted as the preferred value. The method was direct, and in

the same study¹ a number of other rate coefficients for S atom reactions were measured giving results in good agreement with other techniques. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

¹M. A. A. Clyne and L. W. Townsend, *Int. J. Chem. Kinet. Symp.* **1**, 73 (1975).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -50.0 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 210\text{--}350 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

There is a significant scatter in the results which is difficult to attribute to any of the different techniques used. The preferred value at 298 K is a mean of the values of Nesbitt and Leone,¹ Clyne and Ono,² Clyne *et al.*,³ and Nava *et al.*⁴ The result of Lu *et al.*⁵ is not included because of the very

different conditions used. Both studies in which the temperature was varied^{4,5} find a temperature coefficient of zero which is accepted but with substantial error limits. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

References

¹D. J. Nesbitt and S. R. Leone, *J. Chem. Phys.* **72**, 1722 (1980).

²M. A. A. Clyne and Y. Ono, *Chem. Phys. Lett.* **94**, 597 (1983).

³M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, *J. Chem. Soc. Faraday Trans. 2*, **80**, 877 (1984).

⁴D. F. Nava, W. D. Brobst, and L. J. Stief, *J. Phys. Chem.* **89**, 4703 (1985).

⁵E. C. C. Lu, R. S. Iyer, and F. S. Rowland, *J. Phys. Chem.* **90**, 1988 (1986).

⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -117.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.3 \times 10^{-12} \exp(-80/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.08 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 80 \text{ K.}$$

Comments on Preferred Values

The data of Lin *et al.*,¹ Lafage *et al.*,² and Leu and Smith³ are in good agreement and show that *k* exhibits non-Arrhenius behavior over the temperature range 245–450 K

with the Arrhenius plot appearing to have a shallow minimum at approximately 270–300 K. Leu *et al.*³ and Lin *et al.*¹ find that the value of *k* appears to be independent of pressure and nature of the bath gas. These latter results throw some doubt upon the suggestion that the non-Arrhenius behavior is due to the occurrence of both addition and abstraction channels.

Despite the non-Arrhenius behavior of *k* over an extended temperature range, the preferred expression is given in Arrhenius form, which is satisfactory for the limited temperature range covered by our recommendation. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹Y.-L. Lin, N.-S. Wang, and Y.-P. Lee, *Int. J. Chem. Kinet.* **17**, 1201 (1985).
- ²C. Lafage, J.-F. Pauwels, M. Carlier, and P. Devolder, *J. Chem. Soc. Faraday Trans. 2*, **83**, 731 (1987).
- ³M.-T. Leu and R. H. Smith, *J. Phys. Chem.* **86**, 73 (1982).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -127 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 4.0 \times 10^{-31} (T/300)^{-3.3} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 300–400 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 300 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The most recent measurements of Ref. 1 gave smaller rate coefficients than earlier studies. We included these values in the averaging of data which lead to the preferred values. The error limits encompass most of the earlier data. The difference in F_c values between Refs. 2 and 3, which leads to different k_0 and k_∞ values, should be noted.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ over the temperature range 200–300 K.}$$

Comments on Preferred Values

See comment to k_0 . Falloff representation with $F_c = 0.45$ near 300 K. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹Y.-Y. Lee, W.-C. Kao, and Y.-P. Lee, *J. Phys. Chem.* **94**, 4535 (1990).
- ²IUPAC, Supplement III, 1989 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 4 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 4.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

$$k = 1.3 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 290–420 K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at 298 K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

In the earlier studies^{1,2} HO radical decays due to the reaction $\text{HO} + \text{SO}_2 + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$ were monitored in the presence of NO and O₂. The reaction sequence $\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3$ and $\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$ then regenerates HO. Modeling of the NO decay leads to the rate coefficient k . This method of determining k is less direct than the more recent measurements of Gleason *et al.*³ and Gleason and Howard⁴ where HOSO₂ radicals were monitored by

MS. We therefore accept the expression obtained by Gleason and Howard.⁴ The other results, though less precise, are in good agreement with the preferred expression. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

- ¹J. J. Margitan, *J. Phys. Chem.* **88**, 3314 (1984).
- ²D. Martin, J. L. Jourdain, and G. Le Bras, *J. Phys. Chem.* **90**, 4143 (1986).
- ³J. F. Gleason, A. Sinha, and C. J. Howard, *J. Phys. Chem.* **91**, 719 (1987).
- ⁴J. F. Gleason and C. J. Howard, *J. Phys. Chem.* **92**, 3414 (1988).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + OCS → products

No new data have been published since our last evaluation.

Preferred Values

$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.1 \times 10^{-13} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–500 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

Values of k measured by Cheng and Lee¹ and by Wahner and Ravishankara² are approximately a factor of 3 lower at 298 K than the earlier value of Leu and Smith.³ This may be due to the corrections applied by Leu and Smith³ to account for the presence of traces of H₂S in their system since in the absence of such corrections there is reasonable agreement between the studies. Cheng and Lee¹ took care to keep the H₂S level in their OCS very low and this, together with the confirmatory measurements of Wahner and Ravishankara,² leads us to recommend their values. These recommendations are compatible with the earlier upper limit given by Atkinson *et al.*⁴ but not with the higher value obtained by Kurylo⁵

which may be due to interfering secondary chemistry and/or excited state reactions. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

Kurylo and Laufer⁷ have suggested that the reaction proceeds through adduct formation, as found for the reaction of HO with CS₂, followed by decomposition of the adduct to yield mainly HS + CO₂. There is some support for this from the product study of Leu and Smith.³ However, in contrast to the HO + CS₂ reaction, there is no marked effect of O₂ on the rate. Furthermore, very little oxygen atom exchange between H¹⁸O and OCS is found⁸ which may suggest that any adduct formed is weakly bound and short lived.

References

- ¹B.-M. Cheng and Y.-P. Lee, *Int. J. Chem. Kinet.* **18**, 1303 (1986).
- ²A. Wahner and A. R. Ravishankara, *J. Geophys. Res.* **92**, 2189 (1987).
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- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁷M. J. Kurylo and A. H. Laufer, *J. Chem. Phys.* **70**, 2032 (1979).
- ⁸G. D. Greenblatt and C. J. Howard, *J. Phys. Chem.* **93**, 1035 (1989).

$$\Delta H^\circ(1) = -46.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -155 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{01} = 8 \times 10^{-31} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 270–300 K.

Reliability

$\Delta \log k_{01} = \pm 0.5$.

Comments on Preferred Values

Because of the low thermal stability of HOCS₂, experimental studies have to account for the redissociation of the adduct. After clarification of the mechanism, rate coefficients now can be specified. Combining the data for M=N₂ from Refs. 1 and 2 in a falloff representation indicates that the low

pressure limit is approached within 10% only at pressures below about 20 Torr. Because of the rather large scatter, the falloff data do not yet allow for the specification of a temperature dependence. The strong temperature dependence of

k_{01} for M=He derived in Ref. 3 ($E/R = -1610$ K) is apparently not consistent with the results from Refs. 1 and 2. It appears that reaction (2) is slow, with a rate coefficient of $k_2 < 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty 1} = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–300 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.5$ over the temperature range 250–300 K.

Comments on Preferred Values

The preferred rate coefficient $k_{\infty 1}$ is based on a falloff representation of the data from Refs. 1 and 2, with high-pressure data mostly from Ref. 1. The largest weight is given to the measurements near 250 K where decomposition of the adduct and the subsequent kinetics are of comparably minor influence in contrast to the room temperature experiments. A falloff curve with an estimated value of $F_c = 0.8$ was employed for extrapolation. Experiments at 1 bar total pressure are apparently still far below the high-pressure limit. An extensive discussion of the complicated mechanism is given in

Refs. 4–6 as well as in Refs. 1, 2, and 7. Rate expressions combining adduct formation, dissociation, and subsequent reactions with O_2 have been proposed which are not reproduced here. More experiments separating the individual steps are required. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁸

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$$\Delta H^\circ = 46.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 4.8 \times 10^{-14} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

$k_0 = 1.6 \times 10^{-6} \exp(-5160/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on a falloff representation from Refs. 1 and 2 of the data for the reverse process $\text{HO} + \text{CS}_2 + \text{M} \rightarrow \text{HOCS}_2 + \text{M}$ and the determination of the equilibrium constant from the same work. Largest weight is given to the data from Ref. 2 which extend to lower pressures. The data from Ref. 3 are not consistent with this evaluation (with differences of about a factor of 2). HOCS_2 formation and dissociation are characterized by an equilibrium constant of $K_c = 5.16 \times 10^{-25} \exp(5160/T) \text{ cm}^3 \text{ molecule}^{-1}$, as derived from the data of Ref. 2.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_{\infty} = 4.8 \times 10^5 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 1.6 \times 10^{13} \exp(-5160/T) \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the falloff extrapolation of the data for the reverse reaction and the equilibrium constant $K_c = 5.16 \times 10^{-25} \exp(5160/T) \text{ cm}^3 \text{ molecule}^{-1}$ from Ref. 2. Falloff curves are constructed with an estimated value of $F_c = 0.8$. The small pre-exponential factor of k_{∞} can be

explained theoretically as being due to the low bond energy of HOCS_2 . For discussion of the mechanism, see Refs. 1, 2, and 4–7. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁸

References

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 $\text{HOCS}_2 + \text{O}_2 \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(3.1 \pm 0.6) \times 10^{-14}$	298	Diau and Lee, 1991 ¹	(a)
<i>Reviews and Evaluations</i> 2.8×10^{-14}	240–300	IUPAC, 1992 ²	(b)
See comment	200–300	NASA, 1994 ³	(c)

Comments

- (a) Pulsed laser photolysis of H_2O_2 or HNO_3 at 248 nm in He- CS_2 mixtures. Pressure range 26–202 Torr. $[\text{HO}]$ monitored by LIF. Values of $k(\text{HOCS}_2 + \text{NO}) = (7.3 \pm 1.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HOCS}_2 + \text{NO}_2) = (4.2 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were also obtained in this work. The latter is the first measurement of the rate coefficient for the reaction with NO_2 . The value for the reaction with NO is in good agreement with that of Lovejoy *et al.*⁴
- (b) See Comments on Preferred Values.
- (c) Overall reaction between HO and CS_2 considered. Expression of Hynes *et al.*⁵ recommended (see Comments on Preferred Values).

Preferred Values

$$k = 3.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 240\text{--}350 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ over the temperature range } 240\text{--}350 \text{ K.}$$

Comments on Preferred Values

The reaction of HOCS_2 with O_2 is an intermediate step in the overall reaction of HO with CS_2 under atmospheric conditions. The HOCS_2 is formed by the addition of HO to CS_2 ; once formed it may undergo dissociation back to HO and CS_2 or react with O_2 . In previous evaluations, the $\text{HOCS}_2 + \text{O}_2$ reaction has been considered on the data sheet for $\text{HO} + \text{CS}_2$ because only in recent studies has the mechanism of the $\text{HO} + \text{CS}_2$ reaction been clarified and the individual reactions involved studied separately.

The three studies^{1,5,6} of the kinetics of this reaction are in good agreement. Basically the same technique was used in all, and similar results were obtained over a range of temperatures and bath gas pressures.

Over the small temperature range covered (251–348 K) the results of Hynes *et al.*⁵ could equally well be represented by either an Arrhenius expression with a small negative tem-

perature coefficient for k or by a temperature-independent rate coefficient. The results of Murrells *et al.*⁶ favor the latter. For the preferred values we assume the rate coefficient to be temperature independent over the temperature range studied and take a mean of the values of Hynes *et al.*⁵ and Murrells *et al.*⁶ which are in good agreement with the most recent study of Diau and Lee.¹

The main steps in the atmospheric oxidation of CS₂ initiated by HO are

Reaction of the HOCS₂ with O₂ predominates over reaction with NO or NO₂. Because of the nature and number of the steps involved, the overall rate of reaction of HO with CS₂ in the presence of O₂ is a complex function of both the total pressure and the pressure of O₂. Studies over a range of pressures and gas composition have established k_{eff} , the rate coefficient for HO removal in air. Hynes *et al.*⁵ have obtained the following expression of k_{eff} in air at 298 K:

$$k_{\text{eff}} = \frac{1.25 \times 10^{-16} \exp(4550/T)}{T + 1.81 \times 10^{-3} \exp(3400/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Studies by Murrells *et al.*⁶ and Becker *et al.*⁷ are in good agreement with this expression.

Despite the concordancy of such measurements of k_{eff} , significant differences are found between the values for k_{eff} based on measurements of HO removal and those based on relative rate studies of product formation. Becker *et al.*⁷ have carried out both types of study in the same laboratory, employing a number of variations of the relative rate method, but the results have only confirmed the difference. The studies based on product formation give values of k_{eff} up to 50% higher than the real-time studies based on HO removal. These differences point to the need for further studies of the chemistry of the later stages of the reaction involving O₂.

Recent work by Stickel *et al.*⁸ has provided some further insight into the mechanism of this complex reaction. Two

types of experiment were performed. In one, the reaction was initiated by pulsed laser photolysis and product concentrations monitored in real time by tunable diode laser absorption spectroscopy. In the other, continuous photolysis was used with FTIR product detection. Products observed were OCS, SO₂, CO, and CO₂. Both experiments gave concordant values for the yields of OCS and CO of (0.83±0.08) and (0.16±0.03), respectively. The yield of CO₂ was small (<0.01). The overall yield of SO₂ (1.15±0.10) was made up of two components, a "prompt" value of (0.84±0.20) resulting from SO₂ produced in a primary channel of the reaction and a longer time component due to production of SO₂ from reaction of O₂ with SO produced in another primary channel.

The results thus suggest two primary channels, the major one leading to OCS and SO₂ and a minor channel leading to CO and SO. There are a number of possible reaction channels leading directly to these species or to their precursors which subsequently produce them on a very short time scale. The results are compatible with most of the previous product studies but some discrepancies remain, the major one being the small yield of HO found (0.05) as compared with the value of 0.3 found by Becker *et al.*⁷

References

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HO + CH₃SH → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 9.9 \times 10^{-12} \exp(356/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}430 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The preferred values are based upon a least-squares analysis of the absolute rate coefficients of Atkinson *et al.*,¹ Wine *et al.*,^{2,3} and Hynes and Wine,⁴ which are in excellent agreement. The relative rate study of Barnes *et al.*⁵ shows that erroneous rate coefficient data are obtained in the presence of O₂ and NO, thus accounting for the much higher value of Cox and Sheppard.⁶ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁷

The study of Hynes and Wine⁴ shows that there is no

observable effect of O₂ on the measured rate coefficient and the rate coefficients at 298 K for the reactions of the HO radical with CD₃SH⁴ and CH₃SD³ are within 15% of that for HO + CH₃SH. These data indicate^{3,4} that the reaction proceeds via initial addition of HO to form the adduct CH₃S(OH)H.³

Tyndall and Ravishankara⁸ have determined, by monitoring the CH₃S radical by LIF, a CH₃S radical yield from the reaction of the HO radical with CH₃SH of 1.1 ± 0.2 . The reaction then proceeds by HO + CH₃SH → [CH₃S(OH)H] → H₂O + CH₃S.

References

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$$\Delta H^\circ(1) = -107.1 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.35 \times 10^{-11} \exp[-(285 \pm 135/T)]$ $(4.98 \pm 0.46) \times 10^{-12}$	297–368 297 ± 2	Abbatt, Fenter, and Anderson, 1992 ¹	(a)
<i>Branching Ratios</i>			
$k_1/k=0.84 \pm 0.15$	298	Stickel, Zhao, and Wine, 1993 ²	(b)
<i>Reviews and Evaluations</i>			
$k_1=9.6 \times 10^{-12} \exp(-234/T)$ $k_2=1.7 \times 10^{-42} [\text{O}_2]\exp(7810/T)/$ $[1+5.5 \times 10^{-31} [\text{O}_2]\exp(7460/T)]$	250–400 260–360	IUPAC, 1992 ³	(c)
$k_1=1.13 \times 10^{-11} \exp(-254/T)$ $k_2=1.68 \times 10^{-42} [\text{O}_2]\exp(7812/T)/$ $[1+5.53 \times 10^{-31} [\text{O}_2]\exp(7460/T)]$	248–397 ~ 260–360	Atkinson, 1994 ⁴	(d)
$k_1=1.2 \times 10^{-11} \exp(-260/T)$	248–397	NASA, 1994 ⁵	(e)

Comments

- (a) Discharge flow system with generation of HO radicals from the H + NO₂ reaction and detection by LIF. The total pressure was varied over the range 10.6–97.5 Torr of N₂. The measured rate coefficient was invariant of the total pressure over this range.
- (b) For DO radical reaction with CH₃SCH₃. HDO monitored by tunable diode laser absorption spectroscopy from the DO radical reactions with CH₃SCH₃, *n*-hexane and cyclohexane and the branching ratio obtained by assuming (as expected) a unit HDO yield from the DO radical reactions with *n*-hexane and cyclohexane. The branching ratio was independent of total pressure of N₂ (10–30 Torr), temperature (298–348 K) and replacement of 10 Torr total pressure of N₂ by 10 Torr total pressure of O₂. From the temporal profiles of the HDO signals, rate coefficients k_1 for the reaction of the DO radical with CH₃SCH₃ of $(5.4 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 10 Torr

N₂, $(5.8 \pm 1.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 30 Torr N₂, and $(4.4 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 348 K and 10 Torr N₂ were also obtained, in agreement with the rate coefficients for the HO radical reaction.

- (c) The rate coefficient for the H-atom abstraction pathway (1) is based on the studies of Wine *et al.*⁶ and Hynes *et al.*⁷ and the rate coefficient for the HO addition pathway (2) utilizes the data of Hynes *et al.*⁷
- (d) The rate coefficient for the abstraction process [channel (1)] was derived from the data of Wine *et al.*,⁶ Hynes *et al.*,⁷ Hsu *et al.*,⁸ and Abbatt *et al.*¹ The rate coefficient for the addition process [channel (2)] is that of Hynes *et al.*⁷
- (e) The rate coefficient for the abstraction process [channel (1)] was derived from the absolute rate coefficient data of Wine *et al.*,⁶ Hynes *et al.*,⁷ Hsu *et al.*,⁸ and Abbatt *et al.*¹

Preferred Values

$$k = 4.8 \times 10^{-12} + \{ (4.1 \times 10^{-31} [\text{O}_2]) / (1 + 4.1 \times 10^{-20} [\text{O}_2]) \} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

$$k_1 = 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

$$k_1 = 1.13 \times 10^{-11} \exp(-254/T) \text{ over the temperature range 250–400 K.}$$

$$k_2 = (4.1 \times 10^{-31} [\text{O}_2]) / (1 + 4.1 \times 10^{-20} [\text{O}_2]) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

$$k_2 = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K and 1 bar of air.}$$

$$k_2 = 1.7 \times 10^{-42} [\text{O}_2] \exp(7810/T) / \{ 1 + 5.5 \times 10^{-31} [\text{O}_2] \times \exp(7460/T) \} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 260–360 K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at 298 K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.3 \text{ at 298 K and 1 bar of air.}$$

Comments on Preferred Values

It is now recognized^{4,5,7,9} that this reaction proceeds via the two reaction steps (1) and (2). The $\text{CH}_3\text{S(OH)CH}_3$ adduct radical decomposes sufficiently rapidly that in the absence of O_2 only the rate coefficient k_1 is measured. In the presence of O_2 , the $\text{CH}_3\text{S(OH)CH}_3$ radical reacts by

Hence only in the presence of O_2 is the addition channel (2) observed, with the observed rate constant being dependent on the O_2 concentration (but, to at least a first approximation, not on the concentration of other third bodies such as N_2 , Ar or SF_6).⁷

The relative rate study of Wallington *et al.*¹⁰ shows that previous relative rate studies were complicated by secondary reactions, and that all relative rate coefficient studies carried out in the presence of NO are of dubious quality. The most recent absolute rate coefficients measured in the absence of

O_2 ^{1,2,6–12} agree that the earliest absolute rate coefficients of Atkinson *et al.*¹³ and Kurylo¹⁴ are erroneously high, and those of Mac Leod *et al.*¹⁵ were in error owing to heterogeneous wall reactions.¹¹ The preferred rate coefficient k_1 for the H-atom abstraction channel is based upon the studies of Wine *et al.*,⁶ Hynes *et al.*,⁷ Hsu *et al.*,⁸ and Abbatt *et al.*¹ and the rate coefficient for the HO radical addition channel (step 2) utilizes the data of Hynes *et al.*⁷ While the expression for k_2 is strictly valid only for 0.93 bar of air⁷ (in that the rate coefficients for HO addition to CH_3SCH_3 and the reverse dissociation step may be in the fall-off regime), this equation fits well the room temperature data obtained at pressures of air from 0.07 to 0.93 bar.

References

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HO + CH₃SSCH₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.2 \times 10^{-11} \exp[(410 \pm 210)/T]$	297–366	Abbatt, Fenter, and Anderson, 1992 ¹	(a)
$(2.39 \pm 0.30) \times 10^{-10}$	297		
$(2.4 \pm 0.9) \times 10^{-10}$	298	Dominé and Ravishankara, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
$6.0 \times 10^{-11} \exp(380/T)$	250–370	IUPAC, 1992 ³	(c)
$7.00 \times 10^{-11} \exp(350/T)$	249–367	Atkinson, 1994 ⁴	(d)
$6.0 \times 10^{-11} \exp(400/T)$	249–367	NASA, 1994 ⁵	(e)

Comments

- (a) Discharge flow system with generation of HO radicals from the $\text{H} + \text{NO}_2$ reaction and detection by LIF. The total pressure was 10.5–10.9 Torr of N_2 .
- (b) Discharge flow system with photoionization mass spectrometric detection of CH_3SOH and CH_3S product species. The temporal profiles of these product species yielded the cited rate coefficient. The CH_3S yield from the HO radical reaction with CH_3SSCH_3 was measured to be 0.28 ± 0.20 using a pulsed laser photolysis system with LIF detection of CH_3S . The photolysis of CH_3SSCH_3 at 266 nm was used to normalize the CH_3S signal, with the CH_3S yield from the photolysis of CH_3SSCH_3 being 1.8 ± 0.2 at 248 nm.⁶
- (c) The 298 K rate coefficient was the average of the absolute rate coefficients of Wine *et al.*⁷ and the relative rate coefficient of Cox and Sheppard.⁸
- (d) Obtained from a least-squares analysis of the absolute rate coefficients of Wine *et al.*⁷ and Abbatt *et al.*¹
- (e) Based on the absolute rate coefficients of Wine *et al.*⁷ and Abbatt *et al.*¹ and the room temperature relative rate coefficient of Cox and Sheppard.⁸

Preferred Values

$k = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 7.0 \times 10^{-11} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Wine *et al.*,⁷ Abbatt *et al.*,¹ and Dominé and Ravishankara² are in excellent agreement. The preferred values are derived from a least-squares analysis of the absolute rate coefficients of Wine *et al.*⁷ and Abbatt *et al.*¹ The magnitude of the rate coefficient and the negative temperature dependence indicates that the reaction proceeds by initial HO radical addition to the S atoms:

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 $\text{HO}_2 + \text{SO}_2 \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values

$k \leq 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The most recent determination¹ confirms that the reaction is slower than some earlier results² suggest and supports the even lower limit set by Graham *et al.*,³ which we take as the preferred value. The preferred value is identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, *Proc. R. Soc. London Ser. A* **368**, 463 (1979).
- ²W. A. Payne, L. J. Stief, and D. D. Davis, *J. Am. Chem. Soc.* **95**, 7614 (1973).
- ³R. A. Graham, A. M. Winer, R. Atkinson, and J. N. Pitts, Jr., *J. Phys. Chem.* **83**, 1563 (1979).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

 $\text{NO}_3 + \text{H}_2\text{S} \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values $k < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.*Comments on Preferred Values*

The preferred upper limit to the rate coefficient is based upon the absolute rate coefficient study of Dlugokencky and

Howard.¹ The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

¹E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **92**, 1188 (1988).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

NO₃ + CS₂ → products

No new data have been published since our last evaluation.

Preferred Values $k < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.*Comments on Preferred Values*

The preferred value is based upon the absolute study of Burrows *et al.*,¹ which is consistent with the slightly higher upper limit derived by Mac Leod *et al.*² The preferred value is identical to our previous evaluation, IUPAC, 1992.³

References

¹J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, *J. Phys. Chem.* **89**, 4848 (1985).

²H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.* **91**, 5338 (1986).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

NO₃ + OCS → products

No new data have been published since our last evaluation.

Preferred Values $k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.*Comments on Preferred Values*

The preferred value is based upon the sole study of Mac Leod *et al.*,¹ with a somewhat higher upper limit than reported. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

¹H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.* **91**, 5338 (1986).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

NO₃ + SO₂ → products

No new data have been published since our last evaluation.

Preferred Values $k < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.*Comments on Preferred Values*

The preferred value is based upon the relative rate study of Daubendiek and Calvert,¹ with a much higher upper limit.

This preferred upper limit to the 298 K rate coefficient is consistent with the upper limits determined in the absolute rate coefficient studies of Burrows *et al.*,² Wallington *et al.*,³ Dlugokencky and Howard,⁴ and Canosa-Mas *et al.*^{5,6} The preferred value is identical to our previous evaluation, IUPAC, 1992.⁷

References

- ¹R. L. Daubendiek and J. G. Calvert, *Environ. Lett.* **8**, 103 (1975).
- ²J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, *J. Phys. Chem.* **89**, 4848 (1985).
- ³T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 5393 (1986).
- ⁴E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **92**, 1188 (1988).
- ⁵C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **84**, 247 (1988).
- ⁶C. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **84**, 263 (1988).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

NO₃ + CH₃SH → products

No new data have been published since our last evaluation.

Preferred Values

$k = 9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–370 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred value at 298 K is the mean of the four studies carried out to date,^{1–4} which are in reasonably good agreement. Although a significant negative temperature dependence is indicated by the absolute rate coefficient study of Wallington *et al.*,¹ this is due to the rate coefficient measured at 350 K, since the rate coefficients at 280 and 298 K are identical.¹ The temperature independence determined by Dlugokencky and Howard³ is accepted. The experimental data indicate that there is no pressure dependence of the rate coefficient, at least over the range ~ 0.0013 –1 bar. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

The magnitude of the rate coefficient and the lack of temperature dependence of the rate coefficient shows that this reaction proceeds by initial addition, followed by decomposition of the adduct to yield CH₃S radicals.

This conclusion is consistent with the product studies carried out by Mac Leod *et al.*⁴ and Jensen *et al.*⁶ Jensen *et al.*⁶ identified CH₃SO₃H (methanesulfonic acid), SO₂, HCHO, CH₃ONO₂, CH₃SNO, and HNO₃ as products of the NO₃ radical reaction with CH₃SH at 295 ± 2 K and 740 ± 10 Torr of purified air.

References

- ¹T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 5393 (1986).
- ²M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **92**, 91 (1988).
- ³E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **92**, 1188 (1988).
- ⁴H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.* **91**, 5338 (1986).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁶N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.* **14**, 95 (1992).

NO₃ + CH₃SCH₃ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.9 \times 10^{-13} \exp(520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The literature absolute^{1–5} and relative⁶ rate coefficient studies are in reasonable agreement, although the data of

Wallington *et al.*^{3,4} are $\sim 20\%$ lower than the other data. The absolute rate coefficients measured by Tyndall *et al.*,¹ Dlugokencky and Howard,² and Daykin and Wine⁵ and the relative rate coefficient of Atkinson *et al.*⁶ have been fitted to an Arrhenius expression to obtain the preferred values. The experimental data show that the rate coefficient is independent of total pressure over the range ~ 0.0013 –1 bar. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁷

The magnitude of the rate constant and the negative temperature dependence indicates that this reaction proceeds by initial addition of the NO₃ radical to the S atom. The kinetic data of Daykin and Wine⁵ and Jensen *et al.*⁸ for CH₃SCH₃

and CD_3SCD_3 show that the rate determining step involves H- (or D-) atom abstraction, indicating that the reaction is $\text{NO}_3 + \text{CH}_3\text{SCH}_3 \rightleftharpoons [\text{CH}_3\text{S}(\text{ONO}_2)\text{CH}_3]^\ddagger \rightarrow \text{CH}_3\text{SCH}_2 + \text{HNO}_3$. This conclusion is consistent with the product studies of Jensen *et al.*^{8,9}

References

- ¹G. S. Tyndall, J. P. Burrows, W. Schneider, and G. K. Moortgat, *Chem. Phys. Lett.* **130**, 463 (1986).
²E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **92**, 1188 (1988).

- ³T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 5393 (1986).
⁴T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 4640 (1986).
⁵E. P. Daykin and P. H. Wine, *Int. J. Chem. Kinet.* **22**, 1083 (1990).
⁶R. Atkinson, J. N. Pitts, Jr., and S. M. Aschmann, *J. Phys. Chem.* **88**, 1584 (1984).
⁷IUPAC, Supplement IV, 1992 (see references in Introduction).
⁸N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.* **14**, 95 (1992).
⁹N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *Atmos. Environ.* **25A**, 1897 (1991).

$\text{NO}_3 + \text{CH}_3\text{SSCH}_3 \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values

$k = 7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 300–380 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The two absolute studies^{1,2} are in reasonable agreement with respect to the room temperature rate coefficient. While the reported rate coefficient from the relative rate study³ is an order of magnitude lower than the absolute data, the subsequent study of Atkinson *et al.*⁴ shows that this is due to complexities in the experimental system used. Accordingly, the preferred values are based upon the absolute rate studies, and then mainly on the data of Dlugokencky and Howard,² with the error limits being sufficient to encompass the data of Wallington *et al.*¹ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

As for the NO_3 radical reactions with CH_3SH and CH_3SCH_3 , the NO_3 radical reaction with CH_3SSCH_3 is expected to proceed by initial addition, followed by decomposition of the addition adduct, possibly to yield CH_3S radicals³

This initial reaction mechanism is consistent with the product study of Jensen *et al.*⁶

References

- ¹T. J. Wallington, R. Atkinson, A. M. Winer, and J. N. Pitts, Jr., *J. Phys. Chem.* **90**, 5393 (1986).
²E. J. Dlugokencky and C. J. Howard, *J. Phys. Chem.* **92**, 1188 (1988).
³H. Mac Leod, S. M. Aschmann, R. Atkinson, E. C. Tuazon, J. A. Sweetman, A. M. Winer, and J. N. Pitts, Jr., *J. Geophys. Res.* **91**, 5338 (1986).
⁴R. Atkinson, S. M. Aschmann, and J. N. Pitts, Jr., *J. Geophys. Res.* **93**, 7125 (1988).
⁵IUPAC, Supplement IV, 1992 (see references in Introduction).
⁶N. R. Jensen, J. Hjorth, C. Lohse, H. Skov, and G. Restelli, *J. Atmos. Chem.* **14**, 95 (1992).

$\text{HS} + \text{O}_2 \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values

$k \leq 4 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The reaction of HS with O_2 is so slow that attempts to measure the rate coefficient have yielded only upper limits^{1–5} that fall in the range 4×10^{-19} to $4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The preferred value is from the study of Stachnik and Molina,⁴ which gives the lowest value of the limit and seems reliable, and is identical to our previous evaluation, IUPAC, 1992.⁶

References

- ¹G. Black, *J. Chem. Phys.* **80**, 1103 (1984).
²R. R. Friedl, W. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **89**, 5505 (1985).
³G. Schoenle, M. M. Rahman, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **91**, 66 (1987).
⁴R. A. Stachnik and M. J. Molina, *J. Phys. Chem.* **91**, 4603 (1987).
⁵N. S. Wang, E. R. Lovejoy, and C. J. Howard, *J. Phys. Chem.* **91**, 5743 (1987).
⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -290 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 9.5 \times 10^{-12} \exp(-280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

The values of k at 298 K agree reasonably well. A mean of the values from the three available studies^{1–3} is taken as the preferred value. There is only one measurement of the temperature coefficient³ which is the basis of the recommended expression, with the pre-exponential factor chosen to fit the recommended value of k at 298 K.

Since there is only one determination of the temperature dependence of k , and in view of the complexity of the secondary chemistry in these systems, substantial error limits are assigned. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

¹R. R. Friedl, W. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **89**, 5505 (1985).

²G. Schoenle, M. M. Rahman, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **91**, 66 (1987); R. N. Schindler and Th. Benter, *Ber. Bunsenges. Phys. Chem.* **92**, 558 (1988).

³N. S. Wang and C. J. Howard, *J. Phys. Chem.* **94**, 8787 (1990).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -139 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 2.4 \times 10^{-31} (T/300)^{-2.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The pressure- and temperature-dependent measurements from Ref. 1 give a consistent picture for the association reaction and are preferred.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ over the range } 200\text{--}300 \text{ K.}$$

Comments on Preferred Values

The falloff extrapolation with $F_c = 0.6$ of Ref. 1 toward k_∞ appears less certain than that to k_0 . The preferred values are

identical to those in our previous evaluation, IUPAC, 1992.²

Intermediate Falloff Range

The given k_0 and k_∞ values from Ref. 1 were based on an assumed F_c value of 0.6.

References

¹G. Black, R. Patrick, L. E. Jusinski, and T. G. Slanger, *J. Chem. Phys.* **80**, 4065 (1984).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -90 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.6 \times 10^{-11} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

There is considerable scatter on the measured values of k^{1-6} with no obvious correlation with the conditions used or the technique. The presence of H atoms in the system is known to lead to complicating secondary chemistry, and some of the differences may be due to this, particularly where HS has been generated by photolysis of H_2S . In more recent studies^{5,6} care has been taken to eliminate or model such effects, but significant differences persist. The preferred value at 298 K is the mean of the results of Stachnik and

Molina⁵ and Wang *et al.*⁶ The temperature coefficient is that of Wang *et al.*⁶ and the pre-exponential factor is adjusted to fit the recommended value of k at 298 K. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁷

The absence of any pressure effect on the rate coefficient at pressures up to 0.96 bar^{1,5} indicates that any addition channel is unimportant up to these pressures.

References

- ¹G. Black, J. Chem. Phys. **80**, 1103 (1984).
- ²V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).
- ³R. R. Friedl, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **89**, 5505 (1985).
- ⁴G. Schoenle, M. M. Rahman, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **91**, 66 (1987), revised by R. N. Schindler and Th. Benter, Ber. Bunsenges. Phys. Chem. **92**, 558 (1988).
- ⁵R. A. Stachnik and M. J. Molina, J. Phys. Chem. **91**, 4603 (1987).
- ⁶N. S. Wang, E. R. Lovejoy, and C. J. Howard, J. Phys. Chem. **91**, 5743 (1987).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$$k \leq 2.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The reaction is slow and only an upper limit to k is available.¹

References

- ¹E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).

$$\Delta H^\circ(1) = 4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -94 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -361 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_3 = 2.1 \times 10^{-12} \exp[-(1120 \pm 320)/T]$	273–423	Lee, Lee, and Wang, 1994 ¹	(a)
$k_3 = (4.7 \pm 1.0) \times 10^{-14}$	298		
<i>Reviews and Evaluations</i>			
1.1×10^{-13}	298	IUPAC, 1992 ²	(b)
1.0×10^{-13}	298	NASA, 1994 ³	(b)

Comments

- (a) Discharge flow study. HSO generated by $\text{HS} + \text{O}_3$ reaction. Three sources of HS used ($\text{CH}_3\text{SH} + \text{O}$, $\text{H}_2\text{S} + \text{F}$, $\text{C}_2\text{H}_4 + \text{S}$) of which reaction of H with $\text{C}_2\text{H}_4 + \text{S}$ was the most satisfactory. $[\text{HSO}]$ monitored by LIF at 655 nm. $[\text{O}_3]$ determined by light absorption at 245 nm. Channel (1) regenerates HSO by $\text{HS} + \text{O}_3 \rightarrow \text{HSO} + \text{O}_2$; removal of HSO attributed to other channels.
- (b) Based on the studies of Wang and Howard⁴ and Friedl *et al.*⁵

Preferred Values

$$k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_3 = 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta \log k_1 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta \log k_3 = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

In the recent study by Lee *et al.*¹ the rate coefficient measured is that for HSO removal by all channels other than the

channel giving HS as a product (channel 1) which subsequently regenerates HSO by reaction with the O_3 present. However, in our recommendations the rate coefficients measured by Lee *et al.*¹ are assigned to channel 3 on the grounds that Friedl *et al.*⁵ could not detect HO production (channel 2); some further support comes from the work of Lovejoy *et al.*⁶ who found that HSO_2 is readily formed by the $\text{HSO} + \text{NO}_2$ reaction.

The value at 298 K of k_3 found by Lee *et al.*¹ is compatible within the assigned error limits with the overall rate coefficient and the value of k_1 ($7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) found by Wang and Howard.⁴

Although Lee *et al.*¹ have measured a temperature coefficient for k_3 , preferred values are only given at 298 K until further studies are made on the effects of temperature on all of the rate coefficients.

References

- ¹Y.-Y. Lee, Y.-P. Lee, and N. S. Wang, *J. Chem. Phys.* **100**, 387 (1994).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴N. S. Wang and C. J. Howard, *J. Phys. Chem.* **94**, 8787 (1990).
- ⁵R. R. Friedl, W. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **89**, 5505 (1985).
- ⁶E. R. Lovejoy, N. S. Wang, and C. J. Howard, *J. Phys. Chem.* **91**, 5749 (1987).

HSO + NO $\rightarrow$ products

No new data have been published since our last evaluation.

Preferred Values

$$k \leq 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only two available measurements of $k^{1,2}$ differ by at least a factor of 26. This is unlikely to be due to the higher pressures used in the Bulatov *et al.*¹ study but may arise from secondary chemistry in their HSO source, which employed relatively large H₂S concentrations. Provisionally, the

upper limit of Lovejoy *et al.*² is preferred. The preferred value is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khimi. Fiz. **4**, 1353 (1985).
- ²E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

HSO + NO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 9.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only two measurements of $k^{1,2}$ differ by at least a factor of 2. Lovejoy *et al.*² have suggested that the relatively high H₂S concentrations used by Bulatov *et al.*¹ in their work may lead to side reactions regenerating HSO. The value of Lovejoy *et al.*² is preferred, but wide error limits are as-

signed awaiting confirmatory studies. The preferred value is identical to our previous evaluation, IUPAC, 1992.³

HO₂ was observed as a product of the reaction by Lovejoy *et al.*,² which they suggest arises from the sequence HSO + NO₂ → HSO₂ + NO, HSO₂ + O₂ → HO₂ + SO₂.

References

- ¹V. P. Bulatov, M. Z. Kozliner, and O. M. Sarkisov, Khim. Fiz. **3**, 1300 (1984).
- ²E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

HSO₂ + O₂ → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.8 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

There is only one study of this reaction.¹ The method used to obtain the rate coefficient was indirect and this leads us to

suggest substantial error limits despite the high quality of the experimental work. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

- ¹E. R. Lovejoy, N. S. Wang, and C. J. Howard, J. Phys. Chem. **91**, 5749 (1987).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

SO + O₂ → SO₂ + O

$$\Delta H^\circ = -52.6 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 7.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.6 \times 10^{-13} \exp(-2280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–420 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

This reaction is very slow and measurement of k is subject to error due to impurities. For this reason, Black *et al.*^{1,2} favor their lower values of k at 298 K obtained in the tem-

perature dependence study.² The Goede and Schurath³ values are systematically lower than those from Ref. 2 by about 35%, but appear to have less experimental uncertainty at temperatures <300 K. The preferred value for k at 298 K and for E/R are mean values from Refs. 2 and 3. The A factor is adjusted to give the preferred value at 298 K. The preferred values differ slightly from those in our previous evaluation, IUPAC, 1992.⁴

¹G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).

²G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).

³H.-J. Goede and U. Schurath, Bull. Soc. Chim. Belg. **92**, 661 (1983).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -444.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 8.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.5 \times 10^{-12} \exp(-1170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–420 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 150 \text{ K}$.

Comments on Preferred Values

The data of Black *et al.*^{1,2} are in good agreement with earlier work.^{3,4} The preferred value at 298 K is the simple mean of measurements from Refs. 1–4. The temperature dependence from Black *et al.*² is accepted since this study cov-

ered a much larger temperature range than the earlier work,³ which nevertheless gave a value of E/R within the experimental error of the later study.² The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

¹G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).

²G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **93**, 598 (1982).

³C. J. Halstead and B. A. Thrush, Proc. R. Soc. London Ser. A **295**, 380 (1966).

⁴J. S. Robertshaw and I. W. M. Smith, Int. J. Chem. Kinet. **12**, 729 (1980).

⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -244.8 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 210–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The measurements of Brunning and Stief¹ are the only data available on the temperature dependence of k and indicate no measurable change in k over the range 210–363 K. This finding is the basis for our present recommendation for the temperature coefficient. All of the studies^{1–4} of k at 298 K are in good agreement and a mean of them all is taken for our recommended value. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

- ¹J. Brunning and L. J. Stief, *J. Chem. Phys.* **84**, 4371 (1986).
²G. Black, R. L. Sharpless, and T. G. Slanger, *Chem. Phys. Lett.* **90**, 55 (1982).
³M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, *Proc. R. Soc. London, Ser. A* **295**, 355 (1966).
⁴M. A. A. Clyne and A. J. MacRobert, *Int. J. Chem. Kinet.* **12**, 79 (1980).
⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

SO₃ + H₂O → products

No new data have been published since our last evaluation.

Preferred Values

$k < 6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Accepted as our preferred value, which is identical to our previous evaluation, IUPAC, 1992.³

References

Comments on Preferred Values

It was suspected that wall effects were significant in the flow system of Castleman *et al.*¹ and this was confirmed by Wang *et al.*² who were able to reduce wall effects by appropriate wall coatings. The upper limit of Wang *et al.*² is ac-

- ¹A. W. Castleman, Jr., R. E. Davis, H. R. Munkelwitz, I. N. Tang, and W. P. Wood, *Int. J. Chem. Kinet., Symp.* **1**, 629 (1975).
²X. Wang, Y. G. Yin, M. Suto, L. C. Lee, and H. E. O'Neal, *J. Chem. Phys.* **89**, 4853 (1988).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

SO₃ + NH₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(6.9 \pm 1.5) \times 10^{-11}$	298	Shen, Suto, and Lee, 1990 ¹	(a)
<i>Reviews and Evaluations</i>			
6.9×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Flow system with NH₃ in large excess. [SO₃] monitored by observation of SO₂ fluorescence in range 280–390 nm from photofragmentation of SO₃ by 147 nm radiation. He carrier gas (1–2 Torr).
 (b) Accepted the value of Shen *et al.*¹

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available data is from the work of Shen *et al.*¹ Their value of k is accepted with substantial error limits until confirmatory studies are made.

References

- ¹G. Shen, M. Suto, and L. C. Lee, *J. Geophys. Res.* **95**, 13981 (1990).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 6.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$$\Delta H^\circ(1) = -378 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -165 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.9 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.6 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The reaction of CS with O₂ is slow at 298 K and difficult to study. In the reported studies¹⁻⁷ the technique used by Black *et al.*⁴ seems the most suitable for avoiding difficulties associated with the slowness of the reaction and their value at 298 K is preferred.

The relative importance of the two possible reaction channels is in dispute. Evidence from the photochemical and explosion limit studies⁵⁻⁷ indicate comparable importance but in a more direct flow system study³ k_1 was found to be at least an order of magnitude less than k_2 . However, the absolute value of k_2 obtained in the fast flow study³ appears to be unacceptably high. We make no recommendation for the branching ratio.

The one available measurement of k at higher temperatures,³ when combined with the 298 K values leads to an Arrhenius expression with an extremely low pre-exponential factor. No recommendation is made for the temperature dependence. The preferred value is identical to our previous evaluation, IUPAC, 1992.⁸

References

- ¹ A. B. Callear and D. R. Dickson, reported in G. Hancock and I. W. M. Smith, *Trans. Faraday Soc.* **67**, 2586 (1971).
- ² W. H. Breckenridge, W. S. Kolln, and D. S. Moore, *Chem. Phys. Lett.* **32**, 290 (1975).
- ³ R. J. Richardson, *J. Phys. Chem.* **79**, 1153 (1975).
- ⁴ G. Black, L. E. Jusinski, and T. G. Slanger, *Chem. Phys. Lett.* **102**, 64 (1983).
- ⁵ W. P. Wood and J. Heicklen, *J. Phys. Chem.* **75**, 854 (1971).
- ⁶ W. P. Wood and J. Heicklen, *J. Photochem.* **2**, 173 (1973/74).
- ⁷ W. P. Wood and J. Heicklen, *J. Phys. Chem.* **75**, 861 (1971).
- ⁸ IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -556.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only available measurement of k is that of Black

*et al.*¹ Their value is accepted, but substantial error limits are assigned. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

- ¹ G. Black, L. E. Jusinski, and T. G. Slanger, *Chem. Phys. Lett.* **102**, 64 (1983).
- ² IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -357 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 7.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only available measurement of k is that of Black

*et al.*¹ Their value is accepted, but substantial error limits are assigned. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

¹G. Black, L. E. Jusinski, and T. G. Slanger, Chem. Phys. Lett. **102**, 64 (1983).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

CH₂SH + O₂ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(8.5 \pm 1.0) \times 10^{-12}$	298	Anastasi <i>et al.</i> , 1992 ¹	(a)
$(4.6 \pm 1.9) \times 10^{-12}$	298	Rahman <i>et al.</i> , 1992 ²	(b)
Reviews and Evaluations			
6.5×10^{-12}	298	NASA, 1994 ³	(c)

Comments

- (a) Pulse radiolysis of CH₃SH-O₂-SF₆ mixtures at 1 bar total pressure. CH₂SH and CH₃S radicals were generated by reactions of the radiolytically produced F atoms with CH₃SH. [CH₂SH] was monitored by UV absorption over range 220–380 nm.
- (b) Fast flow discharge study. CH₂SH radicals were generated by reaction of F atoms with CH₃SH. [CH₂SH] was monitored by mass spectrometry. Source reactions were simulated to check consumption of F atoms. Total pressure 3 mbar.
- (c) Mean of the rate coefficients of Anastasi *et al.*¹ and Rahman *et al.*²

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only two measurements of k differ by almost a factor of 2. The values of $k(\text{CH}_2\text{SH} + \text{NO}_2)$ measured in these two studies also differ, although the error limits are large enough to encompass the two results. Until further studies are carried out, a mean of the two values is recommended with substantial error limits.

References

¹C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

²M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

CH₂SH + O₃ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(3.5 \pm 1.2) \times 10^{-11}$	298	Rahman <i>et al.</i> , 1992 ¹	(a)
Reviews and Evaluations			
3.5×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Fast-flow discharge study. CH₂SH radicals were generated by the reaction of F atoms with CH₃SH, and monitored by MS. Source reactions were simulated to check consumption of F atoms. Total pressure 3 mbar.
- (b) Accepted the rate coefficient of Rahman *et al.*¹

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available determination of k^1 is accepted, but with substantial error limits until confirmatory studies can be made.

References

¹M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **96**, 783 (1992).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

CH₂SH + NO → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.5 \pm 0.2) \times 10^{-11}$	298	Anastasi <i>et al.</i> , 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
1.9×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis of CH₃SH-O₂-SF₆ mixtures at 1 bar total pressure. CH₂SH and CH₃S radicals were generated by reactions of the radiolytically produced F atoms with CH₃SH. [CH₂SH] was monitored by UV absorption over the wavelength range 220–380 nm.
- (b) Based on the rate coefficient of Anastasi *et al.*¹

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The only available determination of k^1 is accepted, but with substantial error limits until confirmatory studies are made.

References

¹C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, J. Phys. Chem. **96**, 696 (1992).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

CH₂SH + NO₂ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 1.0) \times 10^{-11}$	298	Anastasi <i>et al.</i> , 1992 ¹	(a)
$(6.9 \pm 4) \times 10^{-11}$	298	Rahman <i>et al.</i> , 1992 ²	(b)
<i>Reviews and Evaluations</i>			
5.2×10^{-11}	298	NASA, 1994 ³	(c)

Comments

- (a) Pulse radiolysis of $\text{CH}_3\text{SH}-\text{O}_2-\text{SF}_6$ mixtures at 1 bar total pressure. CH_2SH and CH_3S radicals were generated by reactions of the radiolytically produced F atoms with CH_3SH . $[\text{CH}_2\text{SH}]$ was monitored by UV absorption over the wavelength range 220–380 nm.
- (b) Fast flow discharge study. CH_2SH radicals were generated by the reaction of F atoms with CH_3SH and were monitored by MS. Source reactions were simulated to check consumption of F atoms. Total pressure 3 mbar.
- (c) Average of the rate coefficients of Anastasi *et al.*¹ and Rahman *et al.*²

Preferred Values

$$k = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only two measurements of $k^{1,2}$ differ substantially but because the error limits are large enough to encompass the two results it is difficult to know whether the difference is significant. In the same two studies the values obtained for $k(\text{CH}_2\text{SH} + \text{O}_2)$ differed to the same degree with much smaller error limits.

Until further studies are carried out, we recommend a weighted mean of the two values and substantial error limits.

References

¹C. Anastasi, M. Broomfield, O. J. Nielsen, and P. Pagsberg, *J. Phys. Chem.* **96**, 696 (1992).

²M. M. Rahman, E. Becker, U. Wille, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **96**, 783 (1992).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -49 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
$(1.81 \pm 0.28) \times 10^{-13}$ (80 Torr He)	216	Turnipseed, Barone, and Ravishankara, 1992 ¹	(a)
$(1.55 \pm 0.23) \times 10^{-13}$ (80 Torr He)	222		
$(1.05 \pm 0.20) \times 10^{-13}$ (80 Torr He)	233		
$(9.0 \pm 1.6) \times 10^{-14}$ (80 Torr He)	237		
$(8.62 \pm 0.84) \times 10^{-14}$ (80 Torr He)	242		
$(7.0 \pm 2.0) \times 10^{-14}$ (80 Torr He)	250		

Comments

- (a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The measured rate coefficients were observed to vary with the total pressure and the diluent gas. An upper limit to the rate coefficient for the reaction of the CH_3SOO radical with O_2 of $4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 258 K was also derived. The $\text{CH}_3\text{S}-\text{OO}$ bond energy was determined to be 49 kJ mol^{-1} at 298 K from measurements of the equilibrium constant over the temperature range 216–258 K, with $\Delta H_f(\text{CH}_3\text{SOO}) = 75.7 \pm 4.2 \text{ kJ mol}^{-1}$ at 298 K.¹

Preferred Values

See Table.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 216–250 K at 80 Torr He.

Comments on Preferred Values

The study of Turnipseed *et al.*¹ is the first to observe ad-

dition of O_2 to the CH_3S radical to form CH_3SOO [and not $\text{CH}_3\text{S}(\text{O})\text{O}$] because the reaction was observed to be reversible leading to equilibrium between CH_3S radicals, O_2 and CH_3SOO radicals.¹ Previous studies of the reaction of CH_3S radicals with O_2 at 298 K^{2–4} did not observe the equilibrium addition of O_2 to CH_3S radicals, and the rate coefficients measured^{2–5} correspond to upper limits to the rate coefficients for the reactions

and/or

The reaction of CH_3S radicals with O_2 to form the CH_3SOO radical, and the reverse reaction, result in $\sim 33\%$ of CH_3S radicals being present as the CH_3SOO adduct at 298 K and ground level,¹ with the $[\text{CH}_3\text{SOO}]/[\text{CH}_3\text{S}]$ ratio being strongly temperature dependent.¹

References

- ¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).
²R. J. Balla, H. H. Nelson, and J. R. McDonald, J. Chem. Phys. **109**, 101 (1986).
³G. Black and L. E. Jusinski, J. Chem. Soc. Faraday Trans. 2, **86**, 2143 (1986).
⁴G. S. Tyndall and A. R. Ravishankara, J. Phys. Chem. **93**, 2426 (1989).
⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 49 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Comments
$(1.99 \pm 0.74) \times 10^3$ (80 Torr He)	216	Turnipseed, Barone, and Ravishankara, 1992 ¹	(a)
$(3.20 \pm 0.80) \times 10^3$ (80 Torr He)	222		
$(9.1 \pm 2.6) \times 10^3$ (80 Torr He)	233		
$(1.00 \pm 0.12) \times 10^4$ (80 Torr He)	237		
$(1.28 \pm 0.12) \times 10^4$ (80 Torr He)	242		
$(2.4 \pm 0.4) \times 10^4$ (80 Torr He)	250		
$> 3.5 \times 10^4$ (80 Torr He)	258		

Comments

- (a) Pulsed laser photolysis system with LIF detection of CH_3S radicals. The formation and decay rate coefficients of CH_3SOO radicals were derived from the observed time-concentration profiles of CH_3S radicals in the presence of O_2 . The measured rate coefficients for the reactions $\text{CH}_3\text{S} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{SOO}$ were observed to vary with total pressure and with the diluent gas.

Comments on Preferred Values

The data presented by Turnipseed *et al.*¹ are the first reported for the dissociation of the CH_3SOO radical (see also the data sheet in this evaluation for the reverse reaction $\text{CH}_3\text{S} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{SOO} + \text{M}$). In the atmosphere, ~33% of CH_3S radicals will be present as the CH_3SOO adduct at 298 K and ground level,¹ with the $[\text{CH}_3\text{SOO}]/[\text{CH}_3\text{S}]$ ratio being strongly temperature dependent.¹

Preferred Values

See Table.

Reliability

$\Delta \log k = \pm 0.3$ at 80 Torr He over the temperature range 216–250 K.

References

- ¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **96**, 7502 (1992).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(5.7 \pm 1.4) \times 10^{-12}$	300	Dominé, Ravishankara, and Howard, 1992 ¹	(a)
$1.98 \times 10^{-12} \exp[(290 \pm 40)/T]$	295–359	Turnipseed, Barone, and Ravishankara, 1993 ²	(b)
5.16×10^{-12}	298		
<i>Reviews and Evaluations</i>			
5.4×10^{-12}	298	Tyndall and Ravishankara, 1991 ³	(c)
4.1×10^{-12}	298	IUPAC, 1992 ⁴	(d)
$2.0 \times 10^{-12} \exp(290/T)$	295–359	NASA, 1994 ⁵	(e)

Comments

- (a) Discharge flow study. CH_3S radicals were generated by reaction of Cl with CH_3SH or O with CH_3SSCH_3 . Photoionization mass spectrometry was used to monitor CH_3 , CH_3S , CH_3SO , CH_2S , CH_3SS , CH_3SSO , CH_2SO , C_2H_5 . $\text{C}_2\text{F}_3\text{Cl}$ was added to scavenge OH radicals and hence suppress OH radical-initiated chain reaction which regenerates CH_3S . Some curvature was observed on $[\text{CH}_3\text{S}]$ logarithmic decay plots in excess O_3 . The initial slope was used to calculate k .
- (b) Pulsed laser photolysis of $(\text{CH}_3)_2\text{S}-\text{O}_3$ (193 nm) or $(\text{CH}_3)_2\text{S}_2-\text{O}_3$ (248 nm) mixtures in bath gas of He , N_2 , or SF_6 . $[\text{CH}_3\text{S}]$ was monitored by LIF. Pressure range 20–200 Torr. No evidence for chain reaction was observed under the experimental conditions employed for the rate coefficient determinations.
- (c) Based on the work of Tyndall and Ravishankara⁶ and Dominé *et al.*¹ The corrections made in the work of Tyndall and Ravishankara⁶ to convert the measured value of k ($5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) to the quoted value ($4.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is now known to be unjustified.
- (d) Accepted the value of Tyndall and Ravishankara.⁶
- (e) Derived from the absolute rate coefficients of Tyndall and Ravishankara,⁶ Dominé *et al.*,¹ and Turnipseed *et al.*²

Preferred Values

$$k = 5.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.0 \times 10^{-12} \exp(290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 290\text{--}360 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

It is difficult to study this reaction because in some conditions rapid chain processes involving the reaction products occur to regenerate CH_3S radicals. This complication appears to be absent in the most recent study by Turnipseed *et al.*² Their value of k at 298 K is in good agreement with other studies in which care was taken to allow for this complication.^{1,6} The mean of the values from the two most recent studies^{1,2} is taken as our recommended value at 298 K.

There is only one study of the temperature dependence of k .² Its findings are accepted with substantial error limits and the pre-exponential factor is adjusted to yield the recommended value of k at 298 K.

References

- ¹F. Dominé, A. R. Ravishankara, and C. J. Howard, *J. Phys. Chem.* **96**, 2171 (1992).
- ²A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).
- ³G. S. Tyndall and A. R. Ravishankara, *Int. J. Chem. Kinet.* **23**, 483 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶G. S. Tyndall and A. R. Ravishankara, *J. Phys. Chem.* **93**, 4707 (1989).

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 3.2 \times 10^{-29} (T/300)^{-4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k_0 = 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 2.$$

Comments on Preferred Values

The preferred values are based on the data of Balla *et al.*¹ Although the falloff extrapolations in Ref. 1 were made with a theoretically improbable temperature coefficient of F_c , the low-pressure rate coefficients are much less influenced by this extrapolation than the high-pressure rate coefficients.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 250\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ over the temperature range } 250\text{--}450 \text{ K.}$$

Comments on Preferred Values

The negative temperature coefficient of k_{∞} reported in Ref. 1 is most probably due to an increasing underestimate of the falloff corrections with increasing temperature. We rec-

ommend the use of the extrapolated k_{∞} value at 298 K over large temperature ranges together with $F_c = \exp(-T/580)$. The preferred values of k_0 and k_{∞} are identical to those in our previous evaluation, IUPAC, 1992.³

Intermediate falloff range

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
$(1.69 \pm 0.04) \times 10^{-11}$	21	He	227	Turnipseed, Barone, and Ravishankara, 1993 ²	(a)
$(1.30 \pm 0.09) \times 10^{-11}$	19	He	242		
$(1.89 \pm 0.08) \times 10^{-11}$	19	He	242		

Comments

- (a) CH_3S radicals were generated by either photolysis of dimethyl sulfide at 193 nm or photolysis of dimethyl disulfide at 248 nm. The decay of CH_3S radical concentrations was followed by LIF. Experiments were performed under slow gas flow conditions.

References

- ¹R. J. Balla, H. H. Nelson, and J. R. McDonald, *Chem. Phys.* **109**, 101 (1986)
²A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -135 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-11} \exp[(320 \pm 40)/T]$	242–350	Turnipseed, Barone, and Ravishankara, 1993 ¹	(a)
6.3×10^{-11}	298		
<i>Reviews and Evaluations</i>			
5.5×10^{-11}	298	Tyndall and Ravishankara, 1991 ²	(b)
5.6×10^{-11}	298	IUPAC, 1992 ³	(b)
$2.1 \times 10^{-11} \exp(320/T)$	242–350	NASA, 1994 ⁴	(c)

Comments

- (a) Pulsed laser photolysis at 193 nm or 248 nm of $(\text{CH}_3)_2\text{S}-\text{NO}_2$ or $(\text{CH}_3)_2\text{S}_2-\text{NO}_2$ mixtures respectively in bath gas of He, N_2 or SF_6 . $[\text{CH}_3\text{S}]$ was monitored by LIF. No effect of pressure on k was observed (20–200 Torr of He).
 (b) Based on the results of Tyndall and Ravishankara⁵ and of Dominé *et al.*⁶
 (c) Based on the rate coefficients of Tyndall and Ravishankara⁵ and Turnipseed *et al.*¹

Preferred Values

$$k = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.0 \times 10^{-11} \exp(320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}350 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The recommended value at 298 K is the mean of the three most recent studies,^{1,5,6} which are in good agreement.

There are two studies^{1,7} of the temperature dependence of k , both giving a positive value of E/R but differing significantly in magnitude. Balla *et al.*⁷ obtain a very small value of E/R but obtain values of k nearly twice as large as those found in the other studies. It has been suggested⁵ that this could arise from secondary chemistry arising from the higher radical concentrations used in the work of Balla *et al.*⁷ The alternative value of Turnipseed *et al.*¹ is preferred but substantial error limits are recommended. The preexponential

factor in the expression for k is based on the value of E/R from Turnipseed *et al.*¹ and the recommended value of k at 298 K.

The lack of pressure dependence of k found in the recent¹ and earlier studies^{5,7} is consistent with the main pathway for the reaction proceeding directly to NO and CH₃SO rather than by addition to give CH₃SNO₂. Product studies^{5,8} are in agreement with this conclusion.

References

¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).

²G. S. Tyndall and A. R. Ravishankara, *Int. J. Chem. Kinet.* **23**, 483 (1991).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

⁵G. S. Tyndall and A. R. Ravishankara, *J. Phys. Chem.* **93**, 2426 (1989).

⁶F. Dominé, T. P. Murrells, and C. J. Howard, *J. Phys. Chem.* **94**, 5839 (1990).

⁷R. J. Balla, H. H. Nelson, and J. R. McDonald, *Chem. Phys.* **109**, 101 (1986).

⁸I. Barnes, V. Bastian, K. H. Becker, and H. Niki, *Chem. Phys. Lett.* **140**, 451 (1987).

CH₃SO + O₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(6.0 \pm 3.0) \times 10^{-13}$	300	Dominé, Ravishankara, and Howard, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
1×10^{-12}	298	IUPAC, 1992 ²	(b)
6.0×10^{-13}	298	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow study. CH₃S radicals were generated by reaction of Cl with CH₃SH. Photoionization mass spectrometry was used to monitor [CH₃SO] and [CH₃S] in CH₃S-O₃ system. CH₃SO radicals were produced by CH₃S + O₃ → CH₃SO + O₂ in 15% yield, independent of pressure in the range 0.7–2.2 Torr He. Reaction of O with C₂H₅SCH₃ was used as a source of CH₃SO to measure $k(\text{CH}_3\text{SO} + \text{O}_3)$. Value considered preliminary.
- (b) Accepted the value of Tyndall and Ravishankara.⁴
- (c) Based on the rate coefficient of Dominé *et al.*,¹ which is in agreement with the less direct study of Tyndall and Ravishankara.⁴

Preferred Values

$$k = 6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The measurement of k by Dominé *et al.*¹ is more direct than the previous study of Tyndall and Ravishankara⁴ in which the result was derived by a complex analysis of the reaction system. However, there are still a number of uncertainties in the study by Dominé *et al.*,¹ who consider their quoted value of k to be preliminary. This value¹ is accepted but substantial error limits are recommended.

References

¹F. Dominé, A. R. Ravishankara, and C. J. Howard, *J. Phys. Chem.* **96**, 2171 (1992).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴G. S. Tyndall and A. R. Ravishankara, *J. Phys. Chem.* **93**, 4707 (1989).

CH₃SO + NO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The measured values^{1–3} of k at 298 K agree within their error limits, some of which are substantial. The preferred value is that of Dominé *et al.*,³ which lies between the other two values both of which have much larger error limits. This rate coefficient is difficult to measure because of the lack of a clean primary source of CH₃SO radicals and the complexity of the secondary chemistry; substantial error limits are suggested. The preferred value is identical to that in our previous evaluation IUPAC, 1992.⁴

References

- ¹A. Mellouki, J. L. Jourdain, and G. Le Bras, *Chem. Phys. Lett.* **148**, 231 (1988).
²G. S. Tyndall and A. R. Ravishankara, *J. Phys. Chem.* **93**, 2426 (1989).
³F. Dominé, T. P. Murrells, and C. J. Howard, *J. Phys. Chem.* **94**, 5839 (1990).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

CH₃SOO + O₃ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$<8 \times 10^{-13}$	228	Turnipseed, Barone, and Ravishankara, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$<8.0 \times 10^{-13}$	227	NASA, 1994 ²	(b)

Comments

- (a) Pulsed laser photolysis of (CH₃)₂S-O₂-O₃ mixtures at 193 nm in bath gas of He, N₂, or SF₆. CH₃S + O₂ ⇌ CH₃SO₂ equilibrium established. [CH₃S] was monitored by LIF. [CH₃S] temporal profiles were simulated to obtain k . $k(\text{CH}_3\text{S} + \text{O}_3)$ obtained in the same study was used in the fitting procedure.
- (b) Based on the upper limit to the rate coefficient obtained by Turnipseed *et al.*¹

Comments on Preferred Values

The single study of the rate of this reaction¹ has provided only an upper limit to k at 228 K, which is accepted as the preferred value.

References

- ¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 5926 (1993).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k < 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 228 K.

CH₃SOO + NO → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.10 \pm 0.38) \times 10^{-11}$	227–255	Turnipseed, Barone, and Ravishankara, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
1.1×10^{-11}	227–256	NASA, 1994 ²	(b)

Comments

- (a) Pulsed laser photolysis of (CH₃)₂S₂-O₂-NO mixtures at 248 nm with He or SF₆ as the bath gas. Only a limited pressure range could be studied (16–21 Torr He, 19

Torr SF₆), but no effect of pressure on k was observed. [CH₃S] was monitored by LIF and the temporal profile simulated to obtain k .

- (b) Based on the sole study of Turnipseed *et al.*¹

Preferred Values

$k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 227–255 K.

Reliability

$\Delta \log k = \pm 0.3$ over the range 227–255 K.

Comments on Preferred Values

The value of k obtained in the only study of this reaction¹ is accepted but substantial error limits are assigned until confirmatory studies are made.

References

¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

CH₃SOO + NO₂ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.6) \times 10^{-11}$	227–246	Turnipseed, Barone, and Ravishankara, 1993 ¹	(a)
Reviews and Evaluations			
2.2×10^{-11}	227–246	NASA, 1994 ²	(b)

Comments

- (a) Pulsed laser photolysis of (CH₃)₂S₂-O₂-NO₂ mixtures at 248 nm in He (80–350 Torr) or SF₆ (65 Torr). [CH₃S] was monitored and the temporal profile simulated to obtain k . No variation of k with pressure or temperature was found.
- (b) Based on the sole study of Turnipseed *et al.*¹

Reliability

$\Delta \log k = \pm 0.3$ over the range 227–246 K.

Comments on Preferred Values

The value of k obtained in the only study¹ of this reaction is accepted but substantial error limits are assigned until confirmatory studies are made.

References

¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **97**, 5926 (1993).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 227–246 K.

CH₃SCH₂ + O₂ → CH₃SCH₂O₂**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.7 \pm 0.4) \times 10^{-12}$ (1 bar)	298	Wallington, Ellermann, and Nielsen, 1993 ¹	(a)
2.3×10^{-13} (1 Torr He)	298	Butkovskaya and Le Bras, 1994 ²	(b)
1.9×10^{-13} (1 Torr He)	298		

Comments

- (a) Pulse radiolysis of SF₆-CH₃SCH₃-O₂ mixtures. CH₃SCH₂ radicals were generated by reaction of F atoms with CH₃SCH₃, and monitored in absorption at 290 nm. The total pressure was approximately 1 bar.
- (b) Discharge flow study of the NO₃-CH₃SCH₃-Br₂-O₂ system at 1 Torr He. NO₃ radicals were produced by F + HNO₃ reaction added to CH₃SCH₃ to give

CH₃SCH₂. Subsequent addition of Br₂-O₂ mixtures allowed monitoring of competition between O₂ and Br₂ for CH₃SCH₂. Competition followed by mass spectrometric measurement of [CH₃SCH₂Br] profile. Modeling of profile gave $k = 2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Similar study of Cl-Cl₂-CH₃SCH₃-O₂ system in which CH₃SCH₂ was produced by Cl + CH₃SCH₃ reaction gave $k = 1.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$k = 5.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K and 1 bar.

Comments on Preferred Values

The preferred value of k is taken from the study of Wall-

ington *et al.*¹ Until confirmatory studies are made we confine our recommendations to 1 bar and assign substantial error limits.

References

¹T. J. Wallington, T. Ellermann, and O. J. Nielsen, *J. Phys. Chem.* **97**, 8442 (1993).

²N. I. Butkovskaya and G. Le Bras, *J. Phys. Chem.* **98**, 2582 (1994).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.9 \pm 0.6) \times 10^{-11}$	298	Wallington, Ellermann, and Nielsen, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
1.9×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis of $\text{CH}_3\text{SCH}_3\text{-SF}_6\text{-O}_2\text{-NO}$ mixtures. Generation of $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals occurred by $\text{F} + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{HF}$, followed by $\text{CH}_3\text{SCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{O}_2$. $[\text{NO}_2]$ was monitored at 400 nm. Yield of NO_2 compared with yield of F atoms suggest that 80% of the reaction leads to NO_2 production.
- (b) Based on the rate coefficient of Wallington *et al.*¹

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

Comments on Preferred Values

The preferred value of k is taken from the only study of this reaction.¹ Substantial error limits are assigned until confirmatory studies are made.

References

¹T. J. Wallington, T. Ellermann, and O. J. Nielsen, *J. Phys. Chem.* **97**, 8442 (1993).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 7.9 \times 10^{-12}$	298	Wallington, Ellermann, and Nielsen, 1993 ¹	(a,b)

Comments

- (a) k is defined by $-\text{d}[\text{CH}_3\text{SCH}_2\text{O}_2]/\text{dt} = 2k[\text{CH}_3\text{SCH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CH}_3\text{SCH}_3\text{-O}_2\text{-SF}_6$ mixtures with monitoring of $\text{CH}_3\text{SCH}_2\text{O}_2$ radical concentrations

by UV absorption with $\sigma_{250} = (4.3 \pm 0.7) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The observed value of $k_{\text{obs}} = (7.9 \pm 1.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k because of the possibility of secondary reactions giving rise to an increasing decay rate of $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals (see Comments on Preferred Values).

Preferred Values

$$k \leq 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

We have recommended an upper limit to the overall rate coefficient at 298 K, as determined by Wallington *et al.*¹ There is no information as yet on the products of the self-reactions of the $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals, although it has been

suggested that the alkoxy radical, $\text{CH}_3\text{SCH}_2\text{O}$, could react as follows: $\text{CH}_3\text{SCH}_2\text{O} \rightarrow \text{CH}_3\text{S} + \text{HCHO}$ and that the CH_3S radicals could react with the $\text{CH}_3\text{SCH}_2\text{O}_2$ radicals, leading to an enhanced decay rate of these radicals.

References

- ¹T. J. Wallington, T. Ellermann, and O. J. Nielsen, *J. Phys. Chem.* **97**, 8442 (1993).

 $\text{CH}_3\text{SS} + \text{O}_3 \rightarrow \text{products}$ **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(4.6 \pm 1.1) \times 10^{-13}$	300	Dominé, Ravishankara, and Howard, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
4.6×10^{-13}	298	NASA, 1994 ²	(b)

Comments

- (a) Discharge-flow study. Photoionization mass spectrometry was used to monitor $[\text{CH}_3]$, $[\text{CH}_3\text{S}]$, $[\text{CH}_3\text{SO}]$, $[\text{CH}_2\text{S}]$, $[\text{CH}_3\text{SS}]$, $[\text{CH}_3\text{SSO}]$, $[\text{CH}_2\text{SO}]$, and $[\text{C}_2\text{H}_5]$ produced in reactions of O_3 with CH_3S and CH_3SO . CH_3S radicals were generated by $\text{Cl} + \text{CH}_3\text{SH}$ or $\text{O} + (\text{CH}_3)_2\text{S}_2$ reactions. CH_3SS was observed to be formed in the CH_3S source and thought to be due to the $\text{CH}_3\text{S} + \text{S}_2$ reaction on walls. $[\text{CH}_3\text{SS}]$ was monitored in the presence of excess O_3 to obtain k .
- (b) Accepted the value of Dominé *et al.*¹

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only available measurement of k^1 is accepted but substantial error limits are assigned until confirmatory studies are made.

References

- ¹F. Dominé, A. R. Ravishankara, and C. J. Howard, *J. Phys. Chem.* **96**, 2171 (1992).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$$k = 4.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

 $\text{CH}_3\text{SS} + \text{NO}_2 \rightarrow \text{products}$ **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.8 \pm 0.3) \times 10^{-11}$	297	Dominé, Murrells, and Howard, 1990 ¹	(a)
<i>Reviews and Evaluations</i>			
1.8×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Fast-flow discharge study. CH_3SS radicals were produced as a by-product of CH_3S radical production. CH_3S radicals were mainly produced by $\text{Cl} + \text{CH}_3\text{SH}$ reaction but other sources of CH_3S , e.g., $\text{O} + (\text{CH}_3)_2\text{S}_2$ reaction, also produce CH_3SS . $[\text{CH}_3\text{SS}]$ was monitored by photoionization mass spectrometry in excess NO_2 .
- (b) Accepted the value of Dominé *et al.*¹

Preferred Values

$$k = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The study of Dominé *et al.*¹ has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until confirmatory studies are made.

References

¹F. Dominé, T. P. Murrells, and C. J. Howard, *J. Phys. Chem.* **94**, 5839 (1990).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

 $\text{CH}_3\text{SSO} + \text{NO}_2 \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(4.5 \pm 1.2) \times 10^{-12}$	297	Dominé, Murrells, and Howard, 1990 ¹	(a)
<i>Reviews and Evaluations</i>			
4.5×10^{-12}	298	NASA, 1994 ²	(b)

Comments

- (a) Fast-flow discharge system with photoionization mass spectrometric detection of products. CH_3SSO radicals were produced by $\text{CH}_3\text{SS} + \text{NO}_2 \rightarrow \text{CH}_3\text{SSO} + \text{NO}$. Mass 47 peak was monitored in excess NO_2 and the contributions from CH_3S and CH_3SSO (from $\text{CH}_3\text{SSO} + h\nu \rightarrow \text{CH}_3\text{S}^+ + \text{e}^- + \text{SO}$) separated by modeling using data from other mass peaks.
- (b) Accepted the value of Dominé *et al.*¹

Preferred Values

$$k = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The study of Dominé *et al.*¹ has provided the only available value for the rate coefficient of this reaction. This value is accepted but with substantial error limits until confirmatory studies are made.

References

¹F. Dominé, T. P. Murrells, and C. J. Howard, *J. Phys. Chem.* **94**, 5839 (1990).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

 $\text{O}_3 + \text{CH}_3\text{SCH}_3 \rightarrow \text{products}$

No new data have been published since our last evaluation.

Preferred Values

$$k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

References

¹R. I. Martinez and J. T. Herron, *Int. J. Chem. Kinet.* **10**, 433 (1978).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Comments on Preferred Values

The preferred value is based upon the sole study of Martinez and Herron,¹ and is identical to our previous evaluation, IUPAC, 1992.²

OCS + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OCS + $h\nu \rightarrow \text{CO} + \text{S}(^3\text{P})$ (1)	308	388
$\rightarrow \text{CO} + \text{S}(^1\text{D})$ (2)	419	286

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength region	Reference	Comments
$\phi_1/\phi_2 = 0.055$	222	Nan, Burak, and Houston, 1993 ¹	(a)

Comments

- (a) Pulsed laser photolysis of OCS at 222 nm. Doppler profile of $\text{S}(^3\text{P}_2)$ was monitored by LIF at 147 nm. CO used to quench $\text{S}(^1\text{D})$. $\text{S}(^3\text{P}_2)$ yield of 0.050 relative to $\text{S}(^1\text{D})$ obtained. $\text{S}(^3\text{P}_1)$ and $\text{S}(^3\text{P}_0)$ were not monitored but if they were present in statistical amounts then total triplet yield = 0.055. This work supersedes the earlier study² where a yield of 0.02 was obtained.

Preferred Values

λ/nm	$10^{21} \sigma/\text{cm}^2$		ϕ	ϕ_2
	295 K	225 K		
300	0.0009			
295	0.0023	0.0013		
290	0.0077	0.0035		
285	0.0218	0.0084		
280	0.0543	0.0206		
275	0.1504	0.0607		
270	0.376	0.156		
265	0.960	0.423		
260	2.52	1.16	0.8	0.6
255	6.64	3.46	0.8	0.6
250	16.5	9.79	0.8	0.6
245	38.2	25.1	0.8	0.6
240	81.3	59.3	0.8	0.6
235	153.6	123.7	0.8	0.6
230	243.8	211.8	0.8	0.6
225	310.4	283.0	0.8	0.6
220	304.8	287.5	0.8	0.6
215	241.6	236.2	0.8	0.6
210	150.8	151.6		
205	82.0	82.5		
200	39.3	39.3		
195	20.2	18.9		
190	39.7	26.8		
185	190.3	135.7		

Comments on Preferred Values

There is good agreement among all of the recent cross-section measurements for $\lambda < 280 \text{ nm}$.²⁻⁴ At $\lambda > 280 \text{ nm}$ the data of Molina *et al.*² appear to be the most accurate. The higher values in Ref. 1 may be due to the presence of CS_2 or other unidentified trace contaminants or alternatively dimerization of OCS in the pressurized cell employed. The preferred values are 5 nm averages based on the Molina *et al.* data.² The results of Locker *et al.*,³ whose results were presented in graphical form, agree with these values.

The preferred overall quantum yield of 0.80 is an average of the results of Rudolf and Inn⁴ and the earlier work of Sidhu *et al.*⁵ which gave slightly higher values ($\phi_1 + \phi_2 = 0.9$), with $\phi_2/\phi \geq 0.72$. Breckenridge and Taube⁶ obtained $\phi_2/\phi = 0.74 \pm 0.04$ and their results suggest strongly that $\text{S}(^3\text{P})$ production accounts for the balance. They did not, however, determine absolute values for the quantum yields. There is currently no evidence for fluorescence from OCS. This is difficult to reconcile with a photodissociation yield significantly less than unity.

The study of Nan *et al.*¹ of the triplet channel yield indicates that it is small but we make no recommendation for ϕ_1 at this stage.

References

- ¹G. Nan, I. Burak, and P. L. Houston, Chem. Phys. Lett. **209**, 383 (1993).
- ²L. T. Molina, J. J. Lamb, and M. J. Molina, Geophys. Res. Lett. **8**, 1008 (1981).
- ³J. R. Locker, J. B. Burkholder, E. J. Bair, and H. A. Webster, J. Phys. Chem. **87**, 1864 (1983).
- ⁴R. N. Rudolf and E. C. Y. Inn, J. Geophys. Res. **86**, 9891 (1981).
- ⁵K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, J. Am. Chem. Soc. **88**, 2412 (1966).
- ⁶W. H. Breckenridge and H. Taube, J. Chem. Phys. **53**, 1713 (1970).

CS₂ + $h\nu$ → products**Primary photochemical processes**

Reactions	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CS ₂ + $h\nu$ → CS ₂ [*] (1)		>277
→ CS + S(³ P) (2)	432	281
→ CS + S(¹ D) (3)	543	223

Absorption cross-section data

Wavelength range/nm	Reference	Comments
271–374	Hearn and Joens, 1991 ¹	(a)

Comments

- (a) Spectral resolution 0.06 nm. Deuterium lamp was used as source but results checked using atomic lines (narrow band width) from argon-mercury lamp and by measurements at 260 nm on the well characterized benzene spectrum. Results presented in graphical form in paper but authors provide data points at 0.02 nm intervals on request.

Preferred Values

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
295	10	335	6.0
305	35	345	3.0
315	62	355	0.8
325	37		

Quantum Yields

$\phi_{\text{OCS}} = 1.2 \times 10^{-2}$ for 290–360 nm region in 1 bar air.

Comments on Preferred Values

The recent measurements of Hearn and Joens¹ on the absorption spectrum were carried out using similar conditions of temperature, resolution, pathlength, and gas pressure to those used by Wu and Judge.² In both cases the resolution used (0.06 nm) is higher than in the study of Wine *et al.*³ (0.4 nm). All of the studies^{1–4} confirm the banded nature of the spectrum (280–370 nm). The values of the cross-section obtained by Hearn and Joens¹ are some 10–15% higher than

those obtained by Wu and Judge² and there are minor differences in the band structures observed. When the data of Hearn and Joens are averaged over 10 nm intervals the mean absorption coefficients are in reasonable agreement with our previous recommendations which were based on unpublished data from the AERE Laboratories, Harwell. The preferred values given are mean values of the Harwell results and those of Hearn and Joens.¹

The recommended quantum yield for OCS production from the photoinitiated oxidation of CS₂ in air is that reported by Jones *et al.*,⁴ which is in good agreement with the value estimated by Wine *et al.*³ from the earlier data of Wood and Heicklen⁵ (i.e., $\phi_{\text{OCS}} = 0.01\text{--}0.015$). The recommended value might best be considered an upper limit since the observed slow oxidation of the CS₂ could have been due, at least in part, to other mechanisms.

Since there is insufficient energy to dissociate CS₂ at $\lambda < 281$ nm the photochemical reaction yielding OCS and SO₂, studied by Jones *et al.*⁴ in the range 290–360 nm and others,^{5,6} must arise from reactions involving excited CS₂ molecules.

References

- ¹C. H. Hearn and J. A. Joens, *J. Quant. Spectrosc. Radiat. Trans.* **45**, 69 (1991).
- ²C. Y. R. Wu and D. L. Judge, *Geophys. Res. Lett.* **8**, 769 (1981).
- ³P. H. Wine, W. L. Chameides, and A. R. Ravishankara, *Geophys. Res. Lett.* **8**, 543 (1981).
- ⁴B. M. R. Jones, R. A. Cox, and S. A. Penkett, *J. Atmos. Chem.* **1**, 65 (1983).
- ⁵W. P. Wood and J. Heicklen, *J. Phys. Chem.* **75**, 854 (1971).
- ⁶M. DeSorgo, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.* **43**, 1886 (1965).

CH₃SSCH₃ + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ SSCH ₃ → CH ₃ SS + CH ₃ (1)	238	502
→ 2CH ₃ S (2)	274	437

No new data have been published since our last evaluation.

Preferred Values

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
201	1053.0	280	49.8
205	850.0	285	36.0
210	630.0	290	25.15
215	312.0	295	17.06
220	138.7	300	11.27
225	85.6	305	7.24
228 (min)	82.3	310	4.57
230	84.2	315	2.85
235	96.0	320	1.79
240	110.0	325	1.09
245	120.7	330	0.67
250	125.4	335	0.38
251 (max)	125.6	340	0.22
255	123.3	345	0.14
260	113.9	350	0.07
265	99.3	355	0.04
270	82.7	360	<0.01
275	65.4		

Comments on Preferred Values

The preferred values for σ are those of Hearn *et al.*¹ which agree well with the earlier values cited in Calvert and Pitts.² Sheraton and Murray's spectrum³ agrees qualitatively with the other studies but the reported absorption coefficients are significantly lower.

The thermochemistry suggests that formation of CH₃S is the sole dissociation process at wavelengths of importance to atmospheric photochemistry. Balla and Heicklen⁴ report a quantum yield for CH₃S formation of 2.04 ± 0.06 for light absorption in the range 280–300 nm, but as yet there are no definitive measurements of the quantum yields.

References

- ¹C. H. Hearn, E. Turcu, and J. A. Joens, *Atmos. Environ.* **24A**, 1939 (1990).
- ²J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966), p. 490.
- ³D. F. Sheraton and F. E. Murray, *Can J. Chem.* **59**, 2750 (1981).
- ⁴R. J. Balla and J. Heicklen, *Can. J. Chem.* **62**, 162 (1984).

CH₃SNO + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ SNO → CH ₃ S + NO (1)	-	-
→ CH ₃ + SNO (2)	-	-

No new data have been published since our last evaluation.

Preferred Values

λ/nm	$10^{19} \sigma/\text{cm}^2$	λ/nm	$10^{19} \sigma/\text{cm}^2$
190	5	310	14.9
195	104	320	18.5
200 (max)	162	330	21.3
205	91	335 (max)	21.6
210 (min)	81	340	21.5
215	98	350	19.6
218 (max)	104	360	16.5
220	96	370	12.7
225	73	380	9.6
230	40	390	6.7
240	16	400	4.5
250	3.5	410	2.9
260	1.7	420	2.0
264 (min)	1.5	430	1.3
270	1.8		
280	2.7	510	0.24
290	5.2	545	0.58
300	9.3		

Comments on Preferred Values

The spectrum of CH_3SNO consists of a weak transition in the 500–600 nm region showing some vibrational fine structure and stronger continuous bands at shorter wavelengths.¹ The $\text{CH}_3\text{S-NO}$ dissociation energy has been estimated² to be

approximately 110 kJ mol^{-1} but because more reliable data are not available we do not give wavelength limits for the dissociation channels tabulated.

The only available data for σ values in the gas phase appear to be those of Niki *et al.*³ who have published their results mainly in the form of graphs covering the range 190–430 nm. Their published spectrum shows no fine structure but appears to consist of overlapping continua with three maxima at approximately 200, 218, and 335 nm. The preferred values of σ in the range 190–430 nm are taken from the graphs of Niki *et al.*³ and cannot be considered to be very precise. The two values at 510 and 545 nm are numerical values quoted in the same study.

There have been no quantum yield measurements. By analogy with CH_3ONO photolysis the primary products are expected to be CH_3S and NO . This is supported by the work of McCoustra and Pfab¹ who studied the photodissociation of CH_3SNO in a molecular beam and by the study of Niki *et al.*³ who found CH_3SSCH_3 and NO to be the only major products from CH_3SNO photolysis at 300–400 nm.

References

- ¹M. R. S. McCoustra and J. Pfab, *Chem. Phys. Lett.* **137**, 355 (1987).
- ²S. W. Benson, *Chem. Rev.* **78**, 23 (1978).
- ³H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **87**, 7 (1983).

4.6. Fluorine Species

$$\Delta H^\circ = -279 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.2) \times 10^{-11}$	298	Bedzhanyan <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
5×10^{-11}	298	IUPAC, 1992 ²	(b)
2.7×10^{-11}	200–300	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow system. Pseudo-first-order decays of FO radicals in the presence of excess O(³P) atoms were monitored by LMR. [O] determined by EPR.
- (b) Estimated value.
- (c) Based on the results of Bedzhanyan *et al.*¹

Comments on Preferred Values

The preferred value is based on the results of the recent study of Bedzhanyan *et al.*,¹ the sole study of this reaction. The temperature dependence of the rate constant is expected to be small for such an atom-radical process, as for the analogous ClO radical reaction.

Preferred Values

$$k = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

References

- ¹Yu. R. Bedzhanyan, E. M. Markin, G. G. Politenkova, and Yu. M. Gershenson, *Kinetics and Catalysis* **38**, 797 (1993); original pages 998–1003 (1992).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -166 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.7 \text{ at } 298 \text{ K.}$$

constant for such a radical-atom process is expected to approach the gas collision frequency and is not expected to exhibit a strong temperature dependence. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.¹

References

Comments on Preferred Values

There are no experimental data for this reaction. The rate

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -46.9 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$$k = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

There are no published experimental data for this reaction. k is assumed to be comparable to most other O(¹D) atom rate

constants which approach the gas kinetic collision frequency, and as such is not expected to exhibit a strong temperature dependence. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.¹

References

¹IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -197.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k_1 = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred values for k_1 and k_2 are based on the results reported in the study of Wine and Ravishankara,¹ which is

much more direct than the other studies. Both the overall rate and the branching ratio reported in this study¹ are accepted. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

¹P. H. Wine and A. R. Ravishankara, Chem. Phys. Lett. **96**, 129 (1983).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

O(¹D) + HFC's → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
2.0×10^{-10} CH ₃ CHF ₂	298	Warren, Gierczak, and Ravishankara, 1991 ¹	(a)
4.9×10^{-11} CH ₂ FCF ₃			
1.2×10^{-10} CHF ₂ CF ₃			
1.6×10^{-10} CH ₃ F	298	Schmoltner <i>et al.</i> , 1993 ²	(a)
5.1×10^{-11} CH ₂ F ₂			
9.8×10^{-12} CHF ₃			
2.6×10^{-10} CH ₃ CH ₂ F			
Reviews and Evaluations			
1.4×10^{-10} CH ₃ F	298	IUPAC, 1992 ³	(b)
9×10^{-11} CH ₂ F ₂			
8.4×10^{-12} CHF ₃			
1×10^{-10} CH ₃ CHF ₂			
1×10^{-10} CH ₃ CF ₃			
1×10^{-10} CH ₂ FCF ₃			
5×10^{-11} CHF ₂ CF ₃			
1.5×10^{-10} CH ₃ F	200–300	NASA, 1994 ⁴	(c)
5.1×10^{-11} CH ₂ F ₂			
9.1×10^{-12} CHF ₃			
2.6×10^{-10} CH ₃ CH ₂ F			
2.0×10^{-10} CH ₃ CHF ₂			
1.0×10^{-10} CH ₃ CF ₃			
4.9×10^{-11} CH ₂ FCF ₃			
1.2×10^{-10} CHF ₂ CF ₃			

Comments

- (a) Laser flash photolysis of O₃ at 248 nm. Time-resolved production of O(³P) atoms was monitored by resonance fluorescence at 130 nm.
- (b) CH₃F and CHF₃—based on results of Force and Wiesenfeld.⁵ CH₂F₂, CH₃CF₃, and CH₂FCF₃—based on results of Green and Wayne.⁶ CH₃CHF₂, and CH₂FCF₃—estimated by analogy.
- (c) (c) CH₃F and CHF₃—based on results of Schmoltner *et al.*² and Force and Wiesenfeld.⁵ CH₂F₂ and CH₃CH₂F—based on results of Schmoltner *et al.*² CH₃CF₃—based on results of Green and Wayne.⁶ CH₃CHF₂, CH₂FCF₃, and CHF₂CF₃—based on results of Warren *et al.*¹

Preferred Values

CH ₃ F	$k = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₂ F ₂	$k = 5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CHF ₃	$k = 9.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₃ CH ₂ F	$k = 2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₃ CHF ₂	$k = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₃ CF ₃	$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₂ FCF ₃	$k = 4.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CHF ₂ CF ₃	$k = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K for CH₃F.

$\Delta \log k = \pm 0.3$ at 298 K for CH₂F₂, CHF₃, CH₃CH₂F, CH₃CHF₂, CH₃CF₃, CH₂FCF₃, and CHF₂CF₃.

Comments on Preferred Values

The rate coefficients given are for the total disappearance of O(¹D) atoms and include both physical quenching and chemical reaction. Because these rate coefficients have such high values (nearly collisional) at 298 K, they can be assumed to be temperature-independent. Specific comments are as follows:

CH ₃ F	Based on results of Schmoltner <i>et al.</i> ² who also report 11% physical quenching. Good agreement with results of Force and Wiesenfeld. ⁵
CH ₂ F ₂	Based on results of Schmoltner <i>et al.</i> ² who also report 70% physical quenching.
CHF ₃	Based on results of Schmoltner <i>et al.</i> ² who also report essentially complete physical quenching. Good agreement with the results of Force and Wiesenfeld. ⁵
CH ₃ CH ₂ F	Based on results of Schmoltner <i>et al.</i> ² who also report 18% physical quenching.
CH ₃ CHF ₂	Based on results of Warren <i>et al.</i> ¹ who also report 54% physical quenching.
CH ₃ CF ₃	Based on results of Green and Wayne. ⁶
CH ₂ FCF ₃	Based on results of Warren <i>et al.</i> ¹ who also report 94% physical quenching.
CHF ₂ CF ₃	Based on results of Warren <i>et al.</i> ¹ who also report 85% physical quenching.

References

- ¹R. Warren, T. Gierczak, and A. R. Ravishankara, *Chem. Phys. Lett.* **183**, 403 (1991).
²A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 8976 (1993).
³IUPAC, Supplement IV, 1992 (see references in Introduction).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
⁵A. P. Force and J. R. Wiesenfeld, *J. Phys. Chem.* **85**, 782 (1981).
⁶R. G. Green and R. P. Wayne, *J. Photochem.* **6**, 371 (1976).

$$\Delta H^\circ = -134.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.4 \times 10^{-10} \exp(-500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–375 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The value of k at 298 K seems to be well established, with the results reported by Zhitneva and Pshezhetskii,¹ Heidner *et al.*,² Wurzberg and Houston,³ Dodonov *et al.*,⁴ Clyne *et al.*,⁵ Igoshin *et al.*,⁶ Clyne and Hodgson,⁷ and Stevens *et al.*⁸ being in good agreement; the preferred value at 298 K is the mean of these values. Reported values of E/R range from 433–595 K (Refs. 2, 3, 6, and 8). The preferred value of E/R is derived from a least-squares fit to the data in these studies, and the A -factor was chosen to fit the recommended

room temperature value. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁹

References

- ¹G. P. Zhitneva and S. Ya. Pshezhetskii, *Kinetika i Katalia* **19**, 296 (1978).
²R. F. Heidner, J. F. Bott, C. E. Gardner, and J. E. Melzer, *J. Chem. Phys.* **72**, 4815 (1980).
³E. Wurzberg and P. L. Houston, *J. Chem. Phys.* **72**, 4811 (1980).
⁴A. F. Dodonov, G. K. Lavrovskaya, I. I. Morozov, and V. L. Tal'Roze, *Dokl. Akad. Nauk* **198**, 622 (1971).
⁵M. A. A. Clyne, D. J. McKenney, and R. F. Walker, *Can. J. Chem.* **51**, 3596 (1973).
⁶V. I. Igoshin, L. V. Kulakov, and A. I. Nikitin, *Sov. J. Quantum Electron.* **3**, 306 (1974).
⁷M. A. A. Clyne and A. Hodgson, *J. Chem. Soc. Faraday Trans. 2*, **81**, 443 (1985).
⁸P. S. Stevens, W. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **93**, 4068 (1989).
⁹IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -71.6 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 240–370 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The recommended temperature-independent value is based on the results reported by Stevens *et al.*¹ This value is in good agreement with the room temperature results of Frost *et al.*² and Walther and Wagner.³ The latter authors³ in a limited temperature study reported an E/R value of 400 K.

Although these data have not been used in derivation of the preferred value, with the exception of the one low temperature data point they are within the stated uncertainty limit. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹P. S. Stevens, W. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **93**, 4068 (1989).
²R. J. Frost, D. S. Green, M. K. Osborn, and I. W. M. Smith, *Int. J. Chem. Kinet.* **18**, 885 (1986).
³C. D. Walther and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.* **87**, 403 (1983).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -53.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-32} [\text{SF}_6]$	295	Ellermann <i>et al.</i> , 1994 ¹	(a)
$5.8 \times 10^{-33} (T/300)^{-1.7} [\text{N}_2]$	100–373	Campuzano-Jost <i>et al.</i> , 1995 ²	(b)
<i>Reviews and Evaluations</i>			
$3.7 \times 10^{-33} (T/300)^{-1} [\text{N}_2]$	300–400	IUPAC, 1992 ³	(c)
$4.4 \times 10^{-33} (T/300)^{-1.2} [\text{air}]$	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) Pulse radiolysis of $\text{SF}_6\text{-O}_2$ mixtures at 200–1000 Torr total pressure with kinetic UV spectroscopy detection of FO_2 radicals between 215–254 nm. Falloff extrapolations were made with $F_c=0.6$.
- (b) Flash photolysis system with UV absorption of FO_2 radicals. Experiments were carried out between 100 and 373 K, and up to 1000 bar, and in the bath gases He, Ar, and N_2 . Measurements of the equilibrium constant lead to $\Delta H^\circ = -50.8 \text{ kJ mol}^{-1}$. Falloff extrapolations were made with F_c near 0.5.
- (c) Average of the data of Refs. 5 and 6. It was assumed that k_0 is similar for $\text{M}=\text{Ar}$ and N_2 .
- (d) Based on the study of Pagsberg *et al.*,⁵ which is in agreement with previous measurements.

Preferred Values

$k_0 = 5.8 \times 10^{-33} (T/300)^{-1.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 100–400 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

Because of the large data base of Ref. 2, these values are preferred and are in reasonable agreement with earlier work. Falloff curves were constructed with F_c near 0.5.

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
2.0×10^{-12}	295	Ellermann <i>et al.</i> , 1994 ¹	(a)
1.2×10^{-10}	100–373	Campuzano-Jost <i>et al.</i> , 1995 ²	(b)

Comments

- (a) See comment (a) for k_0 .
- (b) See comment (b) for k_0 .

Preferred Values

$k_\infty = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 100–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the range 100–400 K.

Comments on Preferred Values

Because of the large pressure range studied in Ref. 2, a reliable falloff extrapolation towards k_∞ was possible. The data of Ref. 2, therefore, are preferred together with values of F_c near 0.5.

Intermediate falloff range

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	P/Torr	M	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>					
2.4×10^{-13}	585 mbar	SF ₆	298	Wallington and Nielsen, 1991 ⁷	(a)
$(2.35 \pm 0.2) \times 10^{-13}$	600 mbar	SF ₆	298	Wallington <i>et al.</i> , 1992 ⁸	(b)

Comments

- (a) Pulse radiolysis of a mixture of SF₆ and O₂ (6.1–20 mbar). FO₂ radicals were monitored by UV absorption at 220 nm.
- (b) Pulse radiolysis of a mixture of SF₆ and O₂ (2.5–15 mbar). FO₂ radicals were monitored by UV absorption at 220 nm. The results were analyzed together with those of Ref. 6.

References

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- ²P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, and J. Troe, *J. Chem. Phys.* **102**, 5317 (1995).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, *Chem. Phys. Lett.* **141**, 88 (1987).
- ⁶J. L. Lyman and R. Holland, *J. Phys. Chem.* **92**, 7232 (1988).
- ⁷T. J. Wallington and O. J. Nielsen, *Int. J. Chem. Kinet.* **23**, 785 (1991).
- ⁸T. J. Wallington, M. M. Maricq, T. Ellermann, and O. J. Nielsen, *J. Phys. Chem.* **96**, 982 (1992).

$$\Delta H^\circ = 53.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.0 \times 10^{-5} T^{-1.25} \exp(-5990/T) [\text{N}_2]$	315–420	Campuzano-Jost <i>et al.</i> , 1995 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.2 \times 10^{-17} [\text{N}_2]$	298	IUPAC, 1989 ²	(b)

Comments

- (a) Flash photolysis/UV absorption study monitoring FO₂ radicals. Experiments were carried out between 100 and 375 K at total pressures between 1 and 1000 bar, and in the bath gases He, Ar, and N₂. Measurements of the equilibrium constant lead to $\Delta H^\circ = -49.8 \text{ kJ mol}^{-1}$. Falloff extrapolations were carried out with a value of F_c near 0.5. The expression for k_0 was derived from the recombination rate coefficients of the reverse reaction and the equilibrium constants.
- (b) Based on the experiments of Ref. 3.

$$k_0 = 8.4 \times 10^{-9} (T/300)^{-1.25} \exp(-5990/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range 315–420 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 0.5.$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The results of Ref. 1 are in reasonable agreement with those of Ref. 3 but differ at 298 K by a factor of 6 with the data from Ref. 4. The preferred values are based on the data of Ref. 1.

Preferred Values

$$k_0 = 1.5 \times 10^{-17} [\text{N}_2] \text{ s}^{-1} \text{ at 298 K.}$$

High-pressure rate coefficients

Rate coefficient data

k_{∞}/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{13} T^{0.45} \exp(-5990/T)$	315–420	Campuzano-Jost <i>et al.</i> , 1995 ¹	(a)

Comments

- (a) See comment (a) for k_0 .

Preferred Values

$$k_{\infty} = 3.1 \times 10^5 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 1.7 \times 10^{14} (T/300)^{0.45} \exp(-5990/T) \text{ s}^{-1} \text{ over the temperature range } 315\text{--}420 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at } 300 \text{ K.}$$

$$\Delta n = \pm 0.5.$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

Because of the large pressure range studied in Ref. 1, a reliable falloff extrapolation towards k_{∞} was possible. The data of Ref. 1, therefore, are preferred together with F_c values near 0.5.

References

¹P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, and J. Troe, *J. Chem. Phys.* **102**, 5317 (1995).

²IUPAC, Supplement III, 1989 (see references in Introduction).

³P. Pagsberg, E. Ratajczk, A. Sillesen, and J. T. Jodkowski, *Chem. Phys. Lett.* **141**, 88 (1987).

⁴J. L. Lyman and R. Holland, *J. Phys. Chem.* **92**, 7232 (1988).

$$\Delta H^{\circ} = -113 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-11} \exp[-(226 \pm 200)/T]$	253–365	Wagner, Zetzsch, and Warnatz, 1972 ¹	(a)
1.3×10^{-11}	298		
$(6.2 \pm 0.3) \times 10^{-12}$	298	Bedzhanyan, Markin, and Gershenzon, 1993 ²	(b)
<i>Reviews and Evaluations</i>			
$2.8 \times 10^{-11} \exp(-230/T)$	250–365	IUPAC, 1992 ³	(c)
$2.2 \times 10^{-11} \exp(-230/T)$	250–365	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with MS detection of O_3 decay in excess F atoms. Temporal profiles of F, FO, and O_3 monitored by MS.
- (b) Discharge flow system with excess of O_3 over F atoms. Rate of formation of FO radicals monitored by LMR.
- (c) Based on the data of Wagner *et al.*¹
- (d) Based on the data of Wagner *et al.*¹ and Bedzhanyan *et al.*²

Preferred Values

$$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.2 \times 10^{-11} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}365 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.25 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred room temperature value is the average of the room temperature values from the two studies.^{1,2} The temperature dependence is taken from Wagner *et al.*¹ and the A-factor is fitted to the preferred room temperature value. The value appears to be quite reasonable by analogy with the reactivity of atomic chlorine with ozone.

References

¹H. Gg. Wagner, C. Zetzsch, and J. Warnatz, *Ber. Bunsenges. Phys. Chem.* **76**, 526 (1972).

²Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, *Kinetics and Catalysis* **33**, 594 (1993); original pages 744–752 (1992).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -143.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.5) \times 10^{-11}$	298	Mellouki, Le Bras, and Poulet, 1987 ¹	(a)
$(2.1 \pm 1) \times 10^{-11}$	298	Rahman <i>et al.</i> , 1988 ²	(b)
$6.0 \times 10^{-12} \exp[(400 \pm 120)/T]$	260–320	Wine, Wells, and Nicovich, 1988 ³	(c)
$(2.3 \pm 0.1) \times 10^{-11}$	298		
$(2.2 \pm 0.2) \times 10^{-11}$	298	Becker <i>et al.</i> , 1991 ⁴	(d)
<i>Reviews and Evaluations</i>			
$6.0 \times 10^{-12} \exp(400/T)$	260–320	IUPAC, 1992 ⁵	(e)
$6.0 \times 10^{-12} \exp(400/T)$	200–300	NASA, 1994 ⁶	(e)

Comments

- (a) Discharge flow system with EPR detection of F atoms.
- (b) Discharge flow system with MS detection of HF, NO₃ radicals and HNO₃.
- (c) Pulsed laser photolysis at 351 nm with long-path laser absorption of NO₃ at 662 nm. At higher temperatures (335–373 K) the rate coefficient was found to be independent of temperature with a value of $(2.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Two separate discharge flow systems with different detectors. In one system the formation of NO₃ as a function of time was measured by MS; in the other system, the decay of F atoms as a function of time was measured by EPR.
- (e) Based on results of the temperature-dependent study of Wine *et al.*,³ and the room temperature results of Mellouki *et al.*¹ and Rahman *et al.*²

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The recommendation is based on the results of the temperature-dependent study of Wine *et al.*³ and the room temperature results of Mellouki *et al.*,¹ Rahman *et al.*,² and Becker *et al.*⁴ The values at room temperature are in good agreement. The study of Wine *et al.*³ was over the temperature range 260–373 K; below 320 K the authors fitted their data with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

References

- ¹A. Mellouki, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **91**, 5760 (1987).
- ²M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **92**, 91 (1988).
- ³P. H. Wine, J. R. Wells, and J. M. Nicovich, *J. Phys. Chem.* **92**, 2223 (1988).
- ⁴E. Becker, Th. Benter, R. Kampf, R. N. Schindler, and U. Wille, *Ber. Bunsenges. Phys. Chem.* **95**, 1168 (1991).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁶NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$$k = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.0 \times 10^{-12} \exp(400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}320 \text{ K.}$$

$$\Delta H^\circ = -131.9 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.0 \times 10^{-10} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the room-temperature results of Clyne *et al.*,¹ Kompa and Wanner,² Pollock and

Jones,³ and Fasano and Nogar,⁴ the 298–450 K results of Wagner *et al.*,⁵ and the 253–348 K results of Foon and Reid.⁶ These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

¹M. A. A. Clyne, D. J. McKenney, and R. F. Walker, *Can. J. Chem.* **51**, 3596 (1973).

²K. L. Kompa and J. Wanner, *Chem. Phys. Lett.* **12**, 560 (1972).

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⁴D. M. Fasano and N. S. Nogar, *Chem. Phys. Lett.* **92**, 411 (1982).

⁵H. Gg. Wagner, J. Warnatz, and C. Zetzsch, *An. Assoc. Quim. Argentina* **59**, 169 (1971).

⁶R. Foon and G. P. Reid, *Trans. Faraday Soc.* **67**, 3513 (1971).

⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH₃F (HFC-41) → H₂O + CH₂F

$$\Delta H^\circ = -80.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.75 \times 10^{-12} \exp[-(1300 \pm 100)/T]$ $(2.23 \pm 0.38) \times 10^{-14}$	243–373 298	Schmoltner <i>et al.</i> , 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$(1.61 \pm 0.08) \times 10^{-14}$	296 ± 2	Wallington and Hurley, 1993 ²	(b)
$(1.36 \pm 0.07) \times 10^{-14}$	296 ± 2	Wallington and Hurley, 1993 ²	(c)
$1.96 \times 10^{-18} T^2 \exp[-(634 \pm 35)/T]$	298–363	Hsu and DeMore, 1995 ³	(d)
1.95×10^{-14}	298		
<i>Reviews and Evaluations</i>			
$3.7 \times 10^{-12} \exp(-1600/T)$	270–340	IUPAC, 1992 ⁴	(e)
$5.51 \times 10^{-18} T^2 \exp(-1005/T)$	292–480	Atkinson, 1994 ⁵	(f)
$3.0 \times 10^{-12} \exp(-1500/T)$	243–373	NASA, 1994 ⁶	(g)

Comments

- (a) Pulsed laser photolysis system with LIF detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by photolysis of CH₃ONO at 700 Torr total pressure of air. The decay of CH₃F was inferred from the measured formation of HC(O)F, using a formation yield of HC(O)F of 0.90 as measured in separate Cl₂-CH₃F-NO-air irradiations. The concentrations of HC(O)F and acetylene were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{C}_2\text{H}_2) = 0.0201 \pm 0.0009$ was placed on an absolute basis by using $k(\text{HO} + \text{C}_2\text{H}_2) = 7.99 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{5,7}
- (c) HO radicals generated by the photolysis of O₃ at 254 nm in the presence of H₂. The concentrations of CH₄ and CH₃F were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{CH}_4) = 2.30 \pm 0.11$ was placed on an absolute basis by using $k(\text{HO} + \text{CH}_4) = 5.92 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Relative rate method. HO radicals were generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or O₃-H₂O)-CH₃F-CH₃CHF₂-O₂-N₂ mixtures. The concentrations of CH₃F and

CH₃CHF₂ were measured by IR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{F})/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.99 \pm 0.10) \exp[-(174 \pm 34)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (e) The absolute rate coefficients of Howard and Evenson,⁸ Nip *et al.*,⁹ and Jeong and Kaufman^{10,11} were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 5.51 \times 10^{-18} T^2 \exp(-1005/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 292–480 K. The Arrhenius expression $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.
- (f) Derived from the absolute rate coefficient data of Howard and Evenson,⁸ Nip *et al.*,⁹ and Jeong and Kaufman.^{10,11}
- (g) Derived from the absolute rate coefficients of Howard and Evenson,⁸ Nip *et al.*,⁹ and Schmoltner *et al.*¹ and the relative rate coefficients of Hsu and DeMore.³

Preferred Values

$k = 2.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-12} \exp(-1305/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The absolute laser photolysis-LIF rate coefficients of Schmoltner *et al.*¹ are higher than those reported previously by Jeong and Kaufman,^{10,11} although the discrepancy decreases with increasing temperature. The absolute rate coefficients of Schmoltner *et al.*¹ exhibit a significant amount of scatter at temperatures ≤ 273 K, for unknown reasons. Since secondary reactions of HO radicals with CH₂F radicals and other radical species were expected to have occurred in the study of Bera and Hanrahan,¹² the rate coefficient of Bera and Hanrahan¹² was not used in the evaluation. The absolute rate coefficients of Howard and Evenson,⁸ Nip *et al.*,⁹ Jeong and Kaufman,^{10,11} and Schmoltner *et al.*¹ were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.14 \times 10^{-18} T^2 \exp(-776/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 243–480 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is

derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The relative rate coefficients of Hsu and DeMore³ agree with the preferred values to within 8% over the temperature range 298–363 K.

References

- ¹A. M. Schmoltner, R. K. Talukdar, R. F. Warren, A. Mellouki, L. Goldfarb, T. Gierczak, S. A. McKeen, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 8976 (1993).
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- ³K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
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- ⁸C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 197 (1976).
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- ¹⁰K.-M. Jeong and F. Kaufman, *J. Phys. Chem.* **86**, 1808 (1982).
- ¹¹K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, *J. Phys. Chem.* **88**, 1222 (1984).
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$$\Delta H^\circ = -67.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comment
<i>Absolute Rate Coefficients</i>			
$(2.52 \pm 0.25) \times 10^{-15}$	223	Schmoltner <i>et al.</i> , 1993 ¹	(a)
$(1.09 \pm 0.03) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$1.58 \times 10^{-18} T^2 \exp[-(737 \pm 24)/T]$	297–383	Hsu and DeMore, 1995 ²	(b)
1.14×10^{-14}	297		
<i>Reviews and Evaluations</i>			
$2.0 \times 10^{-12} \exp(-1545/T)$	240–300	IUPAC, 1992 ³	(c)
$3.84 \times 10^{-18} T^2 \exp(-1016/T)$	222–492	Atkinson, 1994 ⁴	(d)
$1.9 \times 10^{-12} \exp(-1550/T)$	222–400	NASA, 1994 ⁵	(e)

Comments

- (a) Pulsed photolysis system with LIF detection of HO radicals.
- (b) Relative rate method. HO radicals were generated from the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or O₃-H₂O)-CH₂F₂-CH₃CHF₂-O₂-N₂ mixtures. The concentrations of CH₂F₂ and CH₃CHF₂ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_2\text{F}_2)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.80 \pm 0.06) \exp[-(277 \pm 24)/T]$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) See Comments on Preferred Values.

- (d) Derived from the absolute rate coefficient data of Howard and Evenson,⁶ Nip *et al.*,⁷ Jeong and Kaufman,⁸ and Talukdar *et al.*⁹
- (e) Derived from the rate coefficients of Howard and Evenson,⁶ Nip *et al.*,⁷ Jeong and Kaufman,⁸ Talukdar *et al.*,⁹ Schmoltner *et al.*,¹ and Hsu and DeMore² below 400 K.

Preferred Values

$k = 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.0 \times 10^{-12} \exp(-1545/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Schmoltner *et al.*¹ at 223 K and 298 K are in excellent agreement with the earlier, and much more extensive, rate coefficient data of this research group (Talukdar *et al.*⁹). Accordingly, our previous evaluation, IUPAC, 1992,³ is unchanged. The room temperature rate coefficients of Nip *et al.*,⁷ Jeong and Kaufman,⁸ Talukdar *et al.*,⁹ and Schmoltner *et al.*¹ are in good agreement, but are $\sim 30\%$ higher than those of Howard and Evenson,⁶ Clyne and Holt,¹⁰ and Bera and Hanrahan.¹¹ The data of Clyne and Holt¹⁰ are not considered reliable,^{3,5} and that of Bera and Hanrahan¹¹ may have been subject to secondary reactions. The rate coefficients measured by Jeong and Kaufman⁸ (250–492 K) and Talukdar *et al.*⁹ (222–381 K) are in good agreement over the temperature range where they overlap. The rate coefficient data of Howard and Evenson,⁶ Nip *et al.*,⁷ Jeong and Kaufman,⁸ and Talukdar *et al.*⁹ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.84 \times 10^{-18} T^2 \exp(-1016/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 222–492 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered

at 265 K and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

The relative rate coefficients of Hsu and DeMore² are in good agreement with the recommended three parameter expression at room temperature, but are $\sim 15\%$ lower at 383 K (and the rate coefficients of Hsu and DeMore² extrapolated to 240 K lead to a rate coefficient which is 30% higher than that predicted from the recommended three parameter equation).

References

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$$\Delta H^\circ = -50.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.93 \times 10^{-13} \exp[-(2300 \pm 100)/T]$ $(3.08 \pm 0.28) \times 10^{-16}$	252–374 298	Schmoltner <i>et al.</i> , 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$1.08 \times 10^{-18} T^2 \exp[-(1780 \pm 44)/T]$ 2.40×10^{-16}	298–383 298	Hsu and DeMore, 1995 ²	(b)
<i>Reviews and Evaluations</i>			
$1.0 \times 10^{-12} \exp(-2490/T)$	270–340	IUPAC, 1992 ³	(c)
$1.49 \times 10^{-18} T^2 \exp(-1887/T)$	387–1445	Atkinson, 1989; ⁴ Atkinson, 1994 ⁵	(d)
$1.5 \times 10^{-12} \exp(-2650/T)$	296–410	NASA, 1994 ⁶	(e)

Comments

- (a) Pulsed laser photolysis system with LIF detection of HO radicals.
- (b) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of O_3 - H_2O mixtures in the UV in H_2O (or H_2O - O_3)- CHF_3 - CHF_2CF_3 - N_2 - O_2 mixtures. The concentrations of CHF_3 and CHF_2CF_3 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_3)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = (1.14 \pm 0.08)$

$\times \exp[-(654 \pm 44)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.46 \times 10^{19} T^2 \exp(-1126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (c) The absolute rate coefficients of Ernst *et al.*⁷ and Jeong and Kaufman^{8,9} were fitted to the three-parameter equation, $k = CT^2 \exp(-D/T)$, resulting in $k = 1.49 \times 10^{-18} T^2 \exp(-1887/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 387–1445 K. The Arrhenius ex-

pression, $k = A \exp(-B/T)$, was centered at 300 K and was derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

- (d) Derived from the absolute rate coefficient data of Ernst *et al.*⁷ and Jeong and Kaufman,^{8,9} using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (e) Derived from the 296 K rate coefficient of Howard and Evenson,¹⁰ the 387 and 410 K rate coefficients of Jeong and Kaufman,^{8,9} and the absolute and relative rate coefficients of Schmoltner *et al.*,¹ Kurylo *et al.* (unpublished data, 1994), and Hsu and DeMore.²

Preferred Values

$k = 2.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 6.0 \times 10^{-13} \exp(-2295/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficient study of Schmoltner *et al.*¹ is the only published temperature-dependent study carried out at temperatures $\leq 298 \text{ K}$. The rate coefficients derived from the relative rate study of Hsu and DeMore² are ~ 10 –20% lower than the absolute rate coefficients of Schmoltner *et al.*¹ over the temperature range common to both studies (298–374 K), with the disagreement increasing with decreasing temperature. The rate coefficients measured at $\sim 298 \text{ K}$ by Howard and Evenson,¹⁰ Nip *et al.*,¹¹ and Clyne and Holt¹² are highly uncertain, due to the low rate coefficient (note, for example, the reported invariance of the rate coefficient over

the range 296–430 K from the study of Clyne and Holt¹²). The absolute rate coefficients of Ernst *et al.*,⁷ Jeong and Kaufman,^{8,9} and Schmoltner *et al.*¹ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.29 \times 10^{-18} T^2 \exp(-1765/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 252–1445 K. At 298 K, this equation yields $k = 3.07 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in agreement within the error limits with the room temperature rate coefficients of Howard and Evenson¹⁰ and Nip *et al.*¹¹

The relative rate coefficients of Hsu and DeMore² are uniformly 21% lower than those predicted from the three parameter expression over the temperature range 240–300 K. Accordingly, the value of C in the three parameter equation has been decreased by 10% to $1.15 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

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$$\Delta H^\circ = 328 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 4 \times 10^{-16}$	296 $\pm$ 2	Howard and Evenson, 1976 ¹	(a)
$< 1 \times 10^{-15}$	293	Clyne and Holt, 1979 ²	(b)
$< 2 \times 10^{-18}$	~ 298	Ravishankara <i>et al.</i> , 1993 ³	(c)
<i>Reviews and Evaluations</i>			
$< 2 \times 10^{-18}$	298	Atkinson, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with LMR detection of HO radicals.
- (b) Discharge flow system with resonance fluorescence detection of HO radicals.
- (c) Not explicitly reported, but expected to be a pulsed photolysis system with LIF detection of HO radicals as carried out by Schmoltner *et al.*⁵ for HO radical reaction rate coefficient measurements with related hydrofluorocarbons.
- (d) Based on the upper limit reported by Ravishankara

et al.,³ which is consistent with the higher upper limits of Howard and Evenson¹ and Clyne and Holt.²

Preferred Values

$$k < 2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Value

The preferred value is the upper limit to the rate coefficient reported by Ravishankara *et al.*³

References

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Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.69 \times 10^{-12} \exp[-(750 \pm 100)/T]$	243–373	Schmoltner <i>et al.</i> , 1993 ¹	(a)
$(2.17 \pm 0.29) \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
$1.76 \times 10^{-17} T^2 \exp[-(657 \pm 36)/T]$	285–364	Hsu and DeMore, 1995 ²	(b)
1.69×10^{-13}	298		
<i>Reviews and Evaluations</i>			
2.3×10^{-13}	298	IUPAC, 1992 ³	(c)
$7.0 \times 10^{-12} \exp(-1100/T)$	243–373	NASA, 1994 ⁴	(d)

Comments

- (a) Pulsed photolysis system with LIF detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of $\text{H}_2\text{O}-\text{O}_3$ mixtures in the UV in H_2O (or $\text{H}_2\text{O}-\text{O}_3$)- $\text{CH}_3\text{CH}_2\text{F}-\text{C}_2\text{H}_6-\text{O}_2-\text{N}_2$ mixtures. The concentrations of $\text{CH}_3\text{CH}_2\text{F}$ and C_2H_6 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CH}_2\text{F})/k(\text{HO} + \text{C}_2\text{H}_6) = (1.16 \pm 0.13) \exp[-(158 \pm 36)/T]$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 1.52 \times 10^{-17} T^2 \times \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the rate coefficient of Nip *et al.*⁵
- (d) Based on the rate coefficients of Nip *et al.*,⁵ Schmoltner *et al.*,¹ and Hsu and DeMore.²

Preferred Values

$$k = 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.4 \times 10^{-12} \exp(-740/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}300 \text{ K.}$$

$$k_1/k = 0.85 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

$$\Delta k_1/k = \pm 0.15 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The absolute room temperature rate coefficients of Nip *et al.*⁵ and Schmoltner *et al.*¹ are in excellent agreement, but are significantly higher than the relative rate coefficient of Hsu and DeMore.² The relative rate coefficients of Hsu and DeMore² are $\sim 10\%$ higher than the absolute rate coefficients of Schmoltner *et al.*¹ at 364 K, but $\sim 25\%$ lower at 285 K, with a significantly higher temperature dependence. The absolute rate coefficients of Nip *et al.*⁵ and Schmoltner *et al.*¹ and the relative rate coefficients of Hsu and DeMore¹ have been fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 4.72 \times 10^{-18} T^2 \exp(-213/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 243–373 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.

The branching ratio is taken from the product study of Singleton *et al.*⁶

References

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Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$3.9 \times 10^{-12} \exp[-(1370 \pm 260)/T]$	295–388	Nielsen, 1991 ¹	(a)
$(4.7 \pm 1.1) \times 10^{-14}$	295		
<i>Relative Rate Coefficients</i>			
$(4.03 \pm 0.69) \times 10^{-14}$	298 ± 2	DeMore, 1992 ²	(b)
$3.44 \times 10^{-18} T^{-2} \exp[-(690 \pm 57)/T]$	298–358	Hsu and DeMore, 1995 ³	(c)
3.07×10^{-14}	298		
$(3.22 \pm 0.34) \times 10^{-14}$	298 ± 2	DeMore, 1992 ²	(d)
$6.18 \times 10^{-20} T^{2.58} \exp[-(483 \pm 67)/T]$	298–358	Hsu and DeMore, 1995 ³	(d)
2.96×10^{-14}	298		
<i>Reviews and Evaluations</i>			
$1.0 \times 10^{-12} \exp(-990/T)$	240–300	IUPAC, 1992 ⁴	(e)
$1.98 \times 10^{-18} T^{-2} \exp(-460/T)$	212–423	Atkinson, 1994 ⁵	(f)
$2.4 \times 10^{-12} \exp(-1260/T)$	298–358	NASA, 1994 ⁶	(g)

Comments

- (a) Pulsed radiolysis system with resonance absorption detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of H₂O at 185 nm in H₂O-CH₃CHF₂-C₂H₆-N₂-O₂ mixtures. The concentrations of CH₃CHF₂ and C₂H₆ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{C}_2\text{H}_6) = 0.161 \pm 0.028$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate method. HO radicals were generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or H₂O-O₃)-CH₃CHF₂-CH₃CCl₃-O₂-N₂ mixtures. The concentrations of CH₃CHF₂ and CH₃CCl₃ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (1.53 \pm 0.28) \times \exp[(220 \pm 57)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Relative rate method. HO radicals were generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in H₂O (or O₃-H₂O)-CH₃CHF₂-CH₄-N₂-O₂ mix-

tures. The concentrations of CH₃CHF₂ and CH₄ were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{CH}_4) = 5.2 \pm 0.54^2$ and $k(\text{HO} + \text{CH}_3\text{CHF}_2)/k(\text{HO} + \text{CH}_4) = (0.64 \pm 0.13) \exp[(599 \pm 67)/T]^3$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (e) Derived from the rate coefficients of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ and Gierczak *et al.*¹¹
- (f) Derived from the rate coefficients of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ and Gierczak *et al.*¹¹ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (g) Derived from the room temperature rate coefficient data of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ Gierczak *et al.*,¹¹ Nielsen,¹ and Hsu and DeMore³ and the temperature dependence measured by Hsu and DeMore.³

Preferred Values

$k = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.0 \times 10^{-12} \exp(-990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$$\Delta \log k = {}^{+0.10}_{-0.20} \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = {}^{+200}_{-400} \text{ K.}$$

Comments on Preferred Values

The rate coefficients of Nielsen¹ over the temperature range 295–388 K are consistently higher than the absolute rate coefficients of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ Brown *et al.*,¹² and Gierczak *et al.*,¹¹ all of which are in reasonably good agreement at room temperature. The 298 K relative rate coefficients of DeMore² are also in good agreement with the room temperature absolute rate coefficients of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ Brown *et al.*,¹² and Gierczak *et al.*¹¹ However, the more recent rate coefficients measured by Hsu and DeMore³ relative to the rate coefficients for the HO radical reactions with CH₄ and CH₃CCl₃ (which are in good agreement) are ~10% lower than the least-squares average of the absolute rate coefficients of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ and Gierczak *et al.*¹¹ at 358 K, and ~15–20% lower at 298 K. While this discrepancy is relatively minor, and within the combined overall uncertainties, the temperature dependence obtained by Hsu and DeMore³ is higher than that derived from the absolute rate coefficients.^{7–11}

The temperature dependent studies of Liu *et al.*,¹⁰ Brown *et al.*,¹² and Gierczak *et al.*¹¹ also agree well. As in previous evaluations^{4–6} the data of Clyne and Holt¹³ are omitted. The absolute rate coefficients measured by Brown *et al.*¹² are subject to large uncertainties, as evidenced by the high standard deviations cited at several temperatures, especially at 220 K and 303 K. Because of this and the observations that in general the rate coefficients of Brown *et al.*¹² are significantly higher than those of other recent studies (see the data

sheets for other OH + HCFC and HFC reactions in this evaluation), these data of Brown *et al.*¹² were not used in the evaluation of the rate coefficient for this reaction.

The absolute rate coefficient data of Howard and Evenson,⁷ Handwerk and Zellner,⁸ Nip *et al.*,⁹ Liu *et al.*,¹⁰ and Gierczak *et al.*¹¹ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.98 \times 10^{-18} \times T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 212–423 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The uncertainties on the preferred values are such that they take into account the lower rate coefficients obtained by Hsu and DeMore,³ which extrapolate to a rate coefficient at 240 K which is 30% lower than that calculated from the preferred Arrhenius expression.

References

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$$\Delta H^\circ = -49.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$4.15 \times 10^{-20} T^{2.58} \exp[-(1305 \pm 90)/T]$	298–403	Hsu and DeMore, 1995 ¹	(a)
1.27×10^{-15}	298		
$2.04 \times 10^{-18} T^2 \exp[-(1496 \pm 21)/T]$	298–383	Hsu and DeMore, 1995 ¹	(a)
1.20×10^{-15}	298		
<i>Reviews and Evaluations</i>			
$1.05 \times 10^{-12} \exp(-1990/T)$	240–300	IUPAC, 1992 ²	(b)
$2.02 \times 10^{-18} T^2 \exp(-1459/T)$	223–374	Atkinson, 1994 ³	(c)
$1.6 \times 10^{-12} \exp(-2100/T)$	251–374	NASA, 1994 ⁴	(d)

Comments

- (a) Relative rate method. HO radicals generated by the photolysis of H₂O at 185 nm or of O₃-H₂O mixtures in the UV in H₂O (or O₃-H₂O)-CH₃CF₃-CH₄ (or CHF₂CF₃)-O₂-N₂ mixtures. The concentrations of CH₃CF₃ and CH₄ (or CHF₂CF₃) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{CF}_3)/k(\text{HO} + \text{CH}_4) = (0.43 \pm 0.12) \times \exp[-(223 \pm 90)/T]$ and $k(\text{HO} + \text{CH}_3\text{CF}_3)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = (2.16 \pm 0.14) \exp[-(370 \pm 21)/T]$ were placed on an absolute basis by use of rate coefficients of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.46 \times 10^{-19} T^2 \exp(-1126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Based on the absolute rate coefficients of Martin and Paraskevopoulos⁵ and Talukdar *et al.*⁶
- (c) Derived from the absolute rate coefficients of Martin and Paraskevopoulos⁵ and Talukdar *et al.*,⁶ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (d) Based on the absolute room temperature rate coefficients of Martin and Paraskevopoulos⁵ and the absolute rate coefficients of Talukdar *et al.*⁶ at temperatures >251 K.

Preferred Values

$k = 1.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.05 \times 10^{-12} \exp(-1990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The room temperature absolute rate coefficients of Martin and Paraskevopoulos⁵ and Talukdar *et al.*⁶ are in reasonable agreement. The rate coefficients of Clyne and Holt⁷ are not used in the evaluation because their rate coefficients at 333 K and 378 K are significantly higher than those of Talukdar *et al.*,⁶ and have large associated cited uncertainties. The absolute rate coefficients of Martin and Paraskevopoulos⁵ and Talukdar *et al.*⁶ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 2.02 \times 10^{-18} T^2 \times \exp(-1459/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 223–374 K. The preferred Arrhenius expression $k = A \times \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The preferred values are identical to our previous evaluation, IUPAC, 1992.² The rate coefficients of Hsu and DeMore,¹ relative to the rate coefficients for the reactions of the HO radical with CH₄ and CHF₂CF₃, are in excellent agreement with each other, and the extrapolated rate coefficients of Hsu and DeMore¹ are 7–13% lower than the preferred values over the temperature range 240–300 K.

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.12 \pm 0.12) \times 10^{-13}$	298	Martin and Paraskevopoulos, 1983 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.7 \times 10^{-11} \exp(-1500/T)$	200–300	NASA, 1994 ²	(b)

Comments

- (a) Flash photolysis system with resonance absorption detection of HO radicals.
- (b) The 298 K rate coefficient was based on the rate coefficient of Martin and Paraskevopoulos.¹ The temperature dependence was estimated.

Preferred Values

$k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the absolute rate coefficient of Martin and Paraskevopoulos.¹

References

- ¹J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$4.97 \times 10^{-18} T^2 \exp(-1012/T)$ $(1.49 \pm 0.05) \times 10^{-14}$	278–323 298 ± 2	Barry <i>et al.</i> , 1995 ¹	(a)
<i>Reviews and Evaluations</i>			
1.8×10^{-14}	298	IUPAC, 1992 ²	(b)
$4.0 \times 10^{-12} \exp(-1650/T)$	278–323	NASA, 1994 ³	(c)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of O₃ in the presence of water vapor at ~250 nm at atmospheric pressure of air. Irradiations of O₃-H₂O-CH₂FCHF₂-CH₃CCl₃-air mixtures were carried out and the concentrations of CH₂FCHF₂ and CH₃CCl₃ measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_2\text{FCHF}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.21 \exp(-102/T)$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Based on the room temperature absolute rate coefficient of Martin and Paraskevopoulos.⁴
- (c) Based on the relative rate coefficients of Barry *et al.*¹

Preferred Values

$k = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.3 \times 10^{-12} \exp(-1610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred rate coefficients are derived from the relative rate study of Barry *et al.*¹ The preferred Arrhenius expression, $k = A \exp(-B/T)$, is derived from the three parameter expression cited in the table, of $k = 4.97 \times 10^{-18} T^2 \exp(-1012/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 278–323 K, and is centered at 300 K with $A = C e^2 T^2$ and $B = D + 2T$. The 298 K rate coefficient of Martin and Paraskevopoulos⁴ is in reasonable agreement with this recommendation.

References

- ¹J. Barry, H. Sidebottom, J. Treacy, and J. Franklin, Int. J. Chem. Kinet. **27**, 27 (1995).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³NASA Evaluation No. 11, 1994 (see references in Introduction).
⁴J.-P. Martin and G. Paraskevopoulos, Can. J. Chem. **61**, 861 (1983).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.38 \pm 0.22) \times 10^{-15}$	270	Zhang, Huie, and Kurylo, 1992 ¹	(a)
$1.03 \times 10^{-12} \exp[-(1588 \pm 52)/T]$	298–460	Orkin and Khamaganov, 1993 ²	(b)
$(5.0 \pm 0.44) \times 10^{-15}$	298		
$9.9 \times 10^{-13} \exp[-(1640 \pm 150)/T]$	255–424	Leu and Lee, 1994 ³	(c)
$(3.9 \pm 0.6) \times 10^{-15}$	298		
<i>Relative Rate Coefficients</i>			
$4.31 \times 10^{-20} T^{2.58} \exp[-(1000 \pm 115)/T]$	298–358	DeMore, 1993 ⁴	(d,e)
3.64×10^{-15}	298		
$1.84 \times 10^{-18} T^2 \exp[-(1129 \pm 44)/T]$	298–358	DeMore, 1993 ⁴	(d,f)
3.70×10^{-15}	298		
$1.97 \times 10^{-18} T^2 \exp[-(1138 \pm 79)/T]$	298–358	DeMore, 1993 ⁴	(d,g)
3.80×10^{-15}	298		
$(3.90 \pm 0.48) \times 10^{-15}$	298 ± 2	Barry <i>et al.</i> , 1995 ⁵	(h)
$(4.19 \pm 0.19) \times 10^{-15}$	298 ± 2	Barry <i>et al.</i> , 1995 ⁵	(i)
<i>Reviews and Evaluations</i>			
$8.4 \times 10^{-13} \exp(-1535/T)$	240–300	IUPAC, 1992 ⁶	(j)
$1.61 \times 10^{-18} T^2 \exp(-1005/T)$	223–450	Atkinson, 1994 ⁷	(k)
$1.5 \times 10^{-12} \exp(-1750/T)$	243–450	NASA, 1994 ⁸	(l)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (b) Discharge flow system with EPR detection of HO radicals.
- (c) Discharge flow system with resonance fluorescence detection of HO radicals.
- (d) Relative rate method. HO radicals were generated by the photolysis of $\text{O}_3\text{-H}_2\text{O-O}_2\text{-Ar}$ mixtures at 254 nm. The CH_2FCF_3 and CH_4 , CH_3CCl_3 , or CHF_2CF_3 concentrations were monitored during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_4)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = (2.24 \pm 0.78) \exp[-(82 \pm 115)/T]$, $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = (1.22 \pm 0.17) \times \exp[(219 \pm 44)/T]$ and $k(\text{HO} + \text{CHF}_2\text{CF}_3)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = (0.48 \pm 0.12) \exp[(12 \pm 79)/T]$ are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation), $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.46 \times 10^{-19} \times T^2 \exp(-1126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (e) Relative to $k(\text{HO} + \text{CH}_4)$.
- (f) Relative to $k(\text{HO} + \text{CH}_3\text{CCl}_3)$.
- (g) Relative to $k(\text{HO} + \text{CHF}_2\text{CF}_3)$.
- (h) Relative rate method. HO radicals were generated by the photolysis of O_3 at ~ 250 nm in the presence of water vapor at atmospheric pressure of air. Irradiations of $\text{O}_3\text{-H}_2\text{O-CH}_2\text{FCF}_3\text{-CH}_3\text{CCl}_3\text{-air}$ mixtures were carried

out at 298 ± 2 K and the concentrations of CH_2FCF_3 and CH_3CCl_3 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_2\text{FCF}_3)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = 0.41 \pm 0.05$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (this evaluation).

- (i) Relative rate method. HO radicals were generated by the photolysis of O_3 in the presence of water vapor. Irradiations of $\text{O}_3\text{-H}_2\text{O-CH}_2\text{FCF}_3\text{-CH}_2\text{FCHF}_2\text{-air}$ mixtures were carried out at 298 ± 2 K and the concentrations of CH_2FCF_3 and CH_2FCHF_2 measured by GC and FTIR spectroscopy. The measured rate coefficient ratio $k(\text{HO} + \text{CH}_2\text{FCHF}_2)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = 3.58 \pm 0.16$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_2\text{FCHF}_2) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (this evaluation).
- (j) Derived from the absolute rate coefficients of Martin and Paraskevopoulos,⁹ Liu *et al.*,¹⁰ and Gierczak *et al.*¹¹
- (k) Derived from the absolute rate coefficients of Martin and Paraskevopoulos,⁹ Liu *et al.*,¹⁰ and Gierczak *et al.*,¹¹ using the three parameter equation $k = CT^2 \times \exp(-D/T)$.
- (l) Derived from the absolute rate coefficients of Martin and Paraskevopoulos,⁹ Liu *et al.*,¹⁰ Gierczak *et al.*,¹¹ (for $T \geq 243$ K), Zhang *et al.*,¹ and Leu and Lee,³ and the relative rate coefficients of DeMore.⁴

Preferred Values

$$k = 4.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$k = 7.3 \times 10^{-13} \exp(-1540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficient of Zhang *et al.*¹ at 270 K is in good agreement with those of Liu *et al.*¹⁰ and Gierczak *et al.*¹¹ at 270–273 K, and the absolute rate coefficients of Orkin and Khamaganov² are in agreement with those of Liu *et al.*¹⁰ and Gierczak *et al.*¹¹ However, the relative rate coefficients of DeMore⁴ and Barry *et al.*⁵ at 298 K are lower than those of Martin and Paraskevopoulos,⁹ Liu *et al.*,¹⁰ Gierczak *et al.*,¹¹ and Orkin and Khamaganov,² by up to 30%. The absolute rate coefficients of Gierczak *et al.*¹¹ are slightly or significantly lower than those of Martin and Paraskevopoulos,⁹ Jeong *et al.*,¹² Liu *et al.*,¹⁰ (especially at 350–400 K), Brown *et al.*,¹³ and Orkin and Khamaganov.² The absolute rate coefficients of Leu and Lee³ are in excellent agreement with the relative rate coefficients of DeMore⁴ and Barry *et al.*,⁵ and are $\sim 10^0$ lower than the absolute rate coefficients of Gierczak *et al.*¹¹

The absolute rate coefficients of Gierczak *et al.*¹¹ (243–450 K), Zhang *et al.*¹ (at 270 K), and Leu and Lee³ and the

298 K relative rate coefficients of DeMore⁴ and Barry *et al.*⁵ have been fitted to the three parameter equation $k = CT^2 \times \exp(-D/T)$, resulting in $k = 1.40 \times 10^{-18} T^2 \exp(-1008/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 243–450 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

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HO + CHF₂CHF₂(HFC-134) → H₂O + CF₂CHF₂

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$2.68 \times 10^{-18} T^2 \exp[-(1122 \pm 37)/T]$	298–358	DeMore, 1993 ¹	(a)
5.51×10^{-15}	298		
$1.65 \times 10^{-18} T^2 \exp[-(928 \pm 25)/T]$	298–358	DeMore, 1993 ¹	(b)
6.46×10^{-15}	298		
$1.97 \times 10^{-18} T^2 \exp[-(1017 \pm 77)/T]$	298–358	DeMore, 1993 ¹	(c)
5.76×10^{-15}	298		
<i>Reviews and Evaluations</i>			
5.7×10^{-15}	298	IUPAC, 1992 ²	(d)
$1.6 \times 10^{-12} \exp(-1680/T)$	298–358	NASA, 1994 ³	(e)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of O₃-H₂O-O₂-Ar mixtures at 254 nm. The concentrations of CHF₂CHF₂ and CH₃CCl₃ were measured during the experiments by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CHF}_2\text{CHF}_2) = (0.84 \pm 0.10) \exp[(212 \pm 37)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (b) Relative rate method. HO radicals were generated by the photolysis of O₃-H₂O-O₂-Ar mixtures at 254 nm. The concentrations of CHF₂CHF₂ and CH₂FCF₃ were measured during the irradiations by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_2\text{FCF}_3)/k(\text{HO} + \text{CHF}_2\text{CHF}_2) = (0.85 \pm 0.07) \times \exp[-(80 \pm 25)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_2\text{FCF}_3) = 1.40 \times 10^{-18} T^2 \exp(-1008/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate method. HO radicals were generated by

photolysis of H₂O-O₃ mixtures at 254 nm. The concentrations of CHF₂CHF₂ and CHF₂CF₃ were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{CF}_3)/k(\text{HO} + \text{CHF}_2\text{CHF}_2) = (0.48 \pm 0.11) \exp[-(109 \pm 77)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.46 \times 10^{-19} T^2 \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (d) Derived from the 298 K rate coefficient of Clyne and Holt.⁴
- (e) Derived from the relative rate coefficients of DeMore.¹

Preferred Values

$k = 5.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.4 \times 10^{-12} \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the relative rate coefficients of DeMore.¹ The 298 K rate coefficients and the temperature dependencies from the three sets of measurements¹ (relative to the reactions of the HO radical with CH₃CCl₃, CH₂FCF₃, and CHF₂CF₃), which are in good agreement, have been averaged and the A-factor calculated from the 298 K rate coefficient and the temperature dependence. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The 298 K preferred rate coefficient and the temperature dependence are in good agreement with the absolute rate coefficient data of Clyne and Holt.⁴

References

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(1.59 \pm 0.21) \times 10^{-15}$	298	DeMore, 1992 ¹	(a,b)
$(2.10 \pm 0.15) \times 10^{-15}$	298	DeMore, 1992 ¹	(a,c)
$6.7 \times 10^{-19} T^2 \exp[-(996 \pm 79)/T]$	298–358	DeMore, 1993 ²	(a,d)
2.10×10^{-15}	298		
<i>Reviews and Evaluations</i>			
$4.9 \times 10^{-13} \exp(-1655/T)$	240–300	IUPAC, 1992 ³	(e)
$9.46 \times 10^{-19} T^2 \exp(-1126/T)$	220–364	Atkinson, 1994 ⁴	(f)
$5.6 \times 10^{-13} \exp(-1700/T)$	220–364	NASA, 1994 ⁵	(g)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of O₃ in the presence of water vapor at 254 nm. Irradiations of O₃-H₂O-CHF₂CF₃-reference organic-O₂-N₂ (or Ar) mixtures were carried out, and the concentrations of CHF₂CF₃ and the reference organic measured by FTIR absorption spectroscopy.
- (b) Relative to $k(\text{HO} + \text{CH}_4)$, and the measured rate coefficient ratio $k(\text{HO} + \text{CH}_4)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = 3.9 \pm 0.50$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_4) = 6.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (this evaluation).
- (c) Relative to $k(\text{HO} + \text{CH}_2\text{FCF}_3)$, and the measured rate coefficient ratio $k(\text{HO} + \text{CH}_2\text{FCF}_3)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = 2.0 \pm 0.14$ is placed on an absolute basis

by use of a rate coefficient of $k(\text{HO} + \text{CH}_2\text{FCF}_3) = 4.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (this evaluation).

- (d) Relative to $k(\text{HO} + \text{CH}_2\text{FCF}_3)$, and the measured rate coefficient ratio $k(\text{HO} + \text{CHF}_2\text{CF}_3)/k(\text{HO} + \text{CH}_2\text{FCF}_3) = (0.48 \pm 0.12) \exp[(12 \pm 79)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_2\text{FCF}_3) = 1.40 \times 10^{-18} T^2 \exp(-1008/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation). Rate coefficients were also measured relative to $k(\text{HO} + \text{CHF}_2\text{CHF}_2)$ but, because these data were used to evaluate the rate coefficient for the reaction of the HO radical with CHF₂CHF₂ (see previous data sheet), they are not used in this data sheet.
- (e) Derived from the absolute rate coefficients of Martin and Paraskevopoulos⁶ and Talukdar *et al.*⁷
- (f) Derived from the absolute rate coefficients of Martin

and Paraskevopoulos⁶ and Talukdar *et al.*,⁷ using the three parameter equation $k = CT^2 \exp(-D/T)$.

- (g) Derived from the absolute rate coefficients of Martin and Paraskevopoulos⁶ and Talukdar *et al.*⁷ and the room temperature relative rate coefficient of DeMore.²

Preferred Values

$k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.9 \times 10^{-13} \exp(-1655/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

At room temperature, the measured rate coefficients^{1,2,6–9} cover a range of a factor of ~ 3 , with the rate coefficients of Talukdar *et al.*⁷ and DeMore^{1,2} being the lowest. Combined with the temperature dependence observed by Talukdar *et al.*⁷ being the highest, this suggests the presence of reactive impurities in the CHF_2CF_3 samples used in the studies of Clyne and Holt⁸ and Brown *et al.*⁹ The preferred rate coefficient is derived from the absolute rate coefficients of Martin and Paraskevopoulos⁶ and Talukdar *et al.*⁷

These rate coefficient data^{6,7} were fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 9.46 \times 10^{-19} T^2 \exp(-1126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–364 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, was centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The preferred values are identical with those of our previous evaluation, IUPAC, 1992.³ The relative rate coefficients of DeMore^{1,2} are in good agreement with this recommendation.

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Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$2.87 \times 10^{-12} \exp[-(1661 \pm 170)/T]$ $(1.09 \pm 0.03) \times 10^{-14}$	260–365 298	Zhang <i>et al.</i> , 1994 ¹	(a)
Relative Rate Coefficients			
$6.47 \times 10^{-20} T^{2.58} \exp[-(918 \pm 34)/T]$ 7.47×10^{-15}	286–364 298	Hsu and DeMore, 1995 ²	(b)
Reviews and Evaluations			
$2.4 \times 10^{-12} \exp(-1660/T)$	260–365	NASA, 1994 ³	(c)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3 - H_2O mixtures in the UV in H_2O (or H_2O - O_3)- $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ - CH_4 - O_2 - N_2 mixtures. The concentrations of $\text{CHF}_2\text{CF}_2\text{CH}_2\text{F}$ and CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient of $k(\text{HO} + \text{CHF}_2\text{CF}_2\text{CH}_2\text{F})/k(\text{HO} + \text{CH}_4)$

$= (0.67 \pm 0.07) \exp[(164 \pm 34)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (c) Based on the absolute and relative rate coefficients of Zhang *et al.*¹ and Hsu and DeMore.²

Preferred Values

$k = 7.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.1 \times 10^{-12} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The relative rate coefficients of Hsu and DeMore² are uniformly a factor of 1.5 lower than the absolute rate coefficients of Zhang *et al.*¹ over the temperature range common to both studies (286–364 K). This suggests the presence of reactive impurities or of secondary reactions in the study of Zhang *et al.*¹ The relative rate coefficients of Hsu and

DeMore² are used to derive the preferred values. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter equation, $k = CT^n \exp(-D/T)$, cited in the table with $A = C e^n T^n$ and $B = D + nT$. The temperature dependence of the resultant Arrhenius expression is almost identical to that of Zhang *et al.*¹

References

¹Z. Zhang, S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.* **98**, 4312 (1994).

²K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.6 \times 10^{-13} \exp[-(1107 \pm 202)/T]$ $(6.4 \pm 0.6) \times 10^{-15}$	256–314 295	Garland <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.5 \times 10^{-12} \exp(-1750/T)$	~200–300	NASA, 1994 ²	(b)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals.
- (b) Estimated by analogy with the reaction of the HO radical with $\text{CF}_3\text{CH}_2\text{F}$.

Preferred Values

$k = 6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is that calculated from the Arrhenius expression of Garland *et al.*¹ Because of the low A factor reported by Garland *et al.*,¹ no temperature dependence is recommended.

References

¹N. L. Garland, L. J. Medhurst, and H. H. Nelson, *J. Geophys. Res.* **98**, 23107 (1993).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.0 \times 10^{-13} \exp[-(1007 \pm 151)/T]$ $(6.5 \pm 0.5) \times 10^{-15}$	251–311 294	Garland, Medhurst, and Nelson, 1993 ¹	(a)
$1.05 \times 10^{-12} \exp[-(1434 \pm 161)/T]$ $(8.51 \pm 0.26) \times 10^{-15}$	260–365 298	Zhang <i>et al.</i> , 1994 ²	(b)
<i>Relative Rate Coefficients</i>			
$3.47 \times 10^{-20} T^{2.58} \exp[-(851 \pm 12)/T]$ 4.94×10^{-15}	298–380 298	Hsu and DeMore, 1995 ³	(c)
<i>Reviews and Evaluations</i>			
$1.2 \times 10^{-12} \exp(-1550/T)$	251–365	NASA, 1994 ⁴	(d)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals.
- (b) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (c) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of $\text{O}_3\text{-H}_2\text{O}$ mixtures in the UV, in H_2O (or $\text{O}_3\text{-H}_2\text{O}$)- $\text{CF}_3\text{CHFCHF}_2$ - $\text{CH}_4\text{-O}_2\text{-N}_2$ mixtures. The concentrations of $\text{CF}_3\text{CHFCHF}_2$ and CH_4 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CF}_3\text{CHFCHF}_2)/k(\text{HO} + \text{CH}_4) = (0.36 \pm 0.01) \exp[(231 \pm 12)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Derived from the absolute rate coefficients of Garland *et al.*¹ and Zhang *et al.*² and the relative rate coefficients of Hsu and DeMore.³

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The three studies carried out to date^{1–3} are not in good agreement, with the relative rate coefficients of Hsu and DeMore³ being the lowest and exhibiting the highest temperature dependence. This observation may suggest the presence of reactive impurities in the two absolute rate studies.^{1,2} Accordingly, the relative rate coefficients of Hsu and DeMore³ are used to derive the preferred values. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter equation, $k = CT^n \exp(-D/T)$, of Hsu and DeMore³ cited in the table with $A = C e^n T^n$ and $B = D + nT$.

Preferred Values

$k = 4.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.1 \times 10^{-12} \exp(-1620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

References

- ¹N. L. Garland, L. J. Medhurst, and H. H. Nelson, *J. Geophys. Res.* **98**, 23107 (1993).
²Z. Zhang, S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.* **98**, 4312 (1994).
³K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.0 \times 10^{-14} \exp[-(906 \pm 151)/T]$ 9.6×10^{-16}	257–311 298	Garland, Medhurst, and Nelson, 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$1.19 \times 10^{-18} T^2 \exp[-(1706 \pm 109)/T]$ 3.71×10^{-16}	298–367 298	Hsu and DeMore, 1995 ²	(b)
<i>Reviews and Evaluations</i>			
$7.1 \times 10^{-13} \exp(-2280/T)$		NASA, 1994 ³	(c)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals.
- (b) Relative rate method. HO radicals were generated from the photolysis of H_2O at 185 nm or of $\text{O}_3\text{-H}_2\text{O}$ mixtures in the UV in H_2O (or $\text{O}_3\text{-H}_2\text{O}$)- $\text{CF}_3\text{CH}_2\text{CF}_3$ - CHF_2CF_3 - $\text{O}_2\text{-N}_2$ mixtures. The concentrations of $\text{CF}_3\text{CH}_2\text{CF}_3$ and CHF_2CF_3 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CF}_3\text{CH}_2\text{CF}_3)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = (1.26 \pm 0.41) \exp[-(580 \pm 109)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.46 \times 10^{-19} T^2 \exp(-1126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the relative rate coefficients of Hsu and DeMore.²

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The relative rate coefficient of Hsu and DeMore² at 312 K is a factor of 2.4 lower than the absolute rate coefficient of Garland *et al.*¹ at 311 K (the only temperature common to both studies). Furthermore, the temperature dependence measured by Garland *et al.*¹ is significantly lower than that of Hsu and DeMore² ($B=900 \text{ K}^1$ versus 2300 K^2), suggesting the presence of reactive impurities in the $\text{CF}_3\text{CH}_2\text{CF}_3$ sample used by Garland *et al.*¹

The preferred values are derived from the relative rate coefficients of Hsu and DeMore.² The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter equation, $k = CT^2 \exp(-D/T)$, cited in the table with $A = C e^2 T^2$ and $B = D + 2T$.

Preferred Values

$k = 3.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.9 \times 10^{-13} \exp(-2305/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

References

- ¹N. L. Garland, L. J. Medhurst, and H. H. Nelson, *J. Geophys. Res.* **98**, 23107 (1993).
²K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).
³NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$3.7 \times 10^{-13} \exp[-(1615 \pm 190)/T]$ $(1.65 \pm 0.28) \times 10^{-15}$	294–369 295	Nelson, Zahniser, and Kolb, 1993 ¹	(a)
$3.8 \times 10^{-13} \exp[-(1596 \pm 77)/T]$ $(1.8 \pm 0.2) \times 10^{-15}$	298–463 298	Zellner <i>et al.</i> , 1994 ²	(a)
$3.63 \times 10^{-13} \exp[-(1613 \pm 135)/T]$ $(1.62 \pm 0.03) \times 10^{-15}$	270–365 298	Zhang <i>et al.</i> , 1994 ³	(b)
<i>Relative Rate Coefficients</i>			
$1.64 \times 10^{-20} T^{2.58} \exp[-(965 \pm 105)/T]$ 1.51×10^{-15}	296–398 296	Hsu and DeMore, 1995 ⁴	(c,d)
$7.85 \times 10^{-19} T^2 \exp[-(1088 \pm 89)/T]$ 1.88×10^{-15}	298–367 298	Hsu and DeMore, 1995 ⁴	(c,e)
<i>Reviews and Evaluations</i>			
$5.0 \times 10^{-13} \exp(-1700/T)$	270–463	NASA, 1994 ⁵	(f)

Comments

- (a) Discharge flow system with LIF detection of HO radicals.
- (b) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (c) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or of O_3 - H_2O mixtures in the UV in H_2O (or H_2O - O_3)- $\text{CF}_3\text{CHF}_2\text{CF}_3$ - CH_4 (or CHF_2CF_3)- O_2 - N_2 mixtures. The concentrations of $\text{CF}_3\text{CHF}_2\text{CF}_3$ and CH_4 (or CHF_2CF_3) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CF}_3\text{CHF}_2\text{CF}_3)/k(\text{HO} + \text{CH}_4) = (0.17 \pm 0.05) \times \exp[(117 \pm 105)/T]$ and $k(\text{HO} + \text{CF}_3\text{CHF}_2\text{CF}_3)/k(\text{HO} + \text{CHF}_2\text{CF}_3) = (0.83 \pm 0.22) \exp[(38 \pm 89)/T]$ are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{CHF}_2\text{CF}_3) = 9.46 \times 10^{-19} T^2 \exp(-1126/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Relative to $k(\text{HO} + \text{CH}_4)$.
- (e) Relative to $k(\text{HO} + \text{CHF}_2\text{CF}_3)$.
- (f) Derived from the rate coefficients of Nelson *et al.*,¹ Zellner *et al.*,² Zhang *et al.*,³ Koch and Zetzsch (unpublished data, 1993), and Hsu and DeMore.⁴

Preferred Values

$k = 1.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.5 \times 10^{-13} \exp(-1675/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–463 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are obtained from a least-squares analysis of the absolute rate coefficients of Nelson *et al.*,¹ Zellner *et al.*,² and Zhang *et al.*,³ which are in good agreement and which also agree well with the relative rate coefficients of Hsu and DeMore.⁴

References

- ¹D. D. Nelson, M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **20**, 197 (1993).
²R. Zellner, G. Bednarek, A. Hoffmann, J. P. Kohlmann, V. Mörs, and H. Saathoff, *Ber. Bunsenges. Phys. Chem.* **98**, 141 (1994).
³Z. Zhang, S. Padmaja, R. D. Saini, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.* **98**, 4312 (1994).
⁴K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).
⁵NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.47 \pm 0.2) \times 10^{-14}$	296	Zhang <i>et al.</i> , 1992 ¹	(a)
$5.4 \times 10^{-13} \exp[-(1560 \pm 202)/T]$	269–312	Garland <i>et al.</i> , 1993 ²	(b)
$(3.0 \pm 0.7) \times 10^{-15}$	295		
<i>Reviews and Evaluations</i>			
3.0×10^{-15}	298	NASA, 1994 ³	(c)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO radicals.
- (b) Laser photolysis system with LIF detection of HO radicals.
- (c) Based on the room temperature rate coefficient of Garland *et al.*²

Comments on Preferred Values

The 296 K rate coefficient of Zhang *et al.*¹ is an order of magnitude higher than that of Garland *et al.*,² presumably due to the presence of impurities in the $\text{CHF}_2\text{OCHF}_2$ sample used by Zhang *et al.*^{1,2} The preferred 298 K rate coefficient is derived from the absolute rate coefficients of Garland *et al.*²

Preferred Values

$$k = 2.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

References

¹Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, *J. Phys. Chem.* **96**, 9301 (1992).

²N. L. Garland, L. J. Medhurst, and H. H. Nelson, *J. Geophys. Res.* **98**, 23107 (1993).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -60.1 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$< 5 \times 10^{-15}$	296 $\pm$ 2	Wallington and Hurley, 1993 ¹	(a)

Comments

- (a) Relative rate method. HO radicals generated from the photolysis of $\text{O}_3\text{-H}_2\text{-O}_2$ mixtures, and HC(O)F formed *in situ* from the oxidation of CH_3F . No losses of HC(O)F were observed, leading to a rate coefficient ratio of $k(\text{HO} + \text{HC(O)F})/k(\text{HO} + \text{CH}_3\text{F}) < 0.25$. This upper limit to the rate coefficient ratio is placed on an absolute basis by use of $k(\text{HO} + \text{CH}_3\text{F}) = 1.95 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

Comments on Preferred Values

The preferred value is derived from the sole study of Wallington and Hurley,¹ with the higher upper limit reflecting uncertainties in the reference reaction rate coefficient.

References

¹T. J. Wallington and M. D. Hurley, *Environ. Sci. Technol.* **27**, 1448 (1993).

Preferred Values

$$k < 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.2) \times 10^{-12}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(a)
Relative Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-12}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(b)

Comments

- (a) Laser photolysis system with resonance fluorescence detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO (or $\text{C}_2\text{H}_5\text{ONO}$)-NO- CHF_2CHO -toluene-air mixtures at 1 bar pressure. The concentrations of CHF_2CHO and toluene were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{CHO})/k(\text{HO} + \text{toluene})$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²

Preferred Values

$k = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The absolute and relative rate coefficients of Scollard *et al.*¹ are in good agreement, and the preferred value is the average of these rate coefficients. The reaction is expected to proceed by pathway (1).¹

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).
- ²R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 1**, 1 (1989); **Monograph 2**, 1 (1994).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(6.5 \pm 0.5) \times 10^{-13}$	298	Scollard <i>et al.</i> , 1993 ¹	(a)
Relative Rate Coefficients			
$(5.4 \pm 1.2) \times 10^{-13}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(b)
Reviews and Evaluations			
1.1×10^{-12}	298	IUPAC, 1992 ²	(c)
5.3×10^{-13}	298	Atkinson, 1994 ³	(d)

Comments

- (a) Laser photolysis system with resonance fluorescence detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO (or $\text{C}_2\text{H}_5\text{ONO}$)-NO- CF_3CHO - CH_3COCH_3 -air mixtures at 1 bar pressure. The concentrations of CF_3CHO and CH_3COCH_3 were measured by GC and FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CF}_3\text{CHO})/$

$k(\text{HO} + \text{CH}_3\text{COCH}_3)$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{COCH}_3) = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (c) Based on the absolute rate coefficients of Dóbé *et al.*⁴
- (d) Based on the (as then unpublished) relative rate coefficient of Scollard *et al.*¹

Preferred Values

$$k = 6.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.20 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Scollard *et al.*,¹

which are a factor of 1.7–2.0 lower than the previous absolute room temperature rate coefficient of Dóbé *et al.*⁴

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).
²IUPAC Supplement IV, 1992 (see references in Introduction).
³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
⁴S. Dóbé, L. A. Khachatryan, and T. Bérces, *Ber. Bunsenges. Phys. Chem.* **93**, 847 (1989).

HO + CF₃COOH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.4) \times 10^{-13}$	315	Møgelberg <i>et al.</i> , 1994 ¹	(a)
$(1.5 \pm 0.2) \times 10^{-13}$	348		
<i>Relative Rate Coefficients</i>			
$2.0 \times 10^{-13} \exp[-(156 \pm 400)/T]$	283–323	Carr <i>et al.</i> , 1994 ²	(b,c)
$(1.18 \pm 0.10) \times 10^{-13}$	298 ± 2		
$(1.21 \pm 0.22) \times 10^{-13}$	298 ± 2	Carr <i>et al.</i> , 1994 ²	(b,d)
$(1.75 \pm 0.44) \times 10^{-13}$	296		
		Møgelberg <i>et al.</i> , 1994 ¹	(e)

Comments

- (a) Pulsed radiolysis system with resonance absorption detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the 254 nm photolysis of O₃ in the presence of water vapor in O₃-H₂O-CF₃COOH-C₂H₆ (or C₃H₈)-O₂ mixtures. The concentrations of CF₃COOH and C₂H₆ (or C₃H₈) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CF}_3\text{COOH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.025 \exp[(874 \pm 400)/T]$ (0.47 ± 0.04 at 298 ± 2 K) and $k(\text{HO} + \text{CF}_3\text{COOH})/k(\text{HO} + \text{C}_3\text{H}_8) = 0.11 \pm 0.02$ at 298 K are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{C}_2\text{H}_6) = 7.9 \times 10^{-12} \exp(-1030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{C}_3\text{H}_8) = 1.10 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (this evaluation).
- (c) Relative to $k(\text{OH} + \text{ethane})$.
- (d) Relative to $k(\text{OH} + \text{propane})$.
- (e) Relative rate method. HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of H₂ in O₃-H₂-CF₃COOH-C₂H₆-O₂ mixtures at 740 Torr total pressure. The concentrations of CF₃COOH and ethane were measured by FTIR spectroscopy. The measured rate coefficient ratio was $k(\text{HO} + \text{CF}_3\text{COOH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.59 \pm 0.04$. If the (CF₃COOH)₂ dimer is unreactive towards the HO radical, then the rate coefficient ratio corrected for dimer formation is

0.84 ± 0.06 .¹ An average value of $k(\text{HO} + \text{CF}_3\text{COOH})/k(\text{HO} + \text{C}_2\text{H}_6) = 0.72 \pm 0.18$ was preferred,¹ and is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{C}_2\text{H}_6) = 2.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (this evaluation).

Preferred Values

$k = 1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 283–348 K.

Reliability

$\Delta \log k = \pm 0.20$ over the temperature range 283–348 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the relative and absolute rate coefficients of Møgelberg *et al.*¹ and Carr *et al.*² The reaction is expected to proceed by overall H-atom abstraction from the -OH group to form H₂O + CF₃CO₂ [see the data sheets on the HO radical reactions with HC(O)OH and CH₃C(O)OH].

References

- ¹T. E. Møgelberg, O. J. Nielsen, J. Sehested, T. J. Wallington, and M. D. Hurley, *Chem. Phys. Lett.* **226**, 171 (1994).
²S. Carr, J. J. Treacy, H. W. Sidebottom, R. K. Connell, C. E. Canosa-Mas, R. P. Wayne, and J. Franklin, *Chem. Phys. Lett.* **227**, 39 (1994).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Branching Ratios</i>			
$k_1/k=0.29 \pm 0.08$	295	Wallington <i>et al.</i> , 1994 ¹	(a)
$k_2/k=0.71 \pm 0.11$	295		

Comments

- (a) HO_2 and CH_2FO_2 radicals were generated from the steady-state photolysis of Cl_2 in the presence of CH_3F - H_2 -air mixtures at total pressures of 300–700 Torr. The branching ratios were derived from FTIR analysis of $\text{CH}_2\text{FO}_2\text{H}$ and HCOF , which accounted for $100 \pm 13\%$ of the loss of CH_3F .

Reliability

$$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The lack of a pressure dependence of the branching ratio determined by Wallington *et al.*¹ indicates that there is no thermal decomposition of the products. The observation of two reaction channels for this reaction is in accord with data for other HO_2 reactions with substituted peroxy radicals, for example, with HOCH_2O_2 and $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals.

Preferred Values

$$k_1/k = 0.3 \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.7 \text{ at } 298 \text{ K.}$$

References

- ¹T. J. Wallington, M. D. Hurley, W. F. Schneider, J. Sehested, and O. J. Nielsen, *Chem. Phys. Lett.* **218**, 34 (1994).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-13} \exp[(910 \pm 220)/T]$	210–363	Maricq <i>et al.</i> , 1994 ¹	(a)
$(4.7 \pm 1.7) \times 10^{-12}$	295		
<i>Branching Ratios</i>			
$k_1/k > 0.95$	296	Maricq <i>et al.</i> , 1994 ¹	(b)
$k_2/k < 0.05$	296		

Comments

- (a) Flash photolysis time-resolved UV absorption study of F_2 - $\text{CF}_3\text{CH}_2\text{F}$ - H_2 - O_2 - N_2 mixtures. The rate coefficients were obtained from a fit of the decay curves for CF_3CHFO_2 , HO_2 , CF_3O_2 , and ROOH , based on a mechanism of 14 reactions.
- (b) Steady-state photolysis of Cl_2 - $\text{CF}_3\text{CH}_2\text{F}$ - H_2 - O_2 - N_2 mixtures with FTIR analysis of the products HCOF , CF_3COF , COF_2 , and $\text{CF}_3\text{O}_3\text{CF}_3$. The branching ratio, k_2/k , cited above was based on measurements of CF_3COF , and the value of k_1/k was inferred.

Preferred Values

$$k = 3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.8 \times 10^{-13} \exp(910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 210\text{--}365 \text{ K.}$$

$$k_1/k > 0.95 \text{ at } 298 \text{ K.}$$

$$k_2/k < 0.05 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

Confirmation of both the overall rate coefficient k and the branching ratios are needed. It is interesting to note that the rate coefficient is quite low for this type of reaction; any increase in the rate coefficient which might be anticipated by the presence of an α -F atom in the RO_2 radical is apparently

offset by the decrease caused by the presence of the CF_3 group.

References

- ¹M. M. Maricq, J. J. Szente, M. D. Hurley, and T. J. Wallington, *J. Phys. Chem.* **98**, 8962 (1994).

$$\Delta H^\circ(1) = -172 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -226 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Comments

The $\text{FO} + \text{O}_3$ reaction has two possible pathways which are exothermic, resulting in the production of $\text{F} + 2\text{O}_2$ or $\text{FO}_2 + \text{O}_2$. Although this reaction has not been studied in a simple direct manner, two studies of complex chemical systems have provided some relevant kinetic information. Starrico *et al.*¹ measured quantum yields for ozone destruction in F_2/O_3 mixtures, and attributed the high values, ~ 4600 , to be due to the rapid regeneration of atomic fluorine via the $\text{FO} + \text{O}_3 \rightarrow \text{F} + 2\text{O}_2$ reaction. However, their results are probably also consistent with the chain propagation process being $\text{FO} + \text{FO} \rightarrow 2\text{F} + \text{O}_2$ (the latter reaction has been studied twice (by Wagner *et al.*² and Clyne and Watson³) but although the value of $[\text{F}]_{\text{produced}}/[\text{FO}]_{\text{consumed}}$ is known to be close to unity it has not been accurately determined). Consequently it is impossible to ascertain from the experimental results of Starrico *et al.*¹ whether or not the high quantum yields for ozone destruction should be attributed to the $\text{FO} + \text{O}_3$ reaction producing either $\text{F} + 2\text{O}_2$ or $\text{FO}_2 + \text{O}_2$ (this process is also a chain propagation step if the resulting FO_2 radical preferentially reacts with ozone rather than with either FO or itself). Wagner *et al.*² utilized a low pressure discharge flow-mass spectrometric system to study the $\text{F} + \text{O}_3$ and $\text{FO} + \text{FO}$ reactions by directly monitoring the time history of the concentrations of F, FO, and O_3 . They concluded that the $\text{FO} + \text{O}_3$ reaction was unimportant in their system. However, their paper does not present enough information to warrant this conclusion. Indeed, their value of

$k(\text{FO} + \text{FO})$ of $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is about a factor of 4 greater than that reported by Clyne and Watson,³ which may possibly be attributed to either reactive impurities being present in their system, e.g., $\text{O}(^3\text{P})$, or that the $\text{FO} + \text{O}_3$ reactions were not of negligible importance in their study. Consequently, it is not possible to determine a value for the $\text{FO} + \text{O}_3$ reaction rate constant from existing experimental data. It is worth noting that the analogous $\text{ClO} + \text{O}_3$ reaction is reported⁴ to be extremely slow ($< 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and upper limits of $8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ref. 5) and $5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ⁶ have been reported for $k(\text{BrO} + \text{O}_3)$.

Preferred Values

None.

References

- ¹E. H. Starrico, S. E. Sicre, and H. J. Schumacher, *Z. Physik Chem. N.F.* **31**, 385 (1962).
²H. Gg. Wagner, C. Zetzsch, and J. Warnatz, *Ber. Bunsenges. Phys. Chem.* **76**, 526 (1972).
³M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **70**, 1109 (1974).
⁴W. B. DeMore, C. L. Lin, and S. Jaffe, results presented at ACS meeting Philadelphia, 1975, and 12th Informal Conference on Photochemistry, Washington, D.C. (1976).
⁵M. A. A. Clyne and H. W. Cruse, *Trans. Faraday Soc.* **66**, 2214 (1970).
⁶S. P. Sander and R. T. Watson, *J. Phys. Chem.* **85**, 4000 (1981).

$$\Delta H^\circ = -87 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.5) \times 10^{-11}$	298	Ray and Watson, 1981 ¹	(a)
$1.86 \times 10^{-11} (T/300)^{-(0.66 \pm 0.13)}$	300–845	Bedzhanyan, Markin, and Gershenzon, 1993 ²	(b)
$(1.9 \pm 0.4) \times 10^{-11}$	300		
<i>Reviews and Evaluations</i>			
2.6×10^{-11}	298	IUPAC, 1992 ³	(c)
$8.2 \times 10^{-12} \exp(300/T)$	200–300	NASA, 1994 ⁴	(d)

Comments

$$\Delta(E/R) = \pm 200 \text{ K.}$$

- (a) Discharge flow system with MS detection of FO.
 (b) Discharge flow system. Pseudo-first-order decays of FO radicals in excess NO were monitored by LMR.
 (c) Based on the data of Ray and Watson.¹
 (d) Based on the data of Ray and Watson¹ and Bedzhanyan *et al.*²

Comments on Preferred Values

The preferred room temperature value is the average of the room temperature values from the only two studies.^{1,2} The temperature dependence is derived from a fit to the data of Bedzhanyan *et al.*² and the A-factor is fitted to the preferred room temperature value. The temperature dependence is similar to that for the analogous ClO and BrO radical reactions.

Preferred Values

$$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.2 \times 10^{-12} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 300\text{--}850 \text{ K.}$$

References

- ¹G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
²Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinetics and Catalysis **34**, 1 (1993); original pages 7–10 (1993).
³IUPAC, Supplement IV, 1992 (see references in Introduction).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta H^\circ(1) = -59 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -113 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -218 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.0 \times 10^{-11} (T/300)^{0.85 \pm 0.5}$	300–435	Bedzhanyan, Markin, and Gershenzon, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
1.5×10^{-11}	298	IUPAC, 1992 ²	(b)
1.0×10^{-11}	298–435	NASA, 1994 ³	(c)

Comments

- (b) Based on the data of Clyne and Watson⁴ and Wagner *et al.*⁵

- (a) Discharge flow system with a combined EPR/IR LMR spectrometer.

- (c) Based on the data of Bezghanyan *et al.*¹ and Clyne and Watson.⁴

Preferred Values

$k = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 298–435 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 250 \text{ K}$.

Comments on Preferred Values

The recommended value is based on the results of Bedzhanyan *et al.*¹ and Clyne and Watson.⁴ In a less direct study, Wagner *et al.*⁵ reported a higher value. Although Bedzhan-

yan *et al.*¹ report a weak temperature dependence, a temperature-independent value fits their data equally well and is recommended in this evaluation. This study¹ shows that the predominant reaction channel is that to produce $2\text{F} + \text{O}_2$.

References

¹Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, *Kinetics and Catalysis* **33**, 601 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **70**, 1109 (1974).

⁵H. Gg. Wagner, C. Zetzsch, and J. Warnatz, *Ber. Bunsenges. Phys. Chem.* **76**, 526 (1972).

$\text{FO}_2 + \text{O}_3 \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $< 3.4 \times 10^{-16}$	298	Sehested <i>et al.</i> , 1994 ¹	(a)
<i>Reviews and Evaluations</i> $< 3.4 \times 10^{-16}$	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of $\text{O}_3\text{-O}_2\text{-SF}_6$ mixtures in a high pressure cell at 18 bar of SF_6 . The decay of FO_2 radicals was monitored in absorption at 220 nm.
- (b) Based on the results of Sehested *et al.*¹

Preferred Values

$k < 3.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*¹ This is the sole reported study of this reaction rate coefficient.

References

¹J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, *J. Phys. Chem.* **98**, 6731 (1994).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

$\text{FO}_2 + \text{NO} \rightarrow \text{FNO} + \text{O}_2$

$\Delta H^\circ = -182 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(1.5 \pm 0.1) \times 10^{-12}$	298	Sehested <i>et al.</i> , 1994 ¹	(a)
<i>Reviews and Evaluations</i> 1.5×10^{-12}	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of NO-O₂-SF₆ mixtures in a low pressure cell at 1 bar SF₆. The formation of FNO was monitored in absorption at 310.5 nm. The yield of FNO was determined to be 100±14%.
- (b) Based on the results of Sehested *et al.*¹

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred room temperature rate coefficient is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*¹ This is the sole reported study of this reaction rate coefficient.

References

¹J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, *J. Phys. Chem.* **98**, 6731 (1994).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

FO₂ + NO₂ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(1.05 \pm 0.15) \times 10^{-13}$	298	Sehested <i>et al.</i> , 1994 ¹	(a)
<i>Reviews and Evaluations</i> 1.0×10^{-13}	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of NO₂-O₂-SF₆ mixtures in a low pressure cell at 1 bar SF₆ and also in a high pressure cell at 18 bar SF₆. The decay of NO₂ was monitored in absorption at 400 nm, and that of FO₂ at 220 nm. The rate coefficient showed no dependence on pressure over the pressure range 1 to 18 bar SF₆.
- (b) Based on the results of Sehested *et al.*¹

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred room temperature rate coefficient is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*¹ This is the sole reported study of this reaction rate coefficient. Although the products have not been determined, this reaction can be expected to yield either FO₂NO₂ or FNO₂ + O₂.

References

¹J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, *J. Phys. Chem.* **98**, 6731 (1994).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

FO₂ + CO → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $< 5.1 \times 10^{-16}$	298	Sehested <i>et al.</i> , 1994 ¹	(a)
<i>Reviews and Evaluations</i> $< 5.1 \times 10^{-16}$	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of CO-O₂-SF₆ mixtures in a high pressure cell at 18 bar SF₆. The decay of FO₂ radicals was monitored in absorption at 220 nm.
- (b) Based on the results of Sehested *et al.*¹

Preferred Values

$$k < 5.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*¹ This is the sole reported study of this reaction rate coefficient.

References

¹J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, *J. Phys. Chem.* **98**, 6731 (1994).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

FO₂ + CH₄ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 4.1 \times 10^{-15}$	298	Sehested <i>et al.</i> , 1994 ¹	(a)
<i>Reviews and Evaluations</i>			
$< 4.1 \times 10^{-15}$	298	NASA, 1994 ²	(b)

Comments

- (a) Pulse radiolysis/UV absorption spectroscopy technique. Pulse radiolysis of CH₄-O₂-SF₆ mixtures in a high pressure cell at 18 bar SF₆. The decay of FO₂ radicals was monitored in absorption at 220 nm.
- (b) Based on the results of Sehested *et al.*¹

Preferred Values

$$k < 4.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis/UV absorption study of Sehested *et al.*¹ This is the sole reported study of this reaction rate coefficient.

References

¹J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, *J. Phys. Chem.* **98**, 6731 (1994).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

CF₃ + O₂ + M → CF₃O₂ + M

$$\Delta H^\circ = -146.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficient

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.9 \times 10^{-29} (T/300)^{-4.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

There is good agreement between Refs. 1 and 2 for M = He. The falloff extrapolation uses $F_c = 0.6$.

High-pressure rate coefficient

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 200–400 K.

Comments on Preferred Values

The preferred values are from Ref. 3 because these measurements were done relatively close to the high pressure

limit. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹F. Caralp, R. Lesclaux, and A. M. Dognon, Chem. Phys. Lett. **129**, 433 (1986).
- ²K. R. Ryan and I. C. Plumb, J. Phys. Chem. **86**, 4678 (1982).
- ³R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, Rad. Phys. Chem. **16**, 169 (1980).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 47.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 2 \times 10^{-17}$	298	Turnipseed, Barone, and Ravishankara, 1994 ¹	(a)
$< 4 \times 10^{-17}$	373		
<i>Reviews and Evaluations</i>			
$< 3 \times 10^{-11} \exp(-5000/T)$	250–370	NASA, 1994 ²	(b)

Comments

- (a) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
- (b) Based on the results of Turnipseed *et al.*¹

Preferred Values

$k < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k < 1 \times 10^{-10} \exp(-5600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.

Comments on Preferred Values

The preferred values are based on the upper limit at 373 K reported by Turnipseed *et al.*¹ Assuming that the activation

energy barrier is at least equal to the reaction endothermicity (5600 K) leads to the preferred limits given for the A-factor and for $k(298 \text{ K})$. This procedure using the high temperature limit yields a room temperature limit an order of magnitude lower than the upper limit to the rate coefficient directly determined at 298 K. Chen *et al.*³ in a long path FTIR study of the reaction of CF_3O with NO found no evidence for the reaction of CF_3O with O_2 in 1 bar of air at room temperature.

References

- ¹A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).
- ²NASA Evaluation No. 11, 1994 (see references in Introduction).
- ³J. Chen, T. Zhu, and H. Niki, J. Phys. Chem. **96**, 6115 (1992).

$$\Delta H^\circ = -101.1 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-13}$	295	Nielsen and Sehested, 1993 ¹	(a)
$<5 \times 10^{-14}$	210–353	Maricq and Szente, 1993 ²	(b)
$<2 \times 10^{-15}$	298	Fockenberg, Saathoff, and Zellner, 1994 ³	(c)
$<4 \times 10^{-14}$	298	Ravishankara <i>et al.</i> , 1994 ⁴	(d)
$(2.5^{+0.7}_{-1.5}) \times 10^{-14}$	298	Turnipseed, Barone, and Ravishankara, 1994 ⁵	(e)
$(3.7 \pm 1.5) \times 10^{-14}$	373		
<i>Relative Rate Coefficients</i>			
$<3 \times 10^{-14}$	295	Wallington, Hurley, and Schneider, 1993 ⁶	(f)
<i>Reviews and Evaluations</i>			
$2 \times 10^{-12} \exp(-1300/T)$	250–370	NASA, 1994 ⁷	(g)

Comments

- (a) Pulse radiolysis/UV absorption technique. Radicals generated by pulse radiolysis of $\text{CHF}_3\text{-O}_2\text{-O}_3\text{-SF}_6$ mixtures. Upper limit for k derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of CF_3O and CF_3O_2 radicals.
- (b) Flash photolysis/UV absorption technique. Radicals generated by 351 nm photolysis of F_2 in a flowing $\text{F}_2\text{-CHF}_3\text{-O}_3\text{-O}_2\text{-N}_2$ mixture. O_3 and CF_3O_2 radicals were monitored by absorption at 255 nm, and 210 nm, respectively.
- (c) Laser photolysis/laser-induced fluorescence technique. CF_3O radicals were generated by excimer laser photolysis of CF_3OCl at 351 nm.
- (d) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3 .
- (e) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
- (f) Relative rate technique. Radicals generated by visible photolysis of $\text{CF}_3\text{NO/O}_3$ mixtures in 700 Torr O_2 . Analysis was by FTIR spectroscopy. Value of k was derived by authors from the measured ratio $k/k(\text{CF}_3\text{O} + \text{NO}_2)$ and an estimated value of $k(\text{CF}_3\text{O} + \text{NO}_2)$.
- (g) Based on the results of Turnipseed *et al.*⁵

Preferred Values

$k = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2 \times 10^{-12} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 1$ at 298 K.
 $\Delta(E/R) = \pm 600 \text{ K}$.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.⁷ The preferred value of k at 298 K is based on the results of Turnipseed *et al.*⁵ Using a similar technique, Fockenberg *et al.*³ reported a room temperature value an order of magnitude lower. The higher value of Turnipseed *et al.*⁵ is recommended for use in atmospheric models, but it should be stressed that the true value may be substantially lower. Upper limits reported in the studies of Nielsen and Sehested,¹ Maricq and Szente,² Ravishankara *et al.*,⁴ and Wallington *et al.*⁵ are all consistent with the recommendation. Because of the large uncertainties in the two values of Turnipseed *et al.*,⁵ Arrhenius parameters have not been derived using these values. Rather, the recommended A factor has been estimated by analogy with other CF_3O reactions, and the value of E/R fitted to the preferred room temperature value.

References

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- T. J. Wallington, M. D. Hurley, and W. F. Schneider, *Chem. Phys. Lett.* **213**, 442 (1993).
- NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = 43.4 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$<1 \times 10^{-16}$	298	Turnipseed <i>et al.</i> , 1995 ¹	(a)
$<2 \times 10^{-16}$	381		
<i>Relative Rate Coefficients</i>			
$>2 \times 10^{-18}$	296	Wallington <i>et al.</i> , 1993 ²	(b)
$<4 \times 10^{-16}$	296		
<i>Reviews and Evaluations</i>			
$<3 \times 10^{-12} \exp(-3600/T)$	250–380	NASA, 1994 ³	(c)

Comments

- (a) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
- (b) Long path FTIR-based study. CF_3O radicals generated by chlorine-initiated oxidation of CF_3CFH_2 (HFC-134a) in photolytic mixture of Cl_2 - CF_3CFH_2 - H_2O in 700 Torr air. Reaction rate studied in competition with the rate of $\text{CF}_3\text{O} + \text{CF}_3\text{CFH}_2$.
- (c) Based on the results of Turnipseed *et al.*¹ at 381 K and an estimated A-factor.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.³ The A-factor is estimated by analogy with similar reactions of CF_3O and the activation energy is fitted to the upper limit at 381 K reported by Turnipseed *et al.*¹ Note that this procedure results in a lower limit for E/R ($E/R > 3600$ K). The preferred value of k (298 K) is calculated from the Arrhenius parameters. The limits reported by Wallington *et al.*² are consistent with this preferred value.

References

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- ³NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k < 2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k < 3 \times 10^{-12} \exp(-3600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–380 K.

$$\Delta H^\circ = -135 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(5.2 \pm 2.7) \times 10^{-11}$	295	Sehested and Nielsen, 1993 ¹	(a)
$3.34 \times 10^{-11} \exp[(160 \pm 45)/T]$	233–360	Turnipseed, Barone, and Ravishankara, 1994 ²	(b)
$(5.62 \pm 0.74) \times 10^{-11}$	298		
$4.1 \times 10^{-11} \exp[(60 \pm 100)/T]$	231–393	Jensen, Hanson, and Howard, 1994 ³	(c)
$(5.0 \pm 1.0) \times 10^{-11}$	298		
<i>Reviews and Evaluations</i>			
$3.7 \times 10^{-11} \exp(110/T)$	230–390	NASA, 1994 ⁴	(d)

Comments

- (a) Pulse radiolysis/UV absorption technique. Radicals generated by pulse radiolysis of $\text{CHF}_3\text{-O}_2\text{-NO-SF}_6$ mixtures. Value of k derived from simulations of FNO absorption transients at 310.5 nm.
- (b) Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
- (c) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3 . A low value of k from the same laboratory reported earlier by Bevilacqua *et al.*⁵ is superseded by these results.
- (d) Based on the results of Turnipseed *et al.*,² Jensen *et al.*,³ and Sehested and Nielsen.¹

Preferred Values

$k = 5.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.7 \times 10^{-11} \exp(110/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–390 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.⁴ The preferred values are based on the 233–360 K values of Turnipseed *et al.*,² the 231–393 K values of Jensen *et al.*,³ and the 295 K value of Sehested and Nielsen.¹ These results are in good agreement. The low value of k reported by Bevilacqua *et al.*⁵ has been superseded by the results of Jensen *et al.*³ The reaction products have been reported by Chen *et al.*,⁶ Bevilacqua *et al.*,⁵ and Li and Francisco.⁷

References

- ¹J. Sehested and O. J. Nielsen, Chem. Phys. Lett. **206**, 369 (1993).
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- ³N. R. Jensen, D. R. Hanson, and C. J. Howard, J. Phys. Chem. **98**, 8574 (1994).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
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- ⁶J. Chen, T. Zhu, and H. Niki, J. Phys. Chem. **96**, 6115 (1992).
- ⁷Z. Li and J. S. Francisco, Chem. Phys. Lett. **186**, 336 (1991).

$$\Delta H^\circ = -16.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.2) \times 10^{-14}$	298	Saathoff and Zellner, 1993 ¹	(a)
$1.92 \times 10^{-12} \exp[-(1370 \pm 85)/T]$	247–360	Barone, Turnipseed, and Ravishankara, 1994 ²	(b)
$(1.93 \pm 0.11) \times 10^{-14}$	298		
$3.1 \times 10^{-12} \exp[-(1470 \pm 250)/T]$	231–385	Jensen, Hanson, and Howard, 1944 ³	(c)
$(2.2 \pm 0.4) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$< 5 \times 10^{-15}$	297	Chen <i>et al.</i> , 1992 ⁴	(d)
$(1.2 \pm 0.1) \times 10^{-14}$	298	Kelly <i>et al.</i> , 1993 ⁵	(e)
<i>Reviews and Evaluations</i>			
$2.5 \times 10^{-12} \exp(-1420/T)$	230–380	NASA, 1994 ⁶	(f)

Comments

- (a) Laser photolysis/laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OF at 248 nm.
- (b) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
- (c) Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O radicals were generated by pyrolysis of CF_3OOCF_3 .
- (d) Long path FTIR-based product study of visible pho-

tolysis of $\text{CF}_3\text{NO-NO-CH}_4$ mixtures in 700 Torr air. Searched for CH_2O product from oxidation of CH_4 initiated by reaction of CF_3O radicals with CH_4 . Upper limit of k given in table is derived from the measured ratio $k/k(\text{CF}_3\text{O} + \text{NO}) < 10^{-4}$ and the value of $k(\text{CF}_3\text{O} + \text{NO})$ given in this evaluation.

- (e) Long-path FTIR-based study. CF_3O radicals were generated by photolysis of CF_3OOCF_3 . The decay of the reactant hydrocarbon was compared with the decay of the reference hydrocarbon. The value of k given in the table is derived from the measured ratio

$k/k(\text{CF}_3\text{O} + \text{C}_2\text{H}_6) = 0.010 \pm 0.001$ and the value of $k(\text{CF}_3\text{O} + \text{C}_2\text{H}_6)$ given in this evaluation.

- (f) Based on the results of Saathoff and Zellner,¹ Barone *et al.*,² and Jensen *et al.*³

Preferred Values

$k = 2.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.5 \times 10^{-12} \exp(-1420/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.⁶ The preferred value at room temperature is the average of the values reported by Saathoff and Zellner,¹ Barone *et al.*,² and Jensen *et al.*³ The temperature dependence is based on the 247–360 K data of Barone *et al.*² and the 231–385 K data of Jensen *et al.*³ Results of these

three direct studies are in excellent agreement. The relative rate measurements of Chen *et al.*⁴ and Kelly *et al.*⁵ are factors of 4 and 2, respectively, lower than the preferred value. Jensen *et al.*³ detected the product CF_3OH by chemical ionization mass spectrometer (CIMS) and observed its formation to correlate with the loss of the CF_3O reactant. The CF_3OH product of this reaction was also observed by Bevilacqua *et al.*⁷

References

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$\Delta H^\circ = -32.2 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-12}$	298	Saathoff and Zellner, 1993 ¹	(a)
$4.84 \times 10^{-12} \exp[-(400 \pm 70)/T]$	233–360	Barone, Turnipseed, and Ravishankara, 1994 ²	(b)
$(1.30 \pm 0.11) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.1 \pm 0.6) \times 10^{-12}$	297	Chen <i>et al.</i> , 1992 ³	(c)
Reviews and Evaluations			
$4.7 \times 10^{-12} \exp(-400/T)$	230–360	NASA, 1994 ⁴	(d)

Comments

- (a) Laser photolysis/laser induced fluorescence technique. CF_3O radicals were generated by the photolysis of CF_3OF at 248 nm.
- (b) Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF_3O radicals were generated by the photolysis of $\text{CF}_3\text{OOFCF}_3$ at 193 nm.
- (c) Long path FTIR-based product study of visible photolysis of $\text{CF}_3\text{NO-NO-C}_2\text{H}_6$ mixtures in 700 Torr air. The upper limit of k given in table is derived from measured ratio $k/k(\text{CF}_3\text{O} + \text{NO}) = 0.02 \pm 0.006$ and the value of $k(\text{CF}_3\text{O} + \text{NO})$ given in this evaluation.
- (d) Based on the results of Saathoff and Zellner¹ and Barone *et al.*²

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.7 \times 10^{-12} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–360 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.⁴ The preferred value at room temperature is the average of the values reported by Saathoff and Zellner¹ and Barone *et al.*² The temperature dependence is based on the 233–360 K data of Barone *et al.*² Results of

these direct studies are in excellent agreement. The relative rate measurement of Chen *et al.*³ is in good agreement with the preferred value. Kelly *et al.*⁵ used a relative rate method with FTIR detection to determine the rate of CF₃O reaction with a number of hydrocarbons relative to the rate of the reaction of CF₃O with C₂H₆. They reported $k(\text{CF}_3\text{O} + \text{CH}_4)/k=0.010\pm0.001$ at 298 K and 1 bar pressure.⁵ This is nearly a factor of 2 lower than the ratio of the preferred values given in this evaluation (0.018).

References

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- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵C. Kelly, J. Treacy, H. W. Sidebottom, and O. J. Nielsen, Chem. Phys. Lett. **207**, 498 (1993).

(R = alkyl, halogenated alkyl, H or halogen atom)

Rate coefficient data

Reactions	$k_1 \cdot k_2^{-1} / \text{cm}^3 \text{ molecule}^{-1}$	Temp./K	Reference	Comments
$CH_2FO + O_2 \rightarrow HCOF + HO_2$ (1)	$k_1 [O_2] \gg k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992 ¹	(a)
$CH_2FO + M \rightarrow HCOF + H + M$ (2)	$k_1 [O_2] \gg k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(a)
$CH_3CF_2O + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992 ¹	(b)
$CH_3CF_2O + M \rightarrow CH_3 + COF_2 + M$ (2)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(c)
$CH_2FCHFO + O_2 \rightarrow CH_2FCOF + HO_2$ (1)	$k_1 [O_2] \gg k_2$ (700 Torr, air)	296	Wallington <i>et al.</i> , 1994 ³	(d)
$CH_2FCHFO + M \rightarrow CH_2F + HCOF + M$ (2)				
$CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2$ (1)	$1.58 \times 10^{-25} \exp(3600/T)$	261–353	Wallington <i>et al.</i> , 1992 ⁴	(e)
$CF_3CHFO + M \rightarrow CF_3 + HCOF + M$ (2)	2.8×10^{-20} (2 atm)	298		
	$3.2 \times 10^{-25} \exp(3510/T)$	273–320	Tuazon and Atkinson, 1993 ⁵	(f)
	4.5×10^{-20} (740 Torr)	298		
	$k_1 = 3.7 \times 10^7 \exp(-2200/T) \text{ s}^{-1}$	211–372	Maricq and Szenté, 1992 ⁶	(g)
	$k_1 = 2.3 \times 10^4 \text{ s}^{-1}$ (230 Torr)	298		
	$1.18 \times 10^{-24} \exp(2860/T)$	235–318	Rattigan <i>et al.</i> , 1994 ⁷	(h)
	1.7×10^{-20} (1 atm)	298		
$CF_3CF_2O + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992 ¹	(i)
$CF_3CF_2O + M \rightarrow CF_3 + COF_2 + M$ (2)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(j)
$CHFCIO + O_2 \rightarrow COFCl + HO_2$ (1)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(k)
$CHFCIO + M \rightarrow HCOF + Cl + M$ (2)				
$CF_2ClO + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992 ¹	(l)
$CF_2ClO + M \rightarrow COF_2 + Cl + M$ (2)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(m)
$CFCl_2O + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(n)
$CFCl_2O + M \rightarrow COFCl + Cl + M$ (2)				
$CF_2ClCH_2O + O_2 \rightarrow CF_2ClCHO + HO_2$ (1)	$k_1 [O_2] \gg k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994 ⁸	(o)
$CF_2ClCH_2O + M \rightarrow CF_2Cl + HCHO + M$ (2)				
$CFCl_2CH_2O + O_2 \rightarrow CFCl_2CHO + HO_2$ (1)	$k_1 [O_2] \gg k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994 ⁸	(p)
$CFCl_2CH_2O + M \rightarrow CFCl_2 + HCHO + M$ (2)				
$CF_3CFCIO + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (700 Torr, air)	298	Edney and Driscoll, 1992 ¹	(q)
$CF_3CFCIO + M \rightarrow CF_3COF + Cl + M$ (2)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(r)
$CF_3CCl_2O + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (700 Torr, air)	296	Edney, Gay, and Driscoll, 1991 ⁹	(s)
$CF_3CCl_2O + M \rightarrow CF_3COCl + Cl + M$ (2)	$k_1 [O_2] \ll k_2$ (102 Torr, O_2)	298	Sato and Nakamura, 1991 ¹⁰	(t)
	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1993 ²	(u)
	$k_1 [O_2] \ll k_2$ (~1 atm, air)	298	Hayman <i>et al.</i> , 1993 ¹¹	(v)
$CF_3CF_2CCl_2O + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (102 Torr, O_2)	298	Sato and Nakamura, 1991 ¹⁰	(w)
$CF_3CF_2CCl_2O + M \rightarrow CF_3CF_2COCl + Cl + M$ (2)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994 ⁸	(x)
$CF_2ClCF_2CFCIO + O_2 \rightarrow \text{products}$ (1)	$k_1 [O_2] \ll k_2$ (102 Torr, O_2)	298	Sato and Nakamura, 1991 ¹⁰	(y)
$CF_2ClCF_2CFCIO + M \rightarrow CF_2ClCF_2COF + Cl + M$ (2)	$k_1 [O_2] \ll k_2$ (740 Torr, air)	298	Tuazon and Atkinson, 1994 ⁸	(z)

Rate coefficient data—Continued

Reactions	$k_1 \cdot k_2^{-1} / \text{cm}^3 \text{ molecule}^{-1}$	Temp./K	Reference	Comments
$\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{HCOCl} + \text{HO}_2$ (1)	4.6×10^{-18} (700 Torr, $\text{O}_2 + \text{N}_2$)	296	Kaiser and Wallington, 1993 ¹²	(aa)
$\text{CH}_2\text{ClO} + \text{M} \rightarrow \text{HCO} + \text{HCl} + \text{M}$ (2)				
$\text{CH}_3\text{CHClO} + \text{O}_2 \rightarrow \text{CH}_3\text{COCl} + \text{HO}_2$ (1)	$k_1 [\text{O}_2] \ll k_2$ (700 Torr, air)	295	Shi, Wallington, and Kaiser, 1993 ¹³	(bb)
$\text{CH}_3\text{CHClO} + \text{M} \rightarrow \text{CH}_3\text{CO} + \text{HCl} + \text{M}$ (2)	$k_1 [\text{O}_2] \ll k_2$ (760 Torr, air)	298	Maricq <i>et al.</i> , 1993 ¹⁴	(cc)
$\text{HOCH}_2\text{CHClO} + \text{O}_2 \rightarrow \text{HOCH}_2\text{COCl} + \text{HO}_2$ (1)	$k_1 [\text{O}_2] \ll k_2$ (740 Torr, air)	298	Tuazon <i>et al.</i> , 1988 ¹⁵	(dd)
$\text{HOCH}_2\text{CHClO} + \text{M} \rightarrow \text{CH}_2\text{OH} + \text{HCOCl} + \text{M}$ (2)				
$\text{HOCHClCH}_2\text{O} + \text{O}_2 \rightarrow \text{HOCHClCHO} + \text{HO}_2$ (1)	$k_1 [\text{O}_2] \ll k_2$ (740 Torr, air)	298	Tuazon <i>et al.</i> , 1988 ¹⁵	(dd)
$\text{HOCHClCH}_2\text{O} + \text{M} \rightarrow \text{CHClOH} + \text{HCHO} + \text{M}$ (2)				
$\text{CH}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$ (1)	$k_1 [\text{O}_2] \ll k_2$ (700 Torr, O_2)	298	Nelson <i>et al.</i> , 1990 ¹⁶	(ee)
$\text{CH}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{COCl} + \text{Cl} + \text{M}$ (2)				
$\text{CCl}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CCl}_3\text{CHO} + \text{HO}_2$ (1)	$k_1 [\text{O}_2] \gg k_2$ (100 Torr, O_2)	298	Nelson <i>et al.</i> , 1990 ¹⁶	(ff)
$\text{CCl}_3\text{CH}_2\text{O} + \text{M} \rightarrow \text{CCl}_3 + \text{HCHO} + \text{M}$ (2)				
$\text{CCl}_3\text{CCl}_2\text{O} + \text{O}_2 \rightarrow \text{products}$ (1)	$k_1 [\text{O}_2] \ll k_2$	298	Sato and Nakamura, 1991 ¹⁰	(gg)
$\text{CCl}_3\text{CCl}_2\text{O} + \text{M} \rightarrow \text{CCl}_3\text{COCl} + \text{Cl} + \text{M}$ (2)				

Comments

- (a) Steady-state photolyses of Cl_2 in the presence of CH_3F -air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a 100% yield of HCOF was observed, consistent with $k_1[\text{O}_2] \gg k_2$.
- (b) Steady-state photolysis of Cl_2 in the presence of CH_3CHF_2 -air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a $100 \pm 5\%$ yield of COF_2 was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (c) Similar experiments to those of Comment (b); a $92.2 \pm 1.2\%$ yield of COF_2 plus other unidentified products was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (d) Steady-state photolysis of Cl_2 in the presence of $\text{CH}_2\text{FCH}_2\text{F}$ -air mixtures (700 Torr) with FTIR analysis; a $91 \pm 10\%$ yield of HCOF was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (e) Steady-state photolyses of Cl_2 in the presence of CF_3CFH_2 - O_2 - N_2 mixtures at total pressures of 2 atm with FTIR analyses of products CF_3COF and HCOF . The ratio k_1/k_2 was found to be pressure dependent over the range 20–550 Torr but approximately independent of pressure above 700 Torr.
- (f) Similar experiments to those of Comment (e) at a total pressure of 740 Torr.
- (g) Flash-photolysis time-resolved UV absorption spectroscopic study of CF_3CHFO_2 radicals from F_2 - $\text{CF}_3\text{CH}_2\text{F}$ - O_2 - N_2 mixtures, k_1 obtained from a fit of CF_3O_2 formation profiles, produced from reaction (1) followed by $\text{CF}_3 + \text{O}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2 + \text{M}$. Experiments were carried out at a total pressure of 230 Torr, well below the high-pressure limit.
- (h) Cl_2 -initiated photooxidation of $\text{CF}_3\text{CH}_2\text{F}$ at 1 atm pressure, with dual-beam diode-array UV spectroscopic determination of CF_3COF and HCOF products.
- (i) Steady-state photolyses of Cl_2 in the presence of CF_3CHF_2 -air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a $109 \pm 5\%$ yield of COF_2 was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (j) Similar experiments to those of comment (i) at a total pressure of 740 Torr; a $\sim 100\%$ yield of COF_2 was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (k) Steady-state photolysis of Cl_2 in the presence of CH_2FCl -air mixtures (740 Torr) with FTIR absorption spectroscopic analyses; a 100% yield of HCOF was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (l) Steady-state photolyses of Cl_2 in the presence of CH_2FCl -air mixtures (700 Torr) with FTIR absorption spectroscopic analysis; a $111 \pm 6\%$ yield of COF_2 was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (m) Similar experiments to those of Comment (l) at a total pressure of 740 Torr; a 100% yield of COF_2 was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (n) Steady-state photolysis of Cl_2 in the presence of CHFCl_2 -air mixtures (740 Torr) with FTIR absorption spectroscopic analyses; a 100% yield of COFCl was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (o) Steady-state photolyses of Cl_2 in the presence of $\text{CH}_3\text{CF}_2\text{Cl}$ -air mixtures (740 Torr) with FTIR spectroscopic analysis. A 100% yield of CF_2ClCHO was observed, consistent with $k_1[\text{O}_2] \gg k_2$. Experiments on this reaction were also carried out by Edney and Driscoll¹ and Tuazon and Atkinson.²
- (p) Steady-state photolysis of Cl_2 in the presence of CH_3CFCl_2 -air mixtures (740 Torr) with FTIR analysis; a 100% yield of CFCl_2CHO was observed, consistent with $k_1[\text{O}_2] \gg k_2$. Experiments on this system were also carried out by Tuazon and Atkinson¹ and Edney *et al.*⁹
- (q) Steady-state photolyses of Cl_2 in the presence of CF_3CHFCl -air mixtures (1 atm) with FTIR absorption spectroscopic analyses; a $100 \pm 4\%$ yield of CF_3COF was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (r) Steady-state photolysis of Cl_2 in the presence of CF_3CHFCl -air mixtures at 740 Torr total pressure with FTIR absorption spectroscopic analyses; a $101 \pm 1\%$ yield of CF_3COF was observed, consistent with $k_2 \gg k_1[\text{O}_2]$.
- (s) Steady-state photolyses of Cl_2 in the presence of CF_3CHCl_2 -air mixtures (700 Torr) with FTIR absorption spectroscopic analysis; a $\sim 100\%$ yield of CF_3COCl was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (t) Similar experiments to those of Comment (s) at a total pressure of 100 Torr. The observed formation of CF_3COCl is consistent with $k_1[\text{O}_2] \ll k_2$.
- (u) Similar experiments to those of Comment (s) at a total pressure of 740 Torr; a 98% yield of CF_3COCl was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (v) Steady-state photolysis of Cl_2 in the presence of CF_3CHCl_2 -air mixtures (~ 1 atm) with broad-band UV absorption analysis; a $\sim 100\%$ yield of CF_3COCl was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (w) Steady-state photolysis of Cl_2 in the presence of $\text{CF}_3\text{CF}_2\text{CHCl}_2$ - O_2 mixtures (100 Torr) with FTIR spectroscopic analysis; observed formation of $\text{CF}_3\text{CF}_2\text{COCl}$ is consistent with $k_1[\text{O}_2] \ll k_2$.
- (x) Steady-state photolysis of Cl_2 in the presence of $\text{CF}_3\text{CF}_2\text{CHCl}_2$ -air mixtures (740 Torr) with FTIR spectroscopic analysis; a 100% yield of $\text{CF}_3\text{CF}_2\text{COCl}$ was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (y) Steady-state photolysis of Cl_2 in the presence of $\text{CF}_2\text{ClCF}_2\text{CHFCl}$ - O_2 mixtures (100 Torr) with FTIR spectroscopic analysis; observed formation of $\text{CF}_2\text{ClCF}_2\text{COF}$ is consistent with $k_1[\text{O}_2] \ll k_2$.
- (z) Steady-state photolysis of Cl_2 in the presence of $\text{CF}_2\text{ClCF}_2\text{CHFCl}$ -air mixtures (740 Torr) with FTIR spectroscopic analysis; a 99% yield of $\text{CF}_2\text{ClCF}_2\text{COF}$ was observed, consistent with $k_1[\text{O}_2] \ll k_2$.
- (aa) Steady-state photolysis of Cl_2 in the presence of CH_3Cl - O_2 - N_2 mixtures with FTIR spectroscopic analysis of HOCl , CO , HCl , and CH_2ClCOOH products. k_1/k_2 based on yields of CO and HOCl , the latter being corrected for secondary formation and removal. The

ratio k_1/k_2 was found to be markedly pressure dependent over the range 12 to 700 Torr, and the cited value refers to 700 Torr total pressure.

- (bb) Steady-state photolysis of Cl_2 in the presence of $\text{C}_2\text{H}_5\text{Cl}-\text{O}_2-\text{N}_2$ mixture with FTIR spectroscopic analysis of products; the observed high yields of HCl (157%) and CO_2 (53%) were explained by reaction (2).
- (cc) Laser flash photolyses of Cl_2 in the presence of $\text{C}_2\text{H}_5\text{Cl}$ -air mixtures with transient infrared absorption detection of HCl. The observed secondary formation of HCl was explained by reaction (2).
- (dd) Steady-state photolysis of CH_3ONO or $\text{C}_2\text{H}_5\text{ONO}$ in the presence of chloroethene-NO-air mixtures, with and without C_2H_6 as an added Cl atom scavenger. FTIR spectroscopic analysis of HCHO and HCOCl products, with close to unit yields of each. These products and their formation yields are consistent with the qualitative relative values of $k_1[\text{O}_2]$ and k_2 as shown above.
- (ee) Steady-state photolyses of $\text{CH}_3\text{CCl}_3-\text{O}_2$ mixtures in the presence of Br_2 or NO (to scavenge Cl atoms), with GC and IR analyses of products. CH_3COCl was the major product observed, consistent with the relative values of $k_1[\text{O}_2]$ and k_2 shown above.
- (ff) Steady-state photolysis of Cl_2 in the presence of $\text{CH}_3\text{CCl}_3-\text{O}_2$ mixtures with GC and IR analyses of CCl_3CHO and COCl_2 , which are consistent with the relative values of $k_1[\text{O}_2]$ and k_2 shown above.
- (gg) Steady-state photolysis of Cl_2 in the presence of $\text{CHCl}_2\text{CCl}_3-\text{O}_2$ mixtures (100 Torr) with FTIR spectroscopic analysis. The observed formation of yields of CCl_3COCl and COCl_2 are consistent with the relative values of $k_1[\text{O}_2]$ and k_2 shown above.

Preferred Values

$k_1/k_2 = 2.7 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K and 1 atm pressure.

$k_1/k_2 = 1.1 \times 10^{-25} \exp(3700/T) \text{ cm}^3 \text{ molecule}^{-1}$ over the temperature range 260–355 K and 1 bar pressure.

$\Delta(E/R) = \pm 500 \text{ K}$.

$k_1/k_2 = 4.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K.

Comments on Preferred Values

The recommended temperature dependence rate coefficient ratio is that evaluated by Rattigan *et al.*⁷ from their own data together with those of Wallington *et al.*,⁴ Tuazon and Atkinson,⁵ and Maricq and Szenté.⁶

The elimination of HCl occurs from the CH_3CHClO radical^{13,14} as well as from the CH_2ClO radical.¹²

For the purposes of atmospheric modeling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or other of the alkoxy radical reaction pathways predominates or if both pathways should be considered.

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(R = CH₂F, CHF₂, CF₃, CH₂FCHF, CHF₂CF₂, CF₃CHF, CF₃CF₂, CF₂Cl, CFCl₂, CF₂ClCH₂, CFCl₂CH₂, CF₃CCl₂, CH₂Cl, CCl₃, CH₂Br)

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
R = CH ₂ F $(1.25 \pm 0.13) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CHF ₂ $(1.26 \pm 0.16) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CF ₃ $(1.78 \pm 0.36) \times 10^{-11}$	295	Plumb and Ryan, 1982 ²	(b)
$1.45 \times 10^{-11} (T/298)^{-(1.2 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985 ³	(c)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
$(1.53 \pm 0.30) \times 10^{-11}$	290	Peeters, Vertommen, and Langhans, 1992 ⁴	(d)
$(1.68 \pm 0.26) \times 10^{-11}$	295	Sehested and Nielsen, 1993 ⁵	(a)
$(1.53 \pm 0.20) \times 10^{-11}$	297	Bevilacqua, Hanson, and Howard, 1993 ⁶	(e)
$(1.57 \pm 0.38) \times 10^{-11}$	298	Turnipseed, Barone, and Ravishankara, 1994 ⁷	(f)
R = CH ₂ FCHF $> 8.7 \times 10^{-12}$	296	Wallington <i>et al.</i> , 1994 ⁸	(a)
R = CHF ₂ CF ₂ $> (9.7 \pm 1.3) \times 10^{-12}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CF ₃ CHF $(1.28 \pm 0.36) \times 10^{-11}$	298	Wallington and Nielsen, 1991 ⁹	(a)
R = CF ₃ CF ₂ $> (1.07 \pm 0.15) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CF ₂ Cl $1.6 \times 10^{-11} (T/298)^{-(1.5 \pm 0.4)}$	230–430	Dognon, Caralp, and Lesclaux, 1985 ³	(c)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$(1.31 \pm 0.12) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CFCl ₂ $(1.6 \pm 0.2) \times 10^{-11}$	298	Lesclaux and Caralp, 1984 ¹⁰	(g)
$1.45 \times 10^{-11} (T/298)^{-(1.3 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985 ³	(c)
$(1.45 \pm 0.2) \times 10^{-11}$	298		
R = CF ₂ ClCH ₂ $(1.18 \pm 0.10) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CFCl ₂ CH ₂ $(1.28 \pm 0.11) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CF ₃ CCl ₂ $(1.5\text{--}2.0) \times 10^{-11}$	298	Hayman <i>et al.</i> , 1994 ¹¹	(h)
R = CH ₂ Cl $(1.87 \pm 0.20) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
R = CCl ₃ $(1.86 \pm 0.28) \times 10^{-11}$	295	Ryan and Plumb, 1984 ¹²	(i)
$1.7 \times 10^{-11} (T/298)^{-(1.0 \pm 0.2)}$	230–430	Dognon, Caralp, and Lesclaux, 1985 ³	(c)
$(1.7 \pm 0.2) \times 10^{-11}$	298		
R = CH ₂ Br $(1.07 \pm 0.11) \times 10^{-11}$	295	Sehested, Nielsen, and Wallington, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
R = CF ₃ $1.6 \times 10^{-11} (T/300)^{-1.2}$	230–430	IUPAC, 1992 ¹³	(j)
$5.4 \times 10^{-12} \exp[(320 \pm 150)/T]$	230–430	NASA, 1994 ¹⁴	(k)
$1.6 \times 10^{-11} (T/298)^{-1.2}$	228–433	Lightfoot <i>et al.</i> , 1992 ¹⁵	(l)
$1.45 \times 10^{-11} (T/298)^{-1.2}$	230–430	Wallington <i>et al.</i> , 1992 ¹⁶	(l)
R = CF ₃ CHF 1.28×10^{-11}	298	Lightfoot <i>et al.</i> , 1992 ¹⁵	(m)

Rate coefficient data—Continued

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
$R = \text{CF}_2\text{Cl} \quad 1.6 \times 10^{-11} (T/300)^{-1.5}$	230–430	IUPAC, 1992 ¹³	(l)
$3.8 \times 10^{-12} \exp[(400 \pm 200)/T]$	230–430	NASA, 1992 ¹⁴	(n)
$1.6 \times 10^{-11} (T/298)^{-1.5}$	228–413	Lightfoot <i>et al.</i> , 1992 ¹⁵	(l)
$1.6 \times 10^{-11} (T/298)^{-1.5}$	230–430	Wallington <i>et al.</i> , 1992 ¹⁶	(l)
$R = \text{CFCl}_2 \quad 1.5 \times 10^{-11} (T/300)^{-1.3}$	230–430	IUPAC, 1992 ¹³	(l)
$4.5 \times 10^{-12} \exp[(350 \pm 200)/T]$	230–430	NASA, 1992 ¹⁴	(l)
$1.5 \times 10^{-11} (T/298)^{-1.3}$	228–413	Lightfoot <i>et al.</i> , 1992 ¹⁵	(l)
$1.45 \times 10^{-11} (T/298)^{-1.3}$	230–430	Wallington <i>et al.</i> , 1992 ¹⁶	(l)
$R = \text{CCl}_3 \quad 1.8 \times 10^{-11} (T/300)^{-1.0}$	230–430	IUPAC, 1992 ¹³	(j)
$5.7 \times 10^{-12} \exp[(330 \pm 200)/T]$	230–430	NASA, 1992 ¹⁴	(j)
$1.8 \times 10^{-11} (T/298)^{-1.0}$	229–413	Lightfoot <i>et al.</i> , 1992 ¹⁵	(l)
$1.7 \times 10^{-11} (T/298)^{-1.0}$	230–430	Wallington <i>et al.</i> , 1992 ¹⁶	(l)

Comments

- (a) Pulse-radiolysis combined with time-resolved UV-VIS absorption spectroscopy; k determined from $+d[\text{NO}_2]/dt$ at a total pressure of 1 bar.
- (b) Discharge flow-mass spectrometry system used. The rate coefficient was independent of pressure over the range 1.9–5.1 Torr.
- (c) Pulsed laser photolysis-mass spectrometry system used. No significant pressure dependence of the rate coefficient over the range 1–10 Torr was observed.
- (d) Fast-flow system with molecular beam sampling MS at total pressures of 2 Torr; k was derived from decay of CF_3O_2 and appearance of NO_2 .
- (e) Flow tube reactor coupled to chemical ionization MS. k determined from decay of CF_3O_2 in the presence of NO; pressure range 0.8–2 Torr.
- (f) Pulsed laser photolysis of CF_3Br in the presence of O_2 and NO at 70 Torr total pressure. CF_3O radicals were detected by LIF and the rate coefficient k was obtained by fitting the measured CF_3O radical temporal profile, with formation through $\text{CF}_3\text{O}_2 + \text{NO}$ and loss through $\text{CF}_3\text{O} + \text{NO}$.
- (g) Pulsed laser photolysis-mass spectrometry system used. Measurements were made at 2 Torr total pressure.
- (h) Laser flash photolysis system with time-resolved UV absorption spectroscopy for $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals at a total pressure of 1 atm. k derived from computer fit of transient absorption traces based on a mechanism of 9 reactions.
- (i) Discharge flow-mass spectrometry system used. The rate coefficient was independent of pressure over the range 1.7–5.4 Torr.
- (j) Based on the rate coefficients of Plumb and Ryan^{2,12} and Dognon *et al.*³
- (k) Based on the rate coefficients of Plumb and Ryan,² Dognon *et al.*,³ Peeters *et al.*,⁴ Sehested and Nielsen,⁵ Bevilacqua *et al.*,⁶ and Turnipseed *et al.*⁷
- (l) Recommendation based on the results of Dognon *et al.*³
- (m) Recommendation based on the results of Wallington and Nielsen.⁹
- (n) Based on the rate coefficients of Dognon *et al.*³ and Sehested *et al.*¹

Preferred Values

$\text{R} = \text{CH}_2\text{F}$
 $k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CHF}_2$
 $k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CF}_3$
 $k = 1.6 \times 10^{-11} (T/298)^{-1.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–430 K.

$\Delta \log k = \pm 0.15$ over the temperature range 230–430 K.

$\text{R} = \text{CH}_2\text{FCHF}$
 $k > 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$\text{R} = \text{CHF}_2\text{CF}_2$
 $k > 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$\text{R} = \text{CF}_3\text{CHF}$
 $k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CF}_3\text{CF}_2$
 $k > 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$\text{R} = \text{CF}_2\text{Cl}$
 $k = 1.5 \times 10^{-11} (T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–430 K.
 $\Delta \log k = \pm 0.2$ over the temperature range 230–430 K.

$\text{R} = \text{CFCl}_2$
 $k = 1.5 \times 10^{-11} (T/298)^{-1.3} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–430 K.
 $\Delta \log k = \pm 0.2$ over the temperature range 230–430 K.

$\text{R} = \text{CF}_2\text{ClCH}_2$
 $k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CFCl}_2\text{CH}_2$
 $k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CF}_3\text{CCl}_2$
 $k = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CH}_2\text{Cl}$
 $k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

$\text{R} = \text{CCl}_3$
 $k = 1.8 \times 10^{-11} (T/298)^{-1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–430 K.
 $\Delta \log k = \pm 0.2$ over the temperature range 230–430 K.

$\text{R} = \text{CH}_2\text{Br}$
 $k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

$\text{R} = \text{CH}_2\text{F}$, CHF_2 , CHF_2CF_2 , CF_3CF_2 , CF_2ClCH_2 , CFCl_2CH_2 , CH_2Cl , CH_2Br

The preferred values are the rounded-off rate coefficients determined by Sehested *et al.*¹

$\text{R} = \text{CF}_3$

The preferred values are based on the temperature dependent data of Dognon *et al.*,³ adjusted to fit the average value of k_{298} from the data of Plumb and Ryan,² Dognon *et al.*,³ Peeters *et al.*,⁴ Sehested and Nielsen,⁵ Bevilacqua *et al.*,⁶ and Turnipseed *et al.*⁷

$\text{R} = \text{CH}_2\text{FCHF}$

The preferred value is the rounded-off lower limit of Wallington *et al.*⁸

$\text{R} = \text{CF}_3\text{CHF}$

The preferred value is the rounded-off rate coefficient determined by Wallington and Nielsen.⁹

$\text{R} = \text{CF}_2\text{Cl}$

The preferred values are based on the temperature depen-

dent data of Dognon *et al.*³ adjusted to fit the average value of k_{298} from the data of Sehested *et al.*¹ and Dognon *et al.*³
 $R = \text{CFCl}_2$

The preferred values are based on the temperature dependent data of Dognon *et al.*,³ adjusted to fit the average value of k_{298} from the data of Lesclaux and Caralp¹⁰ and Dognon *et al.*³

$R = \text{CF}_3\text{CCl}_2$

The preferred value is the mid-point of the range of values determined by Hayman *et al.*¹¹

$R = \text{CCl}_3$

The preferred values are based on the temperature dependent data of Dognon *et al.*,³ adjusted to fit the average value of k_{298} from the data of Ryan and Plumb¹² and Dognon *et al.*³

The temperature dependence expressions are given in the form favored by Dognon *et al.*,³ which best describe the measured data. If Arrhenius expressions are required, then the expressions recommended by NASA, 1994¹⁴ should be employed. In view of the consistent observation of pressure independence, it seems unlikely that RONO_2 is produced as a product. Dognon *et al.*³ measured quantum yields for NO_2 greater than unity for all the RO_2 radicals studied; suggesting that the $\text{RO}_2 + \text{NO}$ reactions form RO and NO_2 exclusively,

with additional NO_2 being produced from secondary chemistry.

References

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- ¹⁰R. Lesclaux and F. Caralp, *Int. J. Chem. Kinet.* **16**, 1117 (1984).
- ¹¹G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, *Atmos. Environ.* **28A**, 421 (1994).
- ¹²K. R. Ryan and I. C. Plumb, *Int. J. Chem. Kinet.* **16**, 591 (1984).
- ¹³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ¹⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ¹⁵P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ¹⁶T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).

$$\Delta H^\circ = -184.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 5 \times 10^{-15}$	295	Nielsen and Sehested, 1993 ¹	(a)
$< 1 \times 10^{-14}$	210–353	Maricq and Sente, 1993 ²	(b)
$< 3 \times 10^{-15}$	298	Ravishankara <i>et al.</i> , 1994 ³	(c)
$< 7 \times 10^{-15}$	298	Turnipseed, Barone, and Ravishankara, 1994 ⁴	(d)
<i>Reviews and Evaluations</i>			
$< 3 \times 10^{-15}$	298	NASA, 1994 ⁵	(e)

Comments

- Pulse radiolysis/UV absorption technique. Radicals were generated by pulse radiolysis of $\text{CHF}_3\text{-O}_2\text{-O}_3\text{-SF}_6$ mixtures. Upper limit for k derived from simulations of ozone absorption transients at 254 nm and 276 nm in the presence of CF_3O and CF_3O_2 .
- Flash photolysis/UV absorption technique. Radicals were generated by 351 nm photolysis of F_2 in a flowing $\text{F}_2\text{-CHF}_3\text{-O}_3\text{-O}_2\text{-N}_2$ mixture. O_3 and CF_3O_2 radicals were monitored by absorption at 255 nm and 210 nm, respectively.

- Flow tube reactor/chemical ionization mass spectrometer technique. CF_3O_2 radicals were generated by pyrolysis of CF_3I in the presence of O_2 .
- Pulsed laser photolysis/pulsed laser-induced fluorescence technique. CF_3O_2 radicals were generated by photolysis of $\text{CF}_3\text{Br-O}_2\text{-NO}$ mixtures.
- Based on the results of Ravishankara *et al.*³

Preferred Values

$$k < 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

This evaluation accepts the recommendation of the NASA Panel for Data Evaluation.⁵ The preferred upper limit at 298 K is based on the results of Ravishankara *et al.*³ In that study the temporal profile of CF₃O₂ radicals was measured in a flow tube reactor with chemical ionization mass spectrometry detection of CF₃O₂ in excess O₃. An excess of isobutane was added to scavenge any CF₃O produced and thereby inhibit the possible regeneration of CF₃O₂ by reaction of the product CF₃O with O₃. No measurable reaction was observed. Less sensitive upper limits were reported in the less

direct studies of Nielsen and Sehested,¹ Maricq and Szenté,² and Turnipseed *et al.*⁴

References

- ¹O. J. Nielsen and J. Sehested, Chem. Phys. Lett. **213**, 433 (1993).
- ²M. M. Maricq and J. J. Szenté, Chem. Phys. Lett. **213**, 449 (1993).
- ³A. R. Ravishankara, A. A. Turnipseed, N. R. Jensen, S. Barone, M. Mills, C. J. Howard, and S. Solomon, Science **263**, 71 (1994).
- ⁴A. A. Turnipseed, S. B. Barone, and A. R. Ravishankara, J. Phys. Chem. **98**, 4594 (1994).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -105 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 4.5 \times 10^{-29} (T/300)^{-6.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 220–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The preferred values correspond to the theoretical analysis of Ref. 1, which was based on the experiments of Ref. 2. A value of $F_c = 0.28$ at 300 K was calculated and used. In contrast to Ref. 1, however, an adjustment of ΔH_0° to the value of $-103.6 \text{ kJ mol}^{-1}$ was made in order to meet the trend for formation of other CX₃O₂NO₂ (X = Cl, F) which were investigated in Ref. 3. This modifies the k_0 values in the indicated way. Falloff curves correspond to $F_c = 0.28$ at 220–300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ over the temperature range 200–300 K.}$$

Comments on Preferred Values

See comment to k_0 . Because the measurements were made at low pressures only, the extrapolation to k_∞ remains fairly

uncertain. F_c was calculated¹ to be close to 0.28 over the temperature range 220–300 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).
- ²F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, J. Chem. Soc. Faraday Trans. 2, **84**, 569 (1988).
- ³D. Köppenastrop and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 105 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 3.6 \times 10^{-19} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 5 \times 10^{-1} (T/300)^{-6} \exp(-12460/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 233\text{--}373 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.4 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred values are from the theoretical analysis of Ref. 1 which is based on measurements of the reverse reaction² and calculated equilibrium constants with $\Delta H_0^\circ = 103.6 \text{ kJ mol}^{-1}$, adjusted to meet the extrapolated value of Ref. 3. $F_c = 0.28$ was calculated¹ for 220–300 K. Direct measurements of the dissociation rate are required together with measurements over a wider pressure range. $F_c = 0.28$ is used for falloff curves over the range 220–300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 5.6 \times 10^{-2} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_\infty = 1.2 \times 10^{17} \exp(-12580/T) \text{ s}^{-1} \text{ over the temperature range } 233\text{--}373 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

See comments on k_0 . The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).
- ²F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, *J. Chem. Soc. Faraday Trans. 2*, **84**, 569 (1988).
- ³D. Köppenastrop and F. Zabel, *Int. J. Chem. Kinet.* **23**, 1 (1991).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 3.3 \times 10^{-13} \exp(700/T)$	228–380	Dagaut, Wallington, and Kurylo, 1988 ¹	(a,b)
$\leq 3.1 \times 10^{-12}$	298	Wallington <i>et al.</i> , 1992 ²	(a,c)
$\leq 4.0 \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_2/k > 0.77$	298	Wallington <i>et al.</i> , 1992 ²	(d)
<i>Reviews and Evaluations</i>			
$k_{\text{obs}} = 3.8 \times 10^{-13} \exp(700/T)$	228–370	Lightfoot <i>et al.</i> , 1992 ³	(e)
$k_{\text{obs}} = 3.3 \times 10^{-13} \exp(700/T)$	228–380	Wallington, Dagaut, and Kurylo, 1992 ⁴	(f)

Comments

- (a) k is defined by $-d[\text{CH}_2\text{FO}_2]/dt = 2k[\text{CH}_2\text{FO}_2]^2$ and has been derived from the measured overall second-order decay of CH_2FO_2 radicals (k_{obs}).
- (b) Flash photolysis of Cl_2 in the presence of CH_3F - O_2 - N_2 mixtures at total pressures of 25–400 Torr. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240} = (3.72 \pm 0.45) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of $k_{\text{obs}} = (3.3 \pm 1.2) \times 10^{-13} \exp[(700 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k , owing to the possibility of secondary reactions producing an enhanced decay of CH_2FO_2 radicals (see Comments on Preferred Values).
- (c) Pulse radiolysis study of CH_3F - O_2 - SF_6 mixtures at a total pressure of 1000 mbar. CH_2FO_2 radicals were monitored by UV absorption with $\sigma_{240} = (4.11 \pm 0.67) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of $k_{\text{obs}} = (4.01 \pm 0.52) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is an upper limit to k , owing to the possibility of secondary reactions producing an enhanced decay of CH_2FO_2 radicals (see Comments on Preferred Values).
- (d) CH_2FO_2 radicals were generated from the steady-state photolysis of Cl_2 - CH_3F mixtures at 700 Torr pressure of air. The decay of CH_3F and the formation of products was monitored by FTIR spectroscopy. No CH_2FOH was observed within the detection limits of the apparatus. Significant amounts of HCOF were observed ($86 \pm 5\%$), and in experiments with high conversions CH_2FOOH was observed ($11 \pm 4\%$).
- (e) Recalculated from the data of Dagaut *et al.*¹ with a revised value of $\sigma_{240} = 4.29 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (f) Based on the data of Dagaut *et al.*¹

Preferred Values

$k = (2.0\text{--}4.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = (2.0\text{--}4.0) \times 10^{-13} \exp(700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–380 K.

$k_2/k > 0.77$ at 298 K.

Comments on Preferred Values

We have recommended a range of values for the overall rate coefficient as a function of temperature, based on the data of Dagaut *et al.*¹ and modified by a re-evaluation of $\sigma_{240}(\text{CH}_2\text{FO}_2)$ by Lightfoot *et al.*³ The upper limit is the measured value of k_{obs} with no correction for possible secondary CH_2FO_2 removal by HO_2 radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the HO_2 radical reaction.

The product study of Wallington *et al.*² showed no formation of CH_2FOH , suggesting that channel (1) is negligible. The high yields of HCOF indicate the occurrence of the reaction $\text{CH}_2\text{FO} + \text{O}_2 \rightarrow \text{HCOF} + \text{HO}_2$, while the low yields of CH_2FOOH led Wallington *et al.*² to suggest that the rate coefficient for the reaction $\text{CH}_2\text{FO}_2 + \text{HO}_2 \rightarrow \text{products}$ is appreciably lower than for other $\text{RO}_2 + \text{HO}_2 \rightarrow \text{reactions}$ or that an alternative channel exists for the reactions. More information is needed on the kinetics and mechanisms of the $\text{CH}_2\text{FO}_2 + \text{HO}_2$ reaction to define k and k_2/k more accurately.

References

- ¹P. Dagaut, T. J. Wallington, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 815 (1988).
²T. J. Wallington, J. C. Ball, O. J. Nielsen, and E. Bartkiewicz, *J. Phys. Chem.* **96**, 1241 (1992).
³P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
⁴T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 5.0 \times 10^{-12}$	298	Nielsen <i>et al.</i> , 1992 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen <i>et al.</i> , 1992 ¹	(c)

Comments

- (a) k is defined by $-d[\text{CHF}_2\text{O}_2]/dt = 2k[\text{CHF}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of CHF_2O_2 radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CH}_2\text{F}_2\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 1000 mbar. CHF_2O_2 radicals were monitored by UV absorption with $\sigma_{240} = (2.66 \pm 0.46) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The reported value of $k_{\text{obs}} = (5.0 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is an upper limit to k , because of the possibility of secondary reactions producing an enhanced decay of CHF_2O_2 radicals (see Comments on Preferred Values).
- (c) CHF_2O_2 radicals were generated from the steady-state photolysis of $\text{Cl}_2\text{-CH}_2\text{F}_2$ mixtures in the presence of air at a total pressure of 920 mbar. The decay of CH_2F_2 and the formation of COF_2 were monitored by FTIR spectroscopy. The yield of COF_2 was $104 \pm 2\%$ of the removal of CH_2F_2 .

Preferred Values

$k = (2.5\text{--}5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k \approx 1.0$ at 298 K.

Comments on Preferred Values

We have recommended a range of values for the rate coefficient at 298 K, based on the determination by Nielsen *et al.*¹ The upper limit is the measured value of k_{obs} with no correction for possible secondary CHF_2O_2 removal by HO_2 radicals, and the lower limit is a factor of two less than the upper limit, corresponding to a maximum correction for the HO_2 radical reaction.

The product study in the same paper¹ showed that the only carbon-containing product was COF_2 , indicating that channel (2) is the predominant, if not the only, pathway, formed followed by the reaction $\text{CHF}_2\text{O} + \text{O}_2 \rightarrow \text{COF}_2 + \text{HO}_2$. The absence of the product CHF_2OOH expected from the reaction $\text{CHF}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{CHF}_2\text{OOH} + \text{O}_2$, raises several possibilities, including a slow reaction between CHF_2O_2 and HO_2 radicals or an alternative reaction pathway, such as $\text{CHF}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{COF}_2 + \text{H}_2\text{O} + \text{O}_2$. More information is needed on the kinetics and mechanism of the $\text{CHF}_2\text{O}_2 + \text{HO}_2$ reaction to define k and k_2/k more accurately.

References

- ¹O. J. Nielsen, T. Ellermann, E. Bartkiewicz, T. J. Wallington, and M. D. Hurley, *Chem. Phys. Lett.* **192**, 82 (1992).

$$\Delta H^\circ(2) = -83.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_2 = (1.8 \pm 0.5) \times 10^{-12}$	298	Nielsen <i>et al.</i> , 1992 ¹	(a,b)
$k_2 = 1.8 \times 10^{-12}$	298	Maricq and Szente, 1992 ²	(a,c)
$k_2 = (1.8 \pm 0.5) \times 10^{-12}$	297	Maricq and Szente, 1992 ³	(a,d)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen <i>et al.</i> , 1992 ¹	(e)

Comments

- (a) k is defined by $-d[\text{CF}_3\text{O}_2]/dt = 2k[\text{CF}_3\text{O}_2]^2$ and has been derived from the measured overall second-order decay of CF_3O_2 radicals (k_{obs}) by correcting for secondary removal of CF_3O_2 radicals.
- (b) Pulse radiolysis study of $\text{CHF}_3\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 1000 mbar. CF_3O_2 radicals were monitored by UV absorption with $\sigma_{230} = (2.06 \pm 0.40) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The cited rate coefficient was derived by the authors from the observed rate coefficient, $k_{\text{obs}} = (3.6 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, on the basis of their product studies [see Comment (e)].
- (c) Flash photolysis of $\text{CHF}_3\text{-F}_2\text{-O}_2$ mixtures with time-resolved absorption spectroscopy for the detection of

CF_3O_2 radicals, with $\sigma_{210} = (4.3 \pm 0.3) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. A value of $k_{\text{obs}} = (3.1 \pm 0.25) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined from the time-dependence of the CF_3O_2 radical absorbance.

- (d) Flash photolysis of F_2 in the presence of N_2 , O_2 , He, and CF_3CFH_2 . CF_3O_2 radicals were produced from the reaction $\text{CF}_3\text{CHFO} \rightarrow \text{CF}_3 + \text{HCOF}$, followed by $\text{CF}_3 + \text{O}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2 + \text{M}$, and monitored by UV absorption. A value of $k_{\text{obs}} = 3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived from the rate of disappearance of CF_3O_2 radicals. The value of k_2 quoted above is based on a correction factor of 0.5 to allow for the secondary removal of CF_3O_2 radicals.
- (e) CF_3O_2 radicals were generated from the steady-state

photolysis of F_2 in the presence of CHF_3 - O_2 - N_2 mixtures at a total pressure of 892 mbar. The decay of CHF_3 and the formation of products were monitored by FTIR spectroscopy. The major product was CF_3OOOCF_3 , which accounted for $\sim 100\%$ of the CHF_3 consumed. No CF_3OOCF_3 was observed as a product. The cited branching ratio was obtained assuming that the trioxide product arises from the reaction $CF_3O + CF_3O_2 + M \rightarrow CF_3OOOCF_3 + M$.

Preferred Values

$$k_2 = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k_2 = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The recommended value of k_2 is obtained by taking the average value of $k_{\text{obs}} = 3.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from the three studies of this reaction¹⁻³ and by assuming a correction factor of 0.5 to allow for the secondary removal of CF_3O_2 radicals.¹ This correction factor is based on the product study of Nielsen *et al.*,¹ which showed that the sole product of the interaction of CF_3O_2 radicals is the trioxide, CF_3OOOCF_3 , which appears to be formed by the reaction $CF_3O + CF_3O_2 + M \rightarrow CF_3OOOCF_3 + M$. The absence of any CF_3OOCF_3 product rules out the participation of channel (1).

References

¹O. J. Nielsen, T. Ellermann, J. Sehested, E. Bartkiewicz, T. J. Wallington, and M. D. Hurley, *Int. J. Chem. Kinet.* **24**, 1009 (1992).

²M. M. Maricq and J. J. Szenté, *J. Phys. Chem.* **96**, 4925 (1992).

³M. M. Maricq and J. J. Szenté, *J. Phys. Chem.* **96**, 10862 (1992).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> (8 ± 3) $\times 10^{-12}$	297	Maricq and Szenté, 1992 ¹	(a)

Comments

- (a) Flash photolysis of F_2 in the presence of CF_3CH_2F - O_2 - N_2 -He mixtures. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{213} = (5.2 \pm 0.3) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of k listed above was obtained by modeling the decay of CF_3CFHO_2 radicals and the formation and decay of CF_3O_2 radicals.

Preferred Values

$$k = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K seems reasonable, but requires independent confirmation. Maricq and Szenté¹ assumed that the reaction proceeds entirely by channel (2) on the basis of studies of the self-reactions of CF_3O_2 and CF_3CHFO_2 radicals.

References

¹M. M. Maricq and J. J. Szenté, *J. Phys. Chem.* **96**, 10862 (1992).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2.7 \times 10^{-12}$	298	Nielsen <i>et al.</i> , 1992 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen <i>et al.</i> , 1992 ¹	(c)

Comments

- (a) k is defined by $-d[\text{CHF}_2\text{CF}_2\text{O}_2]/dt = 2k[\text{CHF}_2\text{CF}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CHF}_2\text{CHF}_2\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 1000 mbar. $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{230} = (3.2 \pm 0.5) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The reported value of $k_{\text{obs}} = (2.7 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k , because of the possibility of secondary reactions producing an enhanced decay of $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals (see Comments on Preferred Values).
- (c) $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals were generated from the steady-state photolysis of Cl_2 in the presence of $\text{CHF}_2\text{CHF}_2\text{-air}$ mixtures at 920 mbar total pressure. The decay of CHF_2CHF_2 and the formation of COF_2 , the only carbon-containing product observed, were monitored by FTIR spectroscopy. The branching ratio given in the table is based on a yield of $98 \pm 2\%$ of COF_2 , relative to the decay of CHF_2CHF_2 .

Preferred Values

$k \leq 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k \approx 1.0$ at 298 K.

Comments on Preferred Values

We have recommended an upper limit for the rate coefficient, as determined by Nielsen *et al.*¹ The product study in

the same paper¹ revealed that the only carbon-containing product was COF_2 , which is assumed to arise from channel (2) followed by the rapid decomposition reaction, $\text{CHF}_2\text{CF}_2\text{O} \rightarrow \text{CHF}_2 + \text{COF}_2$. The absence of any peroxide product, $\text{CHF}_2\text{CF}_2\text{OOCF}_2\text{CHF}_2$, together with the carbon balance between the COF_2 produced and the CHF_2CHF_2 consumed indicates that the major, if not the only, pathway for the interaction of the $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals is via reaction (2). The CHF_2 radicals from the decomposition reaction of the $\text{CHF}_2\text{CF}_2\text{O}$ reaction will result in the formation of CHF_2O_2 radicals, which are known² to interact via the reaction of $2\text{CHF}_2\text{O}_2 \rightarrow 2\text{CHF}_2\text{O} + \text{O}_2$, resulting in the formation of COF_2 and HO_2 from the subsequent reaction $\text{CHF}_2\text{O} + \text{O}_2 \rightarrow \text{COF}_2 + \text{HO}_2$.

The formation of the peroxy radicals, CHF_2O_2 and HO_2 , following the interaction of the initial $\text{CHF}_2\text{CF}_2\text{O}$ radicals leads to complications in the interpretation of the UV absorption spectra, which were assumed to be exclusively from the $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals. In the absence of detailed kinetic data concerning the interaction of these peroxy radicals it is not possible to correct the UV absorption spectra. This means that k_{obs} corresponds to an upper limit value of k_2 .

References

- ¹O. J. Nielsen, T. Ellermann, J. Sehested, and T. J. Wallington, *J. Phys. Chem.* **96**, 10875 (1992).
²O. J. Nielsen, T. Ellermann, E. Bartkiewicz, T. J. Wallington, and M. D. Hurley, *Chem. Phys. Lett.* **192**, 82 (1992).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$7.8 \times 10^{-13} \exp[(605 \pm 40)/T]$ $(7 \pm 1.0) \times 10^{-12}$	211–372 297	Maricq and Szente, 1992 ¹	(a,b)
<i>Branching Ratios</i>			
$k_1/k=0.14$	273	Wallington <i>et al.</i> , 1992 ²	(c)
$k_1/k=0.08$	298		
$k_1/k=0.05$	353	Tuazon and Atkinson, 1993 ³	(d)
$k_1/k=0.055$	273		
$k_1/k=0.049$	298		
$k_1/k=0.046$	320		

Comments

- (a) k is defined by $-d[\text{CF}_3\text{CFHO}_2]/dt = 2k[\text{CF}_3\text{CFHO}_2]$.²
- (b) Flash photolysis of F_2 in the presence of N_2 , O_2 , He, and $\text{CF}_3\text{CH}_2\text{F}$. CF_3CHFO_2 radicals were monitored by UV absorption with $\sigma_{213} = (5.2 \pm 0.3) \times 10^{-13} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of k listed above was obtained by modelling the decay curves for CF_3CFHO_2 radicals with a mechanism of 9 reactions.
- (c) Steady-state photolysis of Cl_2 in the presence of $\text{CF}_3\text{CFH}_2\text{-O}_2$ mixtures at a total pressure of 1000 Torr with FTIR analysis of the products HCOF and CF_3COF . The branching ratio was determined from the yields of CF_3COF as a function of added O_2 , extrapolated to zero O_2 partial pressure.
- (d) Similar experiments to those of Comment (c). The branching ratios were derived from the yields of CF_3COF in the presence of 590 Torr N_2 and 1 Torr O_2 .

Preferred Values

$k = 5.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.8 \times 10^{-13} \exp(605/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210–375 K.
 $k_2/k = 0.93$, independent of temperature over the range 270–350 K.
 $k_1/k = 0.07$, independent of temperature over the range 270–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.05$ over the temperature range 270–350 K.

Comments on Preferred Values

The preferred data for the overall rate coefficient are from Maricq and Szente,¹ which are based on temperature-independent branching ratios k_1/k and k_2/k over the range 273–363 K. This is consistent with our recommendation of a temperature-independent branching ratio, k_1/k , which is the average of the experimental results of Wallington *et al.*² and Tuazon and Atkinson³ over the range 273–353 K. The recommended value of k_2/k is inferred from that of k_1/k .

It should also be noted that the results of Maricq and Szente¹ for k at 216 K appear consistent with temperature-independent branching ratios.

Confirmation of both the overall rate coefficient and the branching ratios is required.

References

- ¹M. M. Maricq and J. J. Szente, *J. Phys. Chem.* **96**, 10862 (1992).
²T. J. Wallington, M. D. Hurley, J. C. Ball, and E. W. Kaiser, *Environ. Sci. Technol.* **26**, 1318 (1992).
³E. C. Tuazon and R. Atkinson, *J. Atmos. Chem.* **16**, 301 (1993).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2.1 \times 10^{-12}$	295	Sehested <i>et al.</i> , 1993 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k=1.0$	295	Sehested <i>et al.</i> , 1993 ¹	(c)

Comments

- (a) k is defined by $-d[\text{CF}_3\text{CF}_2\text{O}_2]=2k[\text{CF}_3\text{CF}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CF}_3\text{CF}_2\text{O}_2$ radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CF}_3\text{CF}_2\text{H}-\text{O}_2-\text{SF}_6$ mixtures at a total pressure of 1000 mbar. $\text{CF}_3\text{CF}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{230}=(2.74 \pm 0.46) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of $k_{\text{obs}}=(2.10 \pm 0.38) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k , because of the possibility of secondary reactions producing an enhanced decay of $\text{CF}_3\text{CF}_2\text{O}_2$ radicals (see Comments on Preferred Values).
- (c) $\text{CF}_3\text{CF}_2\text{O}_2$ radicals were generated from the steady-state photolysis of $\text{Cl}_2-\text{CF}_3\text{CF}_2\text{H}$ mixtures at 700 Torr pressure of air. The decay of $\text{CF}_3\text{CF}_2\text{H}$ and the formation of products were monitored by FTIR spectroscopy. The observed products were COF_2 , $\text{CF}_3\text{O}_3\text{CF}_3$, and $\text{CF}_3\text{O}_3\text{C}_2\text{F}_5$, and accounted for 100% of the $\text{CF}_3\text{CF}_2\text{H}$ loss.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient (k_2) as determined by Sehested *et al.*¹ The product study in the same paper¹ showed no formation of the peroxide product, $\text{CF}_3\text{CF}_2\text{OOCF}_2\text{CF}_3$, and together with the carbon-balance between the products COF_2 , $\text{CF}_3\text{O}_3\text{CF}_3$, $\text{CF}_3\text{O}_3\text{C}_2\text{F}_5$, and the decay of $\text{CF}_3\text{CF}_2\text{H}$ indicates that reaction (2) is the sole channel for the interaction of $\text{CF}_3\text{CF}_2\text{O}_2$ radicals. The observed products are accounted for by the reactions of $\text{CF}_3\text{CF}_2\text{O}$ radicals: $\text{CF}_3\text{CF}_2\text{O} \rightarrow \text{CF}_3 + \text{COF}_2$; $\text{CF}_3 + \text{O}_2 + \text{M} \rightarrow \text{CF}_3\text{O}_2 + \text{M}$; $\text{CF}_3\text{O}_2 + \text{CF}_3\text{CF}_2\text{O} \rightarrow \text{CF}_3\text{O}_3\text{C}_2\text{F}_5$; $\text{CF}_3\text{O} + \text{CF}_3\text{O}_2 \rightarrow \text{CF}_3\text{O}_3\text{CF}_3$. Because it is not possible at present to correct for the secondary removal of $\text{C}_2\text{F}_5\text{O}_2$ radicals in reactions with CF_3O and probably also with CF_3O_2 radicals, the reported k_{obs} value from the second-order removal of $\text{C}_2\text{F}_5\text{O}_2$ radicals is an upper limit.

Preferred Values

$k_2 \leq 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k=1.0$ at 298 K.

References

- ¹J. Sehested, T. Ellermann, O. J. Nielsen, T. J. Wallington, and M. D. Hurley, *Int. J. Chem. Kinet.* **25**, 701 (1993).

HCOF + $h\nu \rightarrow$ products

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{HCOF} + h\nu \rightarrow \text{HF} + \text{CO}$ (1)	8.7	13,730
$\rightarrow \text{H} + \text{FCO}$ (2)	439	272
$\rightarrow \text{F} + \text{HCO}$ (3)	476	251

Absorption cross-section data

Wavelength range/nm	References	Comments
220–300	Rattigan <i>et al.</i> , 1994 ¹	(a)
195–270	Meller and Moortgat, 1992 ¹	(b)

Comments

- (a) The absorption spectrum of HCOF was studied using a purified sample of HCOF and recorded by diode array spectroscopy with a resolution of 1.2 nm. The characteristic banded structure was recorded and the absolute cross-section at 230 nm was $\sigma = 6.65 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ using this resolution. The cross-section was independent of temperature in the range 233–318 K, in agreement with the earlier work of Giddings and Innes.³
- (b) Measurements of the spectrum of HCOF at a resolution of 0.02 nm. The spectrum consists of a vibrational progression of many sharp bands, with an origin of structured absorption at 268 nm and a maximum of intensity near 210 nm. The maximum value of $\sigma = 1.5 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ was observed at this resolution, which is in reasonable agreement with the earlier work of Giddings and Innes³ who reported an absorption coefficient of approximately $50 \text{ l mol}^{-1} \text{ cm}^{-1}$ ($\sigma = 1.9 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$) at the maximum.

Quantum yield data

There are no reported quantum yield data. Klimeck and Berry⁴ have observed infrared laser emission from HF* following flash photolysis of HCOF ($\lambda > 165 \text{ nm}$). These results⁴ indicate the occurrence of reactions (1) and/or (3).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	8.28	223	6.58	245	0.67
201	9.75	224	4.94	246	0.72
202	8.3	225	5.33	247	0.41
203	7.55	226	4.00	248	0.48
204	8.52	227	4.65	249	0.28
205	10.15	228	4.43	250	0.21
206	8.28	229	4.61	251	0.15
207	7.41	230	3.57	252	0.24
208	8.44	231	2.55	253	0.21
209	9.55	232	3.16	254	0.07
210	7.76	233	3.09	255	0.12
211	7.36	234	2.98	256	0.07
212	7.92	235	2.04	257	0.05
213	8.56	236	2.28	258	0.04
214	9.22	237	1.24	259	0.04
215	7.67	238	1.71	260	0.04
216	6.51	239	1.75	261	0.02
217	7.38	240	1.55	262	0.02
218	7.97	241	0.97	263	0.02
219	6.28	242	1.19	264	0.02
220	6.85	243	0.57	265	0.01
221	5.7	244	0.76	266	0.01
222	6.07				

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data for the absolute absorption cross-sections reported by Meller and Moortgat.² The listed values are averaged over 1 nm. The cross-sections of Rattigan *et al.*¹ are higher than those of Meller and Moortgat² by approximately a factor of 2 at 230 nm. Although the two studies are nominally at comparable resolution, the Rattigan *et al.*¹ spectrum does not appear to contain all the features reported by Meller and Moortgat,² indicating possible errors.

References

- ¹O. V. Rattigan, D. M. Rowley, O. Wild, R. L. Jones, and R. A. Cox, J. Chem. Soc. Faraday Trans. **90**, 1819 (1994).
²R. Meller and G. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," Final Report to STEP-0004-C(EDB), 1992.
³L. K. Giddings and K. K. Innes, J. Mol. Spectrosc. **6**, 528 (1961).
⁴E. Klimeck and M. J. Berry, Chem. Phys. Lett. **20**, 141 (1973).

COF₂ + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
COF ₂ + $h\nu$ → COF + F (1)	543	220
→ CO + 2F (2)	683	175
→ CF ₂ + O(³ P) (3)	690	173

Preferred Values**Absorption cross-sections for COF₂ photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
186.0	5.5	205.1	0.74
187.8	4.8	207.3	0.52
189.6	4.2	209.4	0.40
191.4	3.7	211.6	0.28
193.2	3.1	213.9	0.20
195.1	2.6	216.2	0.12
197.0	2.1	218.6	0.081
199.0	1.6	221.0	0.049
201.0	1.3	223.5	0.035
203.0	0.95	226.0	0.024
		228.6	0.018

Comments on Preferred Values

The preferred values of the absorption cross sections are those reported by Molina and Molina¹ over the wavelength range 184 to 199 nm and those reported in the recent study by Nolle *et al.*² at longer wavelengths. These results are in excellent agreement over the range 200–208 nm; from 208–225 nm the results of Molina and Molina¹ are 15–25% smaller than those of Nolle *et al.*² The spectrum shows considerable structure; the values listed are averages over 500 cm^{−1} intervals. The recommended quantum yield ($\phi_1=1.0$) is based on the results of the study of Nolle *et al.* at 193 nm, in which they monitored the decay of COF₂ and reported an apparent quantum yield of 0.47 ± 0.03 . Assuming that all the COF radicals produced in channel (1) regenerate COF₂ by the reaction $2 \text{COF} \rightarrow \text{COF}_2 + \text{CO}$, a value of $\phi_1 = 0.94 \pm 0.06$ can be calculated.

References

- ¹L. T. Molina and M. J. Molina, Results presented at the 182nd American Chemical Society National Meeting, New York, August 1982.
²A. Nolle, H. Heydtmann, R. Meller, W. Schneider, and G. K. Moortgat, *Geophys. Res. Lett.* **19**, 281 (1992).

Quantum Yield for COF₂ Photolysis at 298 K

$\phi_1 = 1.0$ at $\lambda = 193$ nm.

CF₃CHO + $h\nu$ → products**Primary photochemical transitions**

Reaction	$\Delta H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ CHO + $h\nu$ → CF ₃ + HCO (1)		
→ CF ₃ CO + H (2)		
→ CHF ₃ + CO (3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
230–360	Meller, Boglu, and Moortgat, 1993 ¹	(a)

Comments

- (a) Absolute absorption cross-sections were measured using a diode-array spectrometer over the temperature range 240–300 K. The UV spectrum of trifluoroacetal-

dehyde shows a broad band, centered at 305 nm and extending out to 355 nm. Values of σ were given at 5 nm intervals at 298 K.

Quantum Yield Data

There are no reported quantum yield data. The products of photolysis of CF_3CHO have been investigated by Dodd and Smith.² More recently, Richer *et al.*³ have studied the photo-oxidation of CF_3CHO and observed CHF_3 , CO , CO_2 , and COF_2 as products. Photodissociation appears to occur predominantly via reaction (1). However, Richer *et al.*³ observed substantial yields (14%) of CHF_3 in the 254 nm photolysis of CF_3CHO in air, indicating that channel (3) also occurs at that wavelength.

Preferred Values

Absorption cross sections at 298 K

λ/nm	$10^{21} \sigma/\text{cm}^2$	λ/nm	$10^{21} \sigma/\text{cm}^2$
235	0.74	300	29.8
240	1.29	305	29.0
245	2.17	310	27.9
250	3.44	315	25.0
255	5.25	320	21.4
260	7.63	325	17.7
265	10.6	330	13.6
270	13.8	335	9.98
275	17.6	340	6.17
280	21.3	345	3.86
285	24.8	350	2.31
290	27.6	355	0.59
295	29.1	360	0.19

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Meller *et al.*¹ In the absence of data, no recommendation is made for the quantum yields but by analogy with other aldehydes, which show a similar absorption spectrum, photodissociation at wavelengths >300 nm is expected to be predominantly by channel (1).

References

- ¹R. Meller, D. Boglu, and G. K. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 130–138.
- ²R. E. Dodd and J. Watson-Smith, J. Chem. Soc. 1465 (1957).
- ³H. Richer, J. R. Sodeau, and I. Barnes, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 182–188.

 $\text{CF}_3\text{COF} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{COF} + h\nu \rightarrow \text{CF}_3 + \text{FCO}$ (1)		
$\rightarrow \text{CF}_3\text{CO} + \text{F}$ (2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–340	Rattigan <i>et al.</i> , 1993 ¹	(a)
210–265	Meller, Boglu, and Moortgat, 1993 ²	(b)

Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(1) + \phi(2) = 1.05 \pm 0.05$	254	Meller, Boglu, and Moortgat, 1993 ²	(c)

Comments

- (a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the tem-

perature range 240–300 K. The UV spectrum of trifluoroacetyl fluoride shows a single band extending out to 315 nm, where there is significant temperature de-

pendence. Values of σ were given at 5 nm intervals at 298 K and 240 K as well as temperature coefficients in the long wavelength tail at $\lambda > 270$ nm.

- (b) Absolute absorption cross-sections were measured using a diode array spectrometer at 298 K. Cross-sections were averaged over 1 nm, 2 nm, and 5 nm wavelength intervals.
- (c) Average of 10 measurements of the overall loss of CF_3COF by photolysis in 1 atm air at 298 K, relative to the loss of COCl_2 for which $\phi = 1$.

Preferred Values

Absorption cross-sections at 293 and 238 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		$10^3 \times B/\text{K}^{-1}$
	293 K	238 K	
200	9.35	9.46	-0.21
205	11.50	11.60	-0.16
210	12.88	13.10	-0.31
215	13.72	13.70	0.03
220	13.39	13.10	0.40
225	11.93	11.40	0.83
230	9.75	9.11	1.23
235	7.26	6.55	1.87
240	4.93	4.18	2.99
245	3.01	2.30	4.91
250	1.67	1.16	6.60
255	0.82	0.49	9.36
260	0.35	0.18	12.40
265	0.13	0.05	18.77
270	0.04	0.01	26.36
275	0.012	0.003	24.73
280	0.004	0.001	23.32
285	0.0016	0.0004	25.21
290	0.0008	0.00	
295	0.0003	0.00	

^aTemperature dependence: $\log_e\{\sigma(T)/\sigma(293 \text{ K})\} = B(T - 293)$.

Quantum Yields

$\phi(1) + \phi(2) = 1.0$ over the wavelength range 200–315 nm.

Comments on Preferred Values

The preferred values for the cross sections at 293 K are a simple average of the data reported by Rattigan *et al.*¹ and Meller *et al.*² The temperature dependence is based on the 238 K data of Rattigan *et al.*¹ The quantum yield of unity is based on the data of Meller *et al.*,² and is assumed to apply over the wavelength region 200–315 nm.

References

- ¹O. V. Rattigan, O. Wild, R. L. Jones, and R. A. Cox, *J. Photochem. Photobiol. A: Chem.* **73**, 1 (1993).
- ²R. Meller, D. Boglu, and G. K. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 130–138.

4.7. Chlorine Species

$$\Delta H^\circ = -30 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.2) \times 10^{-13}$	298	Vogt and Schindler, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
No recommendation		IUPAC, 1992 ²	(b)
$1.0 \times 10^{-11} \exp(-1300/T)$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Discharge fast flow system with mass spectrometric detection. Pseudo-first-order decay of [HOCl] in excess [O] measured.
- (b) No recommendation because there were no experimental data.
- (c) Based on the results of Vogt and Schindler¹ and an estimated A-factor.

Reliability

$$\Delta \log k = \pm 0.7 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 1000 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the room temperature results of Vogt and Schindler.¹ This is the only experimental study of this reaction. The A factor was estimated based on O-atom reactions with similar compounds, and the E/R value fitted to the value of $k(298 \text{ K})$.

Preferred Values

$$k = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.0 \times 10^{-11} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

References

- ¹R. Vogt and R. N. Schindler, *Geophys. Res. Lett.* **19**, 1935 (1992).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -229.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

The most recent studies all give values of k_{298} about 30% lower than the earlier work of Bemand *et al.*¹ and Clyne and Nip.² The two most recent studies^{3,4} give a negative temperature dependence, in contrast to the earlier work which showed zero or positive temperature coefficients. The preferred value is independent of temperature and is obtained by averaging the 298 K values from Schwab *et al.*,⁵ Nicovich *et al.*,³ Ongstad and Birk,⁴ Leu,⁶ Margitan,⁷ and Zahniser and Kaufman.⁸ The uncertainty on E/R allows for a tempera-

ture dependence consistent with all studies. Leu and Yung⁹ have recently shown that the yields of $\text{O}_2(^1\Delta)$ and $\text{O}_2(^1\Sigma)$ in the reaction are $< 2.5 \times 10^{-2}$ and $(4.4 \pm 1.1) \times 10^{-4}$, respectively. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.¹⁰

References

- ¹P. P. Bemand, M. A. A. Clyne, and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **69**, 1356 (1973).
²M. A. A. Clyne and W. S. Nip, *J. Chem. Soc. Faraday Trans. 1*, **72**, 221 (1976).
³J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, *J. Chem. Phys.* **89**, 5670 (1988).
⁴A. P. Ongstad and J. W. Birks, *J. Chem. Phys.* **85**, 3359 (1986).
⁵J. J. Schwab, D. W. Toohey, W. H. Brune, and J. G. Anderson, *J. Geophys. Res.* **89**, 9581 (1984).
⁶M. T. Leu, *J. Phys. Chem.* **88**, 1394 (1984).
⁷J. J. Margitan, *J. Phys. Chem.* **88**, 3638 (1984).
⁸M. S. Zahniser and F. Kaufman, *J. Chem. Phys.* **66**, 3673 (1977).
⁹M. T. Leu and Y. Yung, *Geophys. Res. Lett.* **14**, 949 (1987).
¹⁰IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -243.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.4 \times 10^{-12} \exp[-(960 \pm 120)/T]$ $(1.0 \pm 0.3) \times 10^{-13}$	243–400 298	Gleason, Nesbitt, and Stief, 1994 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.5 \times 10^{-12} \exp(-950/T)$	240–400	IUPAC, 1992 ²	(b)
$2.4 \times 10^{-12} \exp(-960/T)$	240–400	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow system with resonance fluorescence detection of O(³P) atoms. Measurements were made over the temperature range 200–400 K. The data for the temperature range 243–400 K were fitted with the Arrhenius expression given in the table. Data at lower temperatures showed a negative temperature dependence.
- (b) Based on the results of Gleason *et al.*¹ which were then unpublished and were slightly different from the final values published in Ref. 1.
- (c) Based on the results of Gleason *et al.*¹

Preferred Values

$$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.4 \times 10^{-12} \exp(-960/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the results of the discharge flow-resonance fluorescence study of Gleason *et al.*¹ Over the temperature range of the recommendation (240–300 K), the data were well fit by the Arrhenius expression given, but at lower temperatures down to 200 K there was an abrupt change to a negative temperature dependence. The extrapolated 298 K rate coefficient of Colussi⁴ supports this value. It appears that the experiments of Bemand *et al.*⁵ were complicated by secondary chemistry. The experiments of Colussi⁴ and Colussi *et al.*⁶ over an extended pressure range demonstrate the importance of the termolecular reaction (see separate data sheet on O + OCIO + M). The preferred values are only slightly different from those in our previous evaluation, IUPAC, 1992,² which were based on then unpublished results of Gleason *et al.*¹

References

- ¹J. F. Gleason, F. L. Nesbitt, and L. J. Stief, *J. Phys. Chem.* **98**, 126 (1994).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³NASA Evaluation No. 11, 1994 (see references in Introduction).
⁴A. J. Colussi, *J. Phys. Chem.* **94**, 8922 (1990).
⁵P. P. Bemand, M. A. A. Clyne, and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **69**, 1356 (1973).
⁶A. J. Colussi, S. P. Sander, and R. R. Friedl, *J. Phys. Chem.* **96**, 4442 (1992).

$$\Delta H^\circ = -112.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.8 \times 10^{-31} (T/298)^{-1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 0.5 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the data of Colussi¹ and Colussi *et al.*² and correspond to falloff curves with $F_c = 0.48$ at 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 3.1 \times 10^{-11} (T/298)^1 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

See comment on k_0 . The preferred values for k_0 and k_{∞} are identical to those in our previous evaluation, IUPAC, 1992.³

References

¹A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).

²A. J. Colussi, S. P. Sander, and R. R. Friedl, J. Phys. Chem. **96**, 4442 (1992).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -127.4 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.7 \times 10^{-11} \exp[-(510 \pm 30/T)]$	230–380	Stevens and Anderson, 1992 ¹	(a)
$(4.7 \pm 0.2) \times 10^{-12}$	298		
<i>Reviews and Evaluations</i>			
$2.9 \times 10^{-11} \exp(-630/T)$	235–300	IUPAC, 1992 ²	(b)
$2.7 \times 10^{-11} \exp(-530/T)$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow system. The pseudo-first-order decay of [O] in excess $[\text{Cl}_2\text{O}]$ detected by resonance fluorescence.
- (b) Based on the results of Miziolek and Molina⁴ and of Wecker *et al.*⁵
- (c) Based on the results of Stevens and Anderson¹ and Miziolek and Molina.⁴

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred value at 298 K is based on the results of Stevens and Anderson¹ and Miziolek and Molina,⁴ which are in good agreement. The significantly lower values of Wecker *et al.*⁵ are not included, nor are earlier, higher results of Basco and Dogra⁶ and Freeman and Phillips⁷ due to data analysis difficulties in both studies.

References

¹P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴A. W. Miziolek and M. J. Molina, J. Phys. Chem. **82**, 1769 (1978).

⁵D. Wecker, R. Johanssen, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **86**, 532 (1982).

⁶N. Basco and S. K. Dogra, Proc. R. Soc. London, Ser. A **323**, 29 (1971).

⁷G. G. Freeman and L. F. Phillips, J. Phys. Chem. **72**, 3025 (1968).

Preferred Values

$k = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(-530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$$\Delta H^\circ(1) = -96.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -143.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -216 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$$k = 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.0 \times 10^{-12} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 213\text{--}295 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The results reported by Molina *et al.*,¹ Kurylo,² and Adler-Golden and Wiesenfeld³ are in good agreement and have been used to derive the preferred Arrhenius expression. The value reported by Ravishankara *et al.*⁴ is a factor of two higher, and this may possibly be attributed to secondary ki-

netic complications, the presence of NO_2 as a reactive impurity, or the formation of reactive photolytic products. None of the studies reported identification of the reaction products. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

¹L. T. Molina, J. E. Spencer, and M. J. Molina, *Chem. Phys. Lett.* **45**, 158 (1977).

²M. J. Kurylo, *Chem. Phys. Lett.* **45**, 158 (1977).

³S. M. Adler-Golden and J. R. Wiesenfeld, *Chem. Phys. Lett.* **82**, 281 (1981).

⁴A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, *Geophys. Res. Lett.* **4**, 7 (1977).

⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$\text{O}(^1\text{D}) + \text{HCFCs} \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
1.1×10^{-10} CHF ₂ Cl	298	Warren, Gierczak, and Ravishankara, 1991 ¹	(a)
2.2×10^{-10} CH ₃ CF ₂ Cl			
2.6×10^{-10} CH ₃ CFCl ₂			
1.2×10^{-10} CH ₂ ClCF ₃			
8.6×10^{-11} CHFClCF ₃			
2.0×10^{-10} CHCl ₂ CF ₃			
<i>Reviews and Evaluations</i>			
9.5×10^{-11} CHF ₂ Cl	298	IUPAC, 1992 ²	(b)
1.9×10^{-10} CHFCl ₂			
1.4×10^{-10} CH ₃ CF ₂ Cl			
1.5×10^{-10} CH ₃ CFCl ₂			
1.5×10^{-10} CH ₂ ClCF ₃			
1.6×10^{-10} CH ₂ ClCF ₂ Cl			
1.0×10^{-10} CHFClCF ₃	200–300	NASA, 1994 ³	(c)
2.2×10^{-10} CHCl ₂ CF ₃			
1.0×10^{-10} CHF ₂ Cl			
1.9×10^{-10} CHFCl ₂			
2.2×10^{-10} CH ₃ CF ₂ Cl			
2.6×10^{-10} CH ₃ CFCl ₂			
1.2×10^{-10} CH ₂ ClCF ₃			
1.6×10^{-10} CH ₂ ClCF ₂ Cl			
8.6×10^{-11} CHFClCF ₃			
2.0×10^{-10} CHCl ₂ CF ₃			

Comments

- (a) Laser flash photolysis of O₃ at 248 nm. Time-resolved production of O(³P) monitored by resonance fluorescence at 130 nm.
- (b) CHF₂Cl and CHFCl₂: Based on the results of Davidson *et al.*⁴ CH₃CF₂Cl, CH₂ClCF₃, CH₂ClCF₂Cl, and CHCl₂CF₃: Based on the results of Green and Wayne.⁵ CH₃CFCl₂ and CHFClCF₃: Estimated by analogy.
- (c) CHF₂Cl: Based on the results of Warren *et al.*¹ and Davidson *et al.*⁴ CHFCl₂: Based on the results of Davidson *et al.*⁴ CH₃CF₂Cl, CH₃CFCl₂, CH₂ClCF₃, CHFClCF₃, and CHCl₂CF₃: Based on the results of Warren *et al.*¹ CH₂ClCF₂Cl: Based on the results of Green and Wayne.⁵

Preferred Values

CHF ₂ Cl	$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 175–340 K.
CHFCl ₂	$k = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over range 175–340 K.
CH ₃ CF ₂ Cl	$k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₃ CFCl ₂	$k = 2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₂ ClCF ₃	$k = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CH ₂ ClCF ₂ Cl	$k = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CHFClCF ₃	$k = 8.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
CHCl ₂ CF ₃	$k = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K for CHF₂Cl.

$\Delta \log k = \pm 0.2$ at 298 K for CHFCl₂, CH₃CF₂Cl, CH₃CFCl₂, CH₂ClCF₃, CHFClCF₃, and CHCl₂CF₃.

$\Delta \log k = \pm 0.3$ at 298 K for CH₂ClCF₂Cl.

Comments on Preferred Values

The rate coefficients given are for the total disappearance of O(¹D) atoms and include both physical quenching and

chemical reaction. The rate coefficients for CHF₂Cl and CHFCl₂ have been determined to be temperature-independent over the range 175–340 K. Rate coefficients for the other HCFCs are also assumed to be temperature-independent by analogy with these two species and also considering that they have such high values at 298 K. Specific comments are as follows:

CHF₂Cl: Based on the results of Warren *et al.*¹ and Davidson *et al.*⁴ Addison *et al.*⁶ reported that the dominant channel leads to the formation of ClO (55 ± 10%) and that the second most important channel leads to the elimination of HCl (40%). The latter process is accompanied by formation of CF₂ and O(³P). They also report an OH radical yield of 5%. Warren *et al.*¹ report an O(³P) yield of 28% which they interpret as the product of physical quenching.

CHFCl₂: Based on the results of Davidson *et al.*⁴
 CH₃CF₂Cl: Based on the results of Warren *et al.*,¹ who also report 26% physical quenching.
 CH₃CFCl₂: Based on the results of Warren *et al.*,¹ who also report 31% physical quenching.
 CH₂ClCF₃: Based on the results of Warren *et al.*,¹ who also report 20% physical quenching.
 CH₂ClCF₂Cl: Based on the results of Green and Wayne.⁵
 CHFClCF₃: Based on the results of Warren *et al.*,¹ who also report 31% physical quenching.
 CHCl₂CF₃: Based on the results of Warren *et al.*,¹ who also report 21% physical quenching.

References

- ¹R. Warren, T. Gierczak, and A. R. Ravishankara, *Chem. Phys. Lett.* **183**, 403 (1991).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, *J. Chem. Phys.* **69**, 4277 (1978).
- ⁵R. G. Green and R. P. Wayne, *J. Photochem.* **6**, 371 (1976).
- ⁶M. C. Addison, R. J. Donovan, and J. Garraway, *J. Chem. Soc. Faraday Discuss.* **67**, 286, 1979.

$$\Delta H^\circ(1) = -123.1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -580.3 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(4) = -423 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3 + k_4$)

$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 0.15$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(k_2/k) = \pm 0.1$ K.

Comments on Preferred Values

The preferred values are based on the results of Force and Wiesenfeld¹ and Davidson *et al.*,² which are in excellent agreement. The weight of evidence from many O(¹D) rate studies suggests that the results of Fletcher and Husain³ contain a systematic error. The results from the relative rate coefficient studies⁴⁻⁶ were not considered in this evaluation. However, combining the values of $k/k(\text{O}(\text{}^1\text{D}) + \text{N}_2\text{O})$ reported in Refs. 4 and 5 with the IUPAC preferred value for $k(\text{O}(\text{}^1\text{D}) + \text{N}_2\text{O})$ yields values of k in good agreement with

the preferred value. Both Donovan⁷ and Force and Wiesenfeld¹ report that the quenching channel (2) is a significant removal pathway for O(¹D). Consequently, preferred values are given for both the overall rate constant, k , and for the branching ratio k_2/k . These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁸

References

- ¹A. P. Force and J. R. Wiesenfeld, *J. Phys. Chem.* **85**, 782 (1981).
- ²J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, *J. Chem. Phys.* **69**, 4277 (1978).
- ³I. S. Fletcher and D. Husain, *J. Phys. Chem.* **80**, 1837 (1976).
- ⁴R. K. Jayanty, R. Simonaitis, and J. Heicklen, *J. Photochem.* **4**, 381 (1975).
- ⁵R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, *J. Geophys. Res.* **81**, 5765 (1976).
- ⁶R. G. Green and R. P. Wayne, *J. Photochem.* **6**, 371 (1977).
- ⁷R. J. Donovan, private communication (1980).
- ⁸IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ(1) = -141.5 \text{ kJ}\cdot\text{mol}^{-1}$

$\Delta H^\circ(2) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$

$\Delta H^\circ(3) = -581 \text{ kJ}\cdot\text{mol}^{-1}$

$\Delta H^\circ(4) = -425 \text{ kJ}\cdot\text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3 + k_4$)

$k = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 0.16$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred values are based on the results of Force and Wiesenfeld¹ and Davidson *et al.*,² which are in excellent agreement. The weight of evidence from many O(¹D) rate studies suggests that the results of Fletcher and Husain³ contain a systematic error.

The results from the relative rate coefficient studies^{4,5} were not considered in this evaluation. However, combining the values of $k/k(\text{O}(\text{}^1\text{D}) + \text{N}_2\text{O})$ reported in Refs. 4 and 5 with the IUPAC preferred value for $k(\text{O}(\text{}^1\text{D}) + \text{N}_2\text{O})$ yields

rate coefficients in good agreement with the preferred value. Both Donovan⁶ and Force and Wiesenfeld¹ report that the quenching channel (2) is a significant removal pathway for O(¹D). Consequently, preferred values are given for both the overall rate constant, k , and for the branching ratio k_2/k . These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

- ¹A. P. Force and J. R. Wiesenfeld, *J. Phys. Chem.* **85**, 782 (1981).
- ²J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, *J. Chem. Phys.* **69**, 4277 (1978).
- ³I. S. Fletcher and D. Husain, *J. Phys. Chem.* **80**, 1837 (1976).
- ⁴R. K. Jayanty, R. Simonaitis, and J. Heicklen, *J. Photochem.* **4**, 381 (1975).
- ⁵R. Atkinson, G. M. Breuer, J. N. Pitts, Jr., and H. L. Sandoval, *J. Geophys. Res.* **81**, 5765 (1976).
- ⁶R. J. Donovan, private communication (1980).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -170.4 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -563.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + ik_3$)

$$k = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.14 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the results of Force and Wiesenfeld¹ and Davidson *et al.*,² which are in excellent agreement. The weight of evidence from many O(¹D) rate studies suggests that the data of Fletcher and Husain³ contain a systematic error. The results from the relative rate coefficient study⁴ was not considered in this evaluation. Combining the value of $k/k(\text{O}(^1\text{D}) + \text{N}_2\text{O})$ reported in Ref. 4 with

the IUPAC preferred value of $k(\text{O}(^1\text{D}) + \text{N}_2\text{O})$ yields a value $\sim 25\%$ lower than the preferred value. The observation of a quenching channel in this reaction is consistent with the results from the O(¹D) atom reactions with CF₂Cl₂ and CFCI₃. Consequently, preferred values are given for both the overall rate constant, k , and for the branching ratio k_2/k . These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

¹A. P. Force and J. R. Wiesenfeld, *J. Phys. Chem.* **85**, 782 (1981).

²J. A. Davidson, H. I. Schiff, T. J. Brown, and C. J. Howard, *J. Chem. Phys.* **69**, 4277 (1978).

³I. S. Fletcher and D. Husain, *J. Phys. Chem.* **80**, 1837 (1976).

⁴R. K. Jayanty, R. Simonaitis, and J. Heicklen, *J. Photochem.* **4**, 381 (1975).

⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

O(¹D) + COFCl → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3.$$

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain¹ by use of a scaling factor of 0.5. The weight of evidence from many O(¹D) rate studies suggests that

O(¹D) rates reported by Husain and co-workers¹ contain a systematic error, and that these results can be made consistent with other O(¹D) recommended values in this evaluation by use of this scaling factor. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.²

References

¹I. S. Fletcher and D. Husain, *J. Photochem.* **8**, 355 (1978).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

O(¹D) + COCl₂ → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3.$$

Comments on Preferred Values

The preferred value is derived from the data of Fletcher and Husain¹ by use of the scaling factor of 0.5. The weight of evidence from many O(¹D) atom rate studies suggests that O(¹D) rates reported by Husain and co-workers¹ contain a systematic error, and that these results can be made consis-

tent with other O(¹D) recommended values in this evaluation by use of this scaling factor. Note that Jayanty *et al.*² present evidence, based on high yields of CO, that the reaction channel to produce ClO + ClCO is very important. The preferred value is identical to that in our previous evaluation, IUPAC, 1992.³

References

- ¹I. S. Fletcher and D. Husain, *J. Photochem.* **8**, 355 (1978).
- ²R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, *J. Photochem.* **5**, 217 (1976).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 4.4 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.7 \times 10^{-11} \exp(-2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred value is derived from a least-squares fit to data below 300 K reported by Watson *et al.*,¹ Lee *et al.*,² Miller and Gordon,³ and Kita and Stedman.⁴ The results of these studies are in excellent agreement below 300 K; at higher temperatures the data are in poorer agreement. After extrapolation, the results of Watson *et al.*,¹ Miller and Gordon,³ and Kita and Stedman⁴ agree with the results of Benson *et al.*⁵ and Steiner and Rideal.⁶ Note that the two

most recent studies^{3,4} have measured both the forward and reverse rates and have shown that the rate coefficient ratio agrees with equilibrium constant data. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

- ¹R. T. Watson, E. S. Machado, R. L. Schiff, S. Fischer, and D. D. Davis, Proceedings of the 4th CIAP Conference, DOT-OST-75, 1975.
- ²J. H. Lee, J. V. Michael, W. A. Payne, L. J. Stief, and D. A. Whytock, *J. Chem. Soc. Faraday Trans. 1*, **73**, 1530 (1977).
- ³J. C. Miller and R. J. Gordon, *J. Chem. Phys.* **75**, 5305 (1991).
- ⁴D. Kita and D. H. Stedman, *J. Chem. Soc. Faraday Trans. 2*, **78**, 1249 (1982).
- ⁵S. W. Benson, F. R. Cruickshank, and R. Shaw, *Int. J. Chem. Kinet.* **1**, 29 (1969).
- ⁶H. Steiner and E. K. Rideal, *Proc. R. Soc. London, Ser. A* **173**, 503 (1939).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -228.2 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = 5.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(4.45 \pm 0.06) \times 10^{-11}$	243–368	Dobis and Benson, 1993 ¹	(a)
<i>Branching Ratios</i>			
$k_2/k = 0.05 \pm 0.03$	243–368	Dobis and Benson, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	250–420	IUPAC, 1992 ²	(b)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	250–420		
$k_1 = 1.8 \times 10^{-11} \exp(170/T)$	250–420	NASA, 1994 ³	(c)
$k_2 = 4.1 \times 10^{-11} \exp(-450/T)$	250–420		

Comments

- (a) Ethyl radicals were formed by reaction of Cl atoms with C_2H_6 and allowed to react with O_2 in a very low pressure reactor (VLPR) flow system with mass spectrometric analysis of reactants and products.
- (b) See Comments on Preferred Values.
- (c) Based on the direct study of Lee and Howard⁴ and supported by the room temperature results of Cattell and Cox.⁵

Preferred Values

$$k_1 = 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 1.8 \times 10^{-11} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}420 \text{ K.}$$

$$k_2 = 4.1 \times 10^{-11} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}420 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \Delta(E_2/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

The recommendation is unchanged from our previous evaluation, IUPAC, 1992.² The preferred values for k_1 and k_2

are based on results of the direct study by Lee and Howard.⁴ These expressions were derived by the authors from data on the overall rate and the branching ratio. The total rate constant is temperature independent over the range 250–420 K with a value of $4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The room temperature results of Cattell and Cox⁵ are in good agreement with this recommendation. Based on the combined results of these two studies, neither channel shows any pressure dependence between 1 mbar and 1 bar showing that stabilization of the $\text{HOOC}\dot{\text{C}}\text{l}^*$ intermediate does not occur, the two bimolecular channels making up the entire reaction pathway. The recent study of Dobis and Benson¹ reports a total rate constant in good agreement with this recommendation but a significantly lower value of the branching ratio k_2/k . Results of earlier indirect studies^{6–9} were not used.

References

- ¹O. Dobis and S. W. Benson, *J. Am. Chem. Soc.* **115**, 8798 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴Y.-P. Lee and C. J. Howard, *J. Chem. Phys.* **77**, 756 (1982).
- ⁵F. C. Cattell and R. A. Cox, *J. Chem. Soc. Faraday Trans. 2*, **82**, 1413 (1986).
- ⁶M. T. Leu and W. B. DeMore, *Chem. Phys. Lett.* **41**, 121 (1976).
- ⁷G. Poulet, G. Le Bras, and J. Combourieu, *J. Chem. Phys.* **69**, 767 (1978).
- ⁸J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, *Proc. R. Soc. London, Ser. A* **368**, 436 (1979).
- ⁹R. A. Cox, *Int. J. Chem. Kinet.* **12**, 649 (1980).

$$\Delta H^\circ = -62.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-11} \exp(-980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 265–424 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The room temperature rate coefficients reported in Refs. 1–5 range from $(3.6\text{--}6.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The studies of Michael *et al.*,³ Poulet *et al.*,⁴ and Keyser⁵ are considered to be the most reliable. The recommended Arrhenius expression is that reported by Keyser.⁵ The data of Michael *et al.*³ below 300 K are in good agreement; however, the A-factor reported is considerably lower than that expected from theoretical considerations and may possibly

be attributed to decomposition of H_2O_2 above 300 K. More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson⁶ using mass spectrometry confirmed that this reaction proceeds only by the H-atom abstraction mechanism. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

- ¹R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, *J. Chem. Phys.* **65**, 2126 (1976).
- ²M. T. Leu and W. B. DeMore, *Chem. Phys. Lett.* **41**, 121 (1976).
- ³J. V. Michael, D. A. Whytock, J. H. Lee, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* **67**, 3533 (1977).
- ⁴G. Poulet, G. Le Bras, and J. Combourieu, *J. Chem. Phys.* **69**, 767 (1978).
- ⁵L. F. Keyser, *J. Phys. Chem.* **84**, 11 (1980).
- ⁶S. P. Heneghan and S. W. Benson, *Int. J. Chem. Kinet.* **15**, 1311 (1983).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -23.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.4 \times 10^{-33} (T/300)^{-3.9} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 160–300 K.

$k_0 = 1.6 \times 10^{-33} (T/300)^{-2.9} [\text{O}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 160–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 200 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The two recent determinations^{1,2} are in good agreement and are also consistent with the older data of Ref. 3, if one takes into account the strong temperature dependence of k_0 . The most extensive measurements of Ref. 2 are the basis for

the preferred values. No falloff expressions are reported here, because deviations from third order behavior become apparent only at pressures higher than 10 bar and because the falloff formalism does not apply to the radical-complex mechanism operating in this case. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹J. M. Nicovich, K. D. Kreutter, C. J. Shackelford, and P. H. Wine, *Chem. Phys. Lett.* **179**, 367 (1991).
- ²S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, *J. Chem. Phys.* **95**, 6463 (1991).
- ³J. E. Nicholas and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A* **307**, 391 (1968).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 23.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 6.2 \times 10^{-13} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 2.8 \times 10^{-10} \exp(-1820/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the extensive data of Ref. 1. No deviations from third-order behavior were ob-

served at pressures below 1 bar. The reaction probably does not proceed via an energy transfer mechanism (see comments on the reverse reaction $\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$), but rather by a radical complex mechanism. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

¹S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, *J. Chem. Phys.* **95**, 6463 (1991).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -32.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients**Rate coefficient data**

k_0/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(9.1 \pm 3.0) \times 10^{-34} [\text{Ar}]$	300	Clark, Clyne, and Stedman, 1966 ¹	(a)
$1.05 \times 10^{-34} \exp[(810 \pm 70)/T] [\text{N}_2]$	185–260	Nicovich, Kreutter, and Wine, 1990 ²	(b)
<i>Reviews and Evaluations</i>			
$1.3 \times 10^{-33} (T/300)^{-3.8} [\text{air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Discharge-flow system study of Cl_2 -He mixtures. Cl atom concentrations were measured by titration with nitrosyl chloride using the red chlorine afterglow spectrum. The total pressure was 2–4 Torr. From experiments performed also at 195 K, an activation energy of about 8.4 kJ mol^{-1} was obtained.
- (b) Laser flash photolysis of Cl_2 -CO-M ($\text{M} = \text{N}_2, \text{CO}, \text{Ar}, \text{CO}_2$) mixtures at 355 nm. Detection of $\text{Cl}(^2\text{P}_{3/2})$ was by time-resolved resonance fluorescence spectroscopy. The total pressure was 14–200 Torr. By second- and third-law analysis of the temperature dependence of the equilibrium constant the value of $\Delta H_{298}^\circ = -32.2 \pm 2.5 \text{ kJ mol}^{-1}$ was derived. The relative collision efficiencies were $\beta_c(\text{CO}_2) : \beta_c(\text{CO/N}_2) : \beta_c(\text{Ar}) = 3.2 : 1.0 : 0.8$.
- (c) Value adopted from Ref. 2.

Preferred Values

$$k_0 = 1.3 \times 10^{-33} (T/300)^{-3.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 185\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The recommended rate coefficients are based on the measurements of Ref. 2. At room temperature the preferred value is a factor of two greater than that determined by Clark *et al.*¹

References

¹T. C. Clark, M. A. A. Clyne, and D. H. Stedman, *Trans. Faraday Soc.* **62**, 3354 (1966).

²J. M. Nicovich, K. D. Kreutter, and P. H. Wine, *J. Chem. Phys.* **92**, 3539 (1990).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = 32.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.1 \times 10^{-10} \exp[-(2960 \pm 160)/T] [\text{N}_2]$	185–260	Nicovich, Kreutter, and Wine, 1990 ¹	(a)

Comments

- (a) Laser flash photolysis of $\text{Cl}_2\text{-CO-M}$ ($\text{M}=\text{N}_2, \text{CO}, \text{Ar}, \text{CO}_2$) mixtures at 355 nm. Detection of $\text{Cl}(^2\text{P}_{3/2})$ was by time-resolved resonance fluorescence spectrum. The total pressure was 14–200 Torr. By second- and third-law analysis of the temperature dependence of the equilibrium constant, the value of $\Delta H_{298}^\circ = 32.2 \pm 2.5 \text{ kJ mol}^{-1}$ was derived. The relative collision efficiencies were $\beta_c(\text{CO}_2) : \beta_c(\text{CO/N}_2) : \beta_c(\text{Ar}) = 3.2 : 1.0 : 0.8$.

$k_0 = 4.1 \times 10^{-10} \exp(-2960/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 185–300 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred rate coefficients are based on the reported study of Nicovich *et al.*¹

Preferred Values

$$k_0 = 2.0 \times 10^{-14} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

References

- ¹ J. M. Nicovich, K. D. Kreutter, and P. H. Wine, *J. Chem. Phys.* **92**, 3539 (1990).

$$\Delta H^\circ = -162.4 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.9 \times 10^{-11} \exp(-260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 205–298 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
 $\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The preferred Arrhenius expression is derived from a fit to the data within the temperature range 205–298 K reported from the studies of Watson *et al.*,¹ Zahniser *et al.*,² Kurylo and Braun,³ and Clyne and Nip.⁴ In this temperature range the rate constants at any particular temperature agree to within 30–40%. Results of the study by Nicovich *et al.*⁵ show non-Arrhenius behavior over the temperature range 189–385 K. These results are in very good agreement with the present recommendation above about $\sim 250 \text{ K}$; at lower temperatures they are higher than the recommendation although still within its stated uncertainty down to about 220 K.

Vanderzanden and Birks⁶ have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1–0.5%) of $\text{O}_2(^1\Sigma_g)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore⁷ in connection with the Cl_2 photosensitized decomposition of ozone. However, Choo and Leu⁸ were unable to detect $\text{O}_2(^1\Sigma)$ or $\text{O}_2(^1\Delta)$ in the $\text{Cl} + \text{O}_3$ system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2} , respectively. They suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder *et al.*⁹ in a study of infrared line intensities of the ClO radical present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the $\text{Cl} + \text{O}_3$ reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals. These authors point out the possibility for systematic error from assuming a 1:1 stoichiometry for $[\text{ClO}] : [\text{O}_3]_0$ when using the $\text{Cl} + \text{O}_3$ reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies. The pre-

ferred values are identical to those in our previous evaluation, IUPAC, 1992.¹⁰

References

- ¹R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, *J. Chem. Phys.* **65**, 2126 (1976).
- ²M. S. Zahniser, F. Kaufman, and J. G. Anderson, *Chem. Phys. Lett.* **37**, 226 (1976).
- ³M. J. Kurylo and W. Braun, *Chem. Phys. Lett.* **37**, 232 (1976).

- ⁴M. A. A. Clyne and W. S. Nip, *J. Chem. Soc. Faraday Trans. 2*, **72**, 838 (1976).
- ⁵J. M. Nicovich, K. D. Kreutter, and P. H. Wine, *Int. J. Chem. Kinet.* **22**, 399 (1990).
- ⁶J. W. Vanderzanden and J. W. Birks, *Chem. Phys. Lett.* **88**, 109 (1982).
- ⁷W. B. DeMore, presented at 182nd National Meeting, American Chemical Society, New York, August 1981.
- ⁸K. Y. Choo and M.-T. Leu, *J. Phys. Chem.* **89**, 4832 (1985).
- ⁹J. B. Burkholder, P. D. Hammer, and C. J. Howard, *J. Geophys. Res.* **94**, 2225 (1989).
- ¹⁰IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -4.8 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k < 2.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred upper limit to the rate coefficient is based on the work of Wine *et al.*¹ The data in Refs. 1 and 2 show that the earlier data of Kurylo *et al.*³ were well above the true value for the rate coefficient of this reaction. The preferred

values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹P. H. Wine, J. R. Wells, and J. M. Nicovich, *J. Phys. Chem.* **92**, 2223 (1988).
- ²H. Zagogianni, A. Mellouki, and G. Poulet, *C. R. Acad. Sci., Series 2*, 573 (1987).
- ³M. J. Kurylo, J. L. Murphy, and G. L. Knable, *Chem. Phys. Lett.* **94**, 281 (1983).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -60.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.26 \pm 0.17) \times 10^{-11}$	298	Becker <i>et al.</i> , 1991 ¹	(a)
<i>Reviews and Evaluations</i>			
2.6×10^{-11}	200–300	IUPAC, 1992 ²	(b)
2.4×10^{-11}	200–300	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow-mass spectrometric technique. Two sets of experiments were performed, with monitoring of either the decay of Cl in excess NO₃ or the decay of NO₃ in excess Cl.
- (b) Based on the results of Mellouki *et al.*⁴
- (c) Based on the results of Becker *et al.*¹ and Mellouki *et al.*⁴

Preferred Values

$$k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 400 \text{ K.}$$

Comments on Preferred Values

The preferred value at room temperature is based on the studies of Becker *et al.*¹ and Mellouki *et al.*⁴ The results of these direct absolute rate studies are preferred over those of earlier relative rate studies,^{5–7} in which NO₃ was monitored in the photolysis of Cl₂-ClONO₂-N₂ mixtures. The agreement among these earlier studies^{5–7} is not good and probably arises from complications in the chemistry of the systems used. This radical-radical reaction is expected to have negli-

gible temperature dependence, which is consistent with the results of Cox *et al.*⁷

References

¹E. Becker, U. Wille, A. D. Parr, and R. P. Wayne, *Ber. Bunsenges. Phys. Chem.* **95**, 1173 (1991).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴A. Mellouki, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **91**, 5760 (1987).

⁵R. A. Cox, R. A. Barton, E. Ljungstrom, and D. W. Stocker, *Chem. Phys. Lett.* **108**, 228 (1984).

⁶J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, *J. Phys. Chem.* **89**, 4848 (1985).

⁷R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, *J. Phys. Chem.* **91**, 3361 (1987).

$$\Delta H^\circ = -13.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.4 \times 10^{-11} \exp(160/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 298\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The data of Toohey¹ agree well with the previous work of Bemand *et al.*² at 298 K, but show a small negative temperature dependence over a similar range to that over which Bemand *et al.*² saw little change in *k*. The preferred value is the average of the 298 K values from these two studies^{1,2} and the

temperature dependence of Toohey¹ is accepted but with error limits covering the possibility that *k* is independent of temperature. Earlier work in Refs. 3 and 4 is rejected following the recommendation of Bemand *et al.*² The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

¹D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. Thesis, Harvard University, Cambridge, MA (1988).

²P. P. Bemand, M. A. A. Clyne, and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **69**, 1356 (1973).

³N. Basco and S. K. Dogra, *Proc. R. Soc. London, Ser. A* **323**, 417 (1971).

⁴V. I. Gritsan, V. N. Panfilov, and I. L. Sukhanov, *Reaction Kinetics and Catalysis Letters* **2**, 265 (1975).

⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -101.1 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$6.0 \times 10^{-11} \exp[(127 \pm 30)/T]$	233-373	Stevens and Anderson, 1992 ¹	(a)
$(9.1 \pm 0.4) \times 10^{-11}$	298		
<i>Reviews and Evaluations</i>			
9.8×10^{-11}	200–300	IUPAC, 1992 ²	(b)
$6.2 \times 10^{-11} \exp(130/T)$	230–370	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow system. The pseudo-first-order decay of [Cl] in excess [Cl₂O] was detected by resonance fluorescence.
- (b) Based on the results of Ray *et al.*⁴
- (c) Based on the results of Stevens and Anderson¹ and Ray *et al.*⁴

Preferred Values

$$k = 9.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.2 \times 10^{-11} \exp(130/T) \text{ over the temperature range } 233\text{--}373 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 130 \text{ K.}$$

Comments on Preferred Values

The preferred room temperature value is the mean of the value reported by Stevens and Anderson¹ and the values obtained by Ray *et al.*⁴ using two completely independent techniques. This value has been confirmed by the relative rate study of Burrows and Cox.⁵ The much lower value reported earlier by Basco and Dogra⁶ has been rejected. The recommended temperature dependence is from Stevens and Anderson.¹ The agreement between the low-pressure studies and the high-pressure study implies that there is no pressure dependence over the pressure range 1 mbar–1 bar.

References

- ¹P. S. Stevens and J. G. Anderson, *J. Phys. Chem.* **96**, 1708 (1992).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴G. W. Ray, L. F. Keyser, and R. T. Watson, *J. Phys. Chem.* **84**, 1674 (1980).
- ⁵J. P. Burrows and R. A. Cox, *J. Chem. Soc. Faraday Trans. 1*, **77**, 2465 (1981).
- ⁶N. Basco and S. K. Dogra, *Proc. R. Soc. London, Ser. A* **323**, 401 (1971).

$$\Delta H^\circ = -151.4 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 230\text{--}298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on results of the discharge flow-mass spectrometric study of Friedl¹ and the relative rate

study of Cox and Hayman.² The Arrhenius parameters have not been determined experimentally; however, the agreement of the room temperature value and that at 233 K along with the high value of *k* precludes a significant temperature dependence. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹R. R. Friedl, unpublished data (1991).
- ²R. A. Cox and G. D. Hayman, *Nature* **332**, 796 (1988).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -70.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.8 \times 10^{-12} \exp(160/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 219\text{--}298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.12 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred value averages the results of Margitan¹ and Kurylo *et al.*,² which are in good agreement. These results show that the rate coefficient for this reaction is two orders of magnitude greater than was indicated by the previous study of Kurylo and Manning.³ It now seems likely that the

reaction actually being observed by Kurylo and Manning³ was the slower reaction $\text{O}(^3\text{P}) + \text{ClONO}_2$. Margitan¹ has shown that the reaction proceeds by Cl atom abstraction rather than by O-atom abstraction. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

$$\Delta H^\circ = 7.2 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.08 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

The preferred value at 298 K is obtained by taking the mean from the most reliable absolute (Watson *et al.*,¹ Manning and Kurylo,² Whytock *et al.*,³ Michael and Lee,⁴ Lin *et al.*,⁵ Zahniser *et al.*,⁶ Keyser,⁷ and Ravishankara and Wine⁸) and the most reliable relative (Pritchard *et al.*,^{9,10} Knox,¹¹ Knox and Nelson,¹² and Lin *et al.*⁵) rate coefficient studies. The room temperature absolute rate coefficients of Dobis and Benson¹³ and Sawerysyn *et al.*¹⁴ are in good agreement with the preferred value, which is identical to our previous evaluation, IUPAC, 1992.¹⁵

The preferred Arrhenius expression is derived to best fit all the reliable experimental data between 200 and 300 K. Data obtained above 300 K are not considered due to the nonlinear Arrhenius behavior observed in the absolute rate coefficient studies.^{3,5,7,8} The average values of k at 230 K are: $3.19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (flash photolysis);^{1,2,3,8} $2.67 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (discharge flow);^{6,7} and $2.27 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (competitive chlorination).^{5,9-12} These differences increase at lower temperatures. Ravishankara and Wine⁸ have suggested that the results obtained using the discharge flow and competitive chlorination techniques may be in error at the lower temperatures ($T < 240 \text{ K}$) due to a nonequilibration of the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ states of atomic chlorine. The chemical composition in each of the flash photolysis studies contained an efficient spin equilibrator, whereas this was not the case in the discharge flow studies. However, the reactor walls in the discharge flow studies could have been expected to have acted as an efficient spin equilibrator. Consequently, until the

References

- ¹J. J. Margitan, *J. Phys. Chem.* **87**, 674 (1983).
- ²M. J. Kurylo, G. L. Knable, and J. L. Murphy, *Chem. Phys. Lett.* **95**, 9 (1983).
- ³M. J. Kurylo and R. G. Manning, *Chem. Phys. Lett.* **48**, 279 (1977).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

hypothesis of Ravishankara and Wine⁸ is proven, it is assumed that the discharge flow and competitive chlorination results are reliable. The Arrhenius expression is derived to yield the preferred values of k at 298 K ($1.04 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and at 230 K ($2.71 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, this is a simple mean of the three average values obtained from each of the three techniques). The preferred expression of $9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ yields rate coefficients similar to those obtained in the discharge flow-resonance fluorescence studies. If only flash photolysis-resonance fluorescence results are used, then an alternate expression of $6.4 \times 10^{-12} \exp(-1220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is obtained (k at 298 K = $1.07 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and k at 230 K = $3.19 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). It should be noted that the rate coefficient ratios $k(\text{Cl} + \text{O}_3)/k(\text{Cl} + \text{CH}_4)$ determined by DeMore¹⁶ at 197 K and 217 K are in reasonable agreement with the present evaluations for these reactions (see the data sheet on the $\text{Cl} + \text{O}_3$ reaction).

References

- ¹R. T. Watson, G. Machado, S. Fischer, and D. D. Davis, *J. Chem. Phys.* **65**, 2126 (1976).
- ²R. G. Manning and M. J. Kurylo, *J. Phys. Chem.* **81**, 291 (1977).
- ³D. A. Whytock, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* **66**, 2690 (1977).
- ⁴J. V. Michael and J. H. Lee, *Chem. Phys. Lett.* **51**, 303 (1977).
- ⁵C. L. Lin, M. T. Leu, and W. B. DeMore, *J. Phys. Chem.* **82**, 172 (1978).
- ⁶M. S. Zahniser, B. M. Berquist, and F. Kaufman, *Int. J. Chem. Kinet.* **10**, 15 (1978).
- ⁷L. F. Keyser, *J. Chem. Phys.* **69**, 214 (1978).
- ⁸A. R. Ravishankara and P. H. Wine, *J. Chem. Phys.* **72**, 25 (1980).
- ⁹H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.* **76**, 1201 (1954).
- ¹⁰H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.* **77**, 2629 (1955).
- ¹¹J. H. Knox, *Chem. Indust.* 1631 (1955); modified by authors of reference 5.
- ¹²J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.* **55**, 937 (1959).
- ¹³O. Dobis and S. W. Benson, *Int. J. Chem. Kinet.* **19**, 691 (1987).
- ¹⁴J.-P. Sawerysyn, C. Lafage, B. Meriaux, and A. Tighezza, *J. Chim. Phys.* **84**, 1187 (1987).
- ¹⁵IUPAC, Supplement IV, 1992 (see references in Introduction).
- ¹⁶W. B. DeMore, *J. Geophys. Res.* **96**, 4995 (1991).

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$5.4 \times 10^{-30} (T/300)^{-2.09} [\text{air}]$	252–370	Kaiser, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
$6.0 \times 10^{-30} (T/300)^{-3.5} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$5.4 \times 10^{-30} (T/300)^{-2.1} [\text{air}]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Mixtures of Cl_2 , C_2H_2 , and C_2H_6 and the diluent gases air, N_2 , and SF_6 were irradiated with an UV fluorescence lamp. After irradiation, C_2H_2 and C_2H_6 concentrations were monitored by GC. The measurements were carried out at 25–1300 Torr total pressure. Rate measurements were relative to the rate coefficient for the reaction $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$, for which an average rate coefficient from Refs. 4–6 of $8.68 \times 10^{-11} \exp(-225/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was adopted. Extrapolations were performed with $F_c=0.6$.
- (b) The preferred values are averages of k_0 from Refs. 7 and 8, assuming equal rates for $\text{M}=\text{Ar}$ and N_2 . The temperature dependence is from Ref. 7.

- (c) Based on measurements from Ref. 1.

Preferred Values

$k_0 = 5.7 \times 10^{-30} (T/300)^{-3} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

Our previous preferred values² have been slightly modified to accommodate the recent determination by Kaiser.¹

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$2.13 \times 10^{-10} (T/300)^{-1.05}$	252–370	Kaiser, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
2.3×10^{-10}	200–300	IUPAC, 1992 ²	(b)
$2.1 \times 10^{-10} (T/300)^{-1.0}$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 .
- (b) Based on the measurements from Ref. 8.
- (c) See comment (c) for k_0 .

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

The preferred value is identical to our previous evaluation, IUPAC, 1992.² The temperature dependence of k_∞ given by Kaiser¹ is sensitive to the F_c value employed, which was constant ($F_c=0.6$). The values of Refs. 1 and 2 are in very good agreement at room temperature.

Preferred Values

$k_\infty = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

References

- ¹E. W. Kaiser, *Int. J. Chem. Kinet.* **24**, 179 (1992).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³NASA Evaluation No. 11, 1994 (see references in Introduction).
⁴O. Dobis and S. W. Benson, *J. Am. Chem. Soc.* **112**, 1023 (1990).
⁵R. G. Manning and M. J. Kurylo, *J. Phys. Chem.* **81**, 291 (1977).
⁶R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, *J. Phys. Chem.* **84**, 2009 (1980).
⁷J. Brunning and L. J. Stief, *J. Chem. Phys.* **83**, 1005 (1985).
⁸T. J. Wallington, J. M. Andino, I. M. Lorkovic, E. W. Kaiser, and G. Marston, *J. Phys. Chem.* **94**, 3644 (1990).

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.6 \times 10^{-29} (T/300)^{-3.5} [\text{air}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

Ref. 1 is the only measurement in the falloff range which allows for an extrapolation to k_0 . The preferred values are based on Ref. 1 and an estimated temperature dependence such as observed for $\text{Cl} + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{ClC}_2\text{H}_2 + \text{M}$ (see this evaluation).

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

The falloff extrapolation of the data from Ref. 1 with $F_c = 0.6$ is consistent with results in the intermediate falloff range. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

- ¹T. J. Wallington, J. M. Andino, I. M. Lorkovic, E. W. Kaiser, and G. Marston, *J. Phys. Chem.* **94**, 3644 (1990).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -8.1 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$8.20 \times 10^{-11} \exp[-(86 \pm 10)/T]$	203–343	Dobis and Benson, 1991 ¹	(a)
$(6.10 \pm 0.11) \times 10^{-11}$	298	Kaiser <i>et al.</i> , 1992 ²	(b)
$(7.05 \pm 1.4) \times 10^{-11}$	298	Stickel <i>et al.</i> , 1992 ³	(c)
$(5.9 \pm 0.6) \times 10^{-11}$	297 ± 2		
<i>Reviews and Evaluations</i>			
$8.2 \times 10^{-11} \exp(-100/T)$	220–600	IUPAC, 1992 ⁴	(d)
$7.7 \times 10^{-11} \exp(-90/T)$	220–350	NASA, 1994 ⁵	(e)

Comments

- (a) Very low pressure reactor study. Cl atoms were generated by microwave discharge of Cl₂-He mixtures, with MS analysis of reactants and products.
- (b) Cl atoms were generated by the laser photolysis of Cl₂ at 351 nm, with detection of the HCl product by time-resolved IR spectroscopy. The rate coefficient was obtained from the measured formation rate of HCl.
- (c) Cl atoms were generated by the laser photolysis of C(O)Cl₂ at 266 nm, with detection of the HCl product by time-resolved tunable diode laser absorption spectroscopy. The rate coefficient was obtained from the measured formation rate of HCl.
- (d) The 298 K rate coefficient was the average of the room temperature rate coefficients of Davis *et al.*,⁶ Manning and Kurylo,⁷ Ray *et al.*,⁸ Lewis *et al.*,⁹ and Dobis and Benson.¹⁰ The temperature dependence was the average of those from the studies of Manning and Kurylo⁷ and Lewis *et al.*⁹
- (e) The 298 K rate coefficient was the mean of the absolute rate coefficients of Davis *et al.*,⁶ Manning and Kurylo,⁷ Ray *et al.*,⁸ and Lewis *et al.*,⁹ with the temperature dependence being that which best fit the data of Manning and Kurylo⁷ and Lewis *et al.*⁹

Preferred Values

$k = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 8.1 \times 10^{-11} \exp(-95/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–600 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The 298 K rate coefficient is the average of the room temperature rate coefficients of Davis *et al.*⁶ (reduced by 10% as discussed previously⁴), Manning and Kurylo,⁷ Ray *et al.*,⁸ Lewis *et al.*,⁹ Dobis and Benson,^{1,10} and Stickel *et al.*,³ all of which are in excellent agreement. The temperature dependence is the average of those from the temperature-dependent studies of Manning and Kurylo,⁷ Lewis *et al.*,⁹ and Dobis and Benson.¹ The room temperature rate coefficients of Poulet *et al.*¹¹ and Kaiser *et al.*² are in agreement with the preferred 298 K rate coefficient.

References

- ¹O. Dobis and S. W. Benson, J. Am. Chem. Soc. **113**, 6377 (1991).
- ²E. W. Kaiser, L. Rimai, E. Schwab, and E. C. Lim, J. Phys. Chem. **96**, 303 (1992).
- ³R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, J. Phys. Chem. **96**, 9875 (1992).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. **2**, 101 (1970).
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- ⁸G. W. Ray, L. F. Keyser, and R. T. Watson, J. Phys. Chem. **84**, 1674 (1980).
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- ¹⁰O. Dobis and S. W. Benson, J. Am. Chem. Soc. **112**, 1023 (1990).
- ¹¹G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **85**, 1892 (1981).

$\Delta H^\circ(1) = -11.6 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta H^\circ(2) = -19.1 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.2 \times 10^{-10} \exp(40/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–600 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the absolute rate coefficient of Lewis *et al.*¹ and the relative rate measurements of Pritchard *et al.*² Knox and Nelson,³ Atkinson and Aschmann,⁴ and Wallington *et al.*,⁵ all of which are

in reasonable agreement. The temperature dependence is that determined by Lewis *et al.*¹ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

References

- ¹R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. **84**, 2009 (1980).
- ²H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. **77**, 2629 (1955).
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- ⁴R. Atkinson and S. M. Aschmann, Int. J. Chem. Kinet. **17**, 33 (1985).
- ⁵T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -63.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 7.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.2 \times 10^{-11} \exp(-34/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}500 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.06 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The preferred temperature dependence is based on a least-squares fit to the 200–500 K data of Michael *et al.*¹ and the 223–323 K data of Anderson and Kurylo.² The preferred 298

K rate coefficient is based on these absolute studies and the room temperature data of Niki *et al.*,³ Fasano and Nogar,⁴ and Poulet *et al.*,⁵ all of which are in good agreement. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

References

- ¹J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* **70**, 1147 (1979).
- ²P. C. Anderson and M. J. Kurylo, *J. Phys. Chem.* **83**, 2053 (1979).
- ³H. Niki, P. D. Maker, L. P. Breitenbach, and C. M. Savage, *Chem. Phys. Lett.* **57**, 596 (1978).
- ⁴D. M. Fasano and N. S. Nogar, *Int. J. Chem. Kinet.* **13**, 325 (1981).
- ⁵G. Poulet, G. Laverdet, and G. Le Bras, *J. Phys. Chem.* **85**, 1892 (1981).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -72.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -35.2 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(9.2 \pm 0.7) \times 10^{-11}$	298 ± 2	Scollard <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
7.2×10^{-11}	210–340	IUPAC, 1992 ²	(b)

Comments

- (a) Relative rate method. Cl atoms were generated by the photolysis of Cl_2 in Cl_2 - CH_3CHO -dimethyl ether- N_2 mixtures, and the concentrations of CH_3CHO and dimethyl ether measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio $k(\text{Cl} + \text{CH}_3\text{CHO})/k(\text{Cl} + \text{dimethyl ether})$ is placed on an absolute basis by using a rate coefficient of $k(\text{Cl} + \text{dimethyl ether}) = 1.76 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³
- (b) See Comments on Preferred Values.

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficient of Payne *et al.*⁴ and the relative rate coefficients of Niki *et al.*,⁵ Wallington *et al.*,⁶ and Bartels *et al.*⁷ The lack of a temperature dependence of the rate coefficient is consistent with the data of Payne *et al.*⁴ The branching ratio is derived from the data of Niki *et al.*⁵ and Bartels *et al.*⁷ The relative rate coefficient of Scollard *et al.*¹ is ~30% higher than the preferred values, which are identical to our previous evaluation, IUPAC, 1992.²

Preferred Values

$$k = 7.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 210\text{--}340 \text{ K.}$$

$$k_2/k < 0.05 \text{ at } 298 \text{ K.}$$

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* **70**, 3652 (1979).

⁴W. A. Payne, D. F. Nava, F. L. Nesbitt, and L. J. Stief, *J. Phys. Chem.* **94**, 7190 (1990).

⁵H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *J. Phys. Chem.* **89**, 588 (1985).

⁶T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, *Int. J. Chem. Kinet.* **20**, 867 (1988).

⁷M. Bartels, K. Hoyer, and U. Lange, *Ber. Bunsenges Phys. Chem.* **93**, 423 (1989).

Cl + C₂H₅CHO → products

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the relative rate study of Wallington *et al.*,¹ with expanded uncertainty limits, and is identical to our previous evaluation, IUPAC, 1992.²

References

¹T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, *Int. J. Chem. Kinet.* **20**, 867 (1988).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + CH₃COCH₃ → HCl + CH₃COCH₂

$\Delta H^\circ = -20.3 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

tive rate study of Wallington *et al.*,¹ with expanded uncertainties, and is identical to our previous evaluation, IUPAC, 1992.²

References

¹T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, *J. Atmos. Chem.* **10**, 301 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the rela-

Cl + CH₃OH → HCl + CH₂OH

$\Delta H^\circ = -21.0 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(6.14 \pm 0.67) \times 10^{-11}$	298 ± 2	Dóbé <i>et al.</i> , 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$(5.3 \pm 1.2) \times 10^{-11}$	248-573	Lightfoot <i>et al.</i> , 1990 ²	(b)
<i>Reviews and Evaluations</i>			
5.3×10^{-11}	200-500	IUPAC, 1992 ³	(c)
5.4×10^{-11}	200-500	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with EPR detection of Cl atoms.
- (b) Derived from the measured initial HO₂ and CH₃O₂ radical concentrations in flash photolyzed Cl₂-CH₃OH-CH₄-N₂-O₂ mixtures, with the HO₂ and CH₃O₂ concentrations being measured by time-resolved UV absorption. Placed on an absolute basis by use of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) The 298 K rate coefficient was the average of the rate coefficients of Michael *et al.*,⁵ Wallington *et al.*,⁶ and Nelson *et al.*⁷ The zero temperature dependence was taken from the study of Michael *et al.*⁵
- (d) Based on the absolute rate coefficients of Michael *et al.*,⁵ Payne *et al.*,⁸ and Dóbé *et al.*,¹ and the relative rate coefficients of Wallington *et al.*,⁶ Nelson *et al.*,⁷ and Lightfoot *et al.*²

Preferred Values

$k = 5.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–573 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K value is the average of the rate coefficients of Michael *et al.*,⁵ Wallington *et al.*,⁶ Nelson *et al.*,⁷ Lightfoot *et al.*,² and Dóbé *et al.*,¹ and is in excellent agreement with the absolute rate coefficient of $(5.1 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K determined by Payne *et al.*⁸ for the reaction $\text{Cl} + \text{CH}_3\text{OD} \rightarrow \text{HCl} + \text{CH}_2\text{OD}$. The zero temperature dependence is taken from the studies of Michael *et al.*⁵ and Lightfoot *et al.*²

References

- ¹S. Dóbé, M. Otting, F. Temps, H. Gg. Wagner, and H. Ziemer, Ber. Bunsenges. Phys. Chem. **97**, 877 (1993).
- ²P. D. Lightfoot, B. Veyret, and R. Lesclaux, J. Phys. Chem. **94**, 708 (1990).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 10, 1994 (see references in Introduction).
- ⁵J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. **70**, 3652 (1979).
- ⁶T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
- ⁷L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
- ⁸W. A. Payne, J. Brunning, M. B. Mitchell, and L. J. Stief, Int. J. Chem. Kinet. **20**, 63 (1988).

Cl + C₂H₅OH → products

No new data have been published since our last evaluation.

Preferred Values

$k = 9.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Wallington *et al.*¹ and Nelson *et al.*,² which are in good

agreement, and is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, Int. J. Chem. Kinet. **20**, 867 (1988).
- ²L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, Int. J. Chem. Kinet. **22**, 1111 (1990).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + *n*-C₃H₇OH → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the data of Wallington *et al.*¹ and Nelson *et al.*,² which are in excellent

agreement, and is identical to our previous evaluation, IUPAC, 1992.³

References

¹T. J. Wallington, L. M. Skewes, W. O. Siegl, C.-H. Wu, and S. M. Japar, *Int. J. Chem. Kinet.* **20**, 867 (1988).

²L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 1111 (1990).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + *i*-C₃H₇OH → products

No new data have been published since our last evaluation.

Preferred Values

$$k = 8.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the relative rate study of Nelson *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.²

References

¹L. Nelson, O. Rattigan, R. Neavyn, H. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 1111 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -72 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$$k = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The only study carried out to date is that of Wallington *et al.*¹ The reaction may occur by the two pathways,

and the formation of HO radicals may have led to secondary reactions involving HO radicals. Since the room-temperature rate coefficient for the Cl atom reaction with H₂O₂ (this evaluation) is two orders of magnitude lower than that for Cl + CH₃OOH, it is expected that channel (2) will dominate. Wallington *et al.*¹ concluded that secondary reactions involving HO radicals did not contribute $\geq 15\%$ to the observed CH₃OOH consumption. The cited uncertainty limits on the preferred values reflect this possibility of HO radical involvement in the Wallington *et al.*¹ study. The preferred value is identical to our previous evaluation, IUPAC, 1992.²

References

¹T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, *J. Atmos. Chem.* **10**, 301 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(2) = -58 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$$k = 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the rate coefficients obtained by Wallington *et al.*¹ relative to $k(\text{Cl} + \text{CH}_3\text{Cl})$ and $k(\text{Cl} + \text{CH}_4)$, which are in good agreement, and is identical to our previous evaluation, IUPAC, 1992.²

Tyndall *et al.*³ have observed that CO_2 is the sole carbon-containing product formed from this reaction in air or N_2 diluent, and conclude from comparison of the rate coefficients for the reactions of the Cl atom with HCOOH , CH_3COOH ,⁴ and CD_3COOH ⁴ that reaction channel (2) dominates.

References

¹T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, *J. Atmos. Chem.* **10**, 301 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³G. S. Tyndall, T. J. Wallington, and A. R. Potts, *Chem. Phys. Lett.* **186**, 149 (1991).

⁴S. Koch and G. K. Moortgat, *Chem. Phys. Lett.* **173**, 531 (1990).

$$\Delta H^\circ(2) = 10.9 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k=k_1+k_2$)

$$k = 2.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole

study of Koch and Moortgat,¹ and is identical to our previous evaluation, IUPAC, 1992.² The measured rate coefficient ratio of $k(\text{Cl} + \text{CH}_3\text{COOH})/k(\text{Cl} + \text{CD}_3\text{COOH}) = 3.7$ at $298 \pm 1 \text{ K}$ ¹ indicates that channel (1) dominates at 298 K.

References

¹S. Koch and G. K. Moortgat, *Chem. Phys. Lett.* **173**, 531 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the relative rate study of

Nielsen *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.² The reaction probably occurs via H-atom abstraction from the $-\text{CH}_3$ group.¹

References

¹O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **178**, 163 (1991).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + C₂H₅ONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*¹ and Nielsen *et al.*,² and is identical

to our previous evaluation, IUPAC, 1992.³ The reaction probably proceeds by H-atom abstraction from the C-H bonds.²

References

¹T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, *Int. J. Chem. Kinet.* **22**, 665 (1990).

²O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **178**, 163 (1991).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + *n*-C₃H₇ONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington *et al.*¹ and Nielsen *et al.*,² and is identical

to our previous evaluation, IUPAC, 1992.³ The reaction probably proceeds by H-atom abstraction from the C-H bonds.²

References

¹T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, *Int. J. Chem. Kinet.* **22**, 665 (1990).

²O. J. Nielsen, H. W. Sidebottom, M. Donlon, and J. Treacy, *Chem. Phys. Lett.* **178**, 163 (1990).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + *i*-C₃H₇ONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$k = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.²

References

¹T. J. Wallington, M. M. Hinman, J. M. Andino, W. O. Siegl, and S. M. Japar, *Int. J. Chem. Kinet.* **22**, 665 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + CH₃C(O)OONO₂ → products

No new data have been published since our last evaluation.

Preferred Values

$$k < 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the relative rate coefficient measurement of Wallington *et al.*,¹ in which no reaction of $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ was observed in the presence of Cl atoms. In both the relative rate study of Wallington *et al.*¹ and the absolute rate study of Tsalkani *et al.*,² the major impurity in the $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ samples would be the C_{12} or C_{13} alkane solvent, respectively. While this was of no consequence in the relative rate study of Wallington *et al.*,¹ the presence of $\sim 0.1\%$ tridecane in the $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ sample used by

Tsalkani *et al.*² could account for the Cl reaction rate observed; their $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ sample was $>99\%$ pure from IR measurements. The upper limit cited here is a factor of ~ 3 higher than measured by Wallington *et al.*¹ to allow for higher uncertainties, and is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, *J. Atmos. Chem.* **10**, 301 (1990).
- ²N. Tsalkani, A. Mellouki, G. Poulet, G. Toupance, and G. Le Bras, *J. Atmos. Chem.* **7**, 409 (1988).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

Cl + CH_3CN → products

No new data have been published since our last evaluation.

Preferred Values

$$k \leq 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the upper limit to the rate coefficient determined by Kurylo and Knable,¹ and is identical to our previous evaluation, IUPAC, 1992.² The low temperature (≤ 410 K) rate coefficient data of Poulet *et al.*³ could have been influenced by a heteroge-

neous reaction. The rate coefficients of Olbregts *et al.*⁴ at 370 and 413 K are in good agreement with the higher temperature data of Poulet *et al.*³

References

- ¹M. J. Kurylo and G. L. Knable, *J. Phys. Chem.* **88**, 3305 (1984).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, *J. Phys. Chem.* **88**, 6259 (1984).
- ⁴J. Olbregts, G. Brasseur, and E. Arijs, *J. Photochem.* **24**, 315 (1984).

Cl + $\text{HC}(\text{O})\text{Cl}$ → HCl + ClCO

No new data have been published since our last evaluation.

Preferred Values

$$k = 7.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.2 \times 10^{-11} \exp(-815/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 265\text{--}325 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

At 298 K, the rate coefficients of Niki *et al.*¹ and Libuda *et al.*² are in excellent agreement and are in reasonably good agreement with the 305 K rate coefficient data of Sanhueza

and Heicklen.³ The preferred 298 K rate coefficient is that of Niki *et al.*¹ and Libuda *et al.*,² and the temperature dependence is that derived from the study of Libuda *et al.*² The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Int. J. Chem. Kinet.* **12**, 915 (1980).
- ²H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, *J. Phys. Chem.* **94**, 5860 (1990).
- ³E. Sanhueza and J. Heicklen, *J. Phys. Chem.* **79**, 7 (1975).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -12.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{-12} \exp[-(770 \pm 55)/T]$	216–296	Manning and Kurylo, 1977 ¹	(a)
3.6×10^{-13}	298		
<i>Relative Rate Coefficients</i>			
$1.9 \times 10^{-11} \exp(-1160/T)$	273–368	Tschuikow-Roux <i>et al.</i> , 1988 ²	(b)
3.8×10^{-13}	298		
$(3.4 \pm 0.7) \times 10^{-13}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ³	(c)
$(3.24 \pm 0.51) \times 10^{-13}$	298	Wallington <i>et al.</i> , 1992 ⁴	(d)
<i>Reviews and Evaluations</i>			
$2.0 \times 10^{-11} \exp(-1200/T)$	200–300	NASA, 1994 ⁵	(e)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of Cl atoms.
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \times \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FT-IR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by IR absorption. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (e) Based on the results of Tschuikow-Roux *et al.*,² Tuazon *et al.*,³ and Wallington *et al.*⁴

Preferred Values

$$k = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.7 \times 10^{-11} \exp(-1160/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 273\text{--}368 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended value is based on results of the temperature-dependent relative rate study of Tschuikow-Roux *et al.*² and the relative rate studies of Tuazon *et al.*³ and Wallington *et al.*⁴ The results of the absolute rate study of Manning and Kurylo¹ are in good agreement at room temperature but show a weaker temperature dependence, which is encompassed within the error limits.

References

- ¹R. G. Manning and M. J. Kurylo, *J. Phys. Chem.* **81**, 291 (1977).
²E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, *J. Phys. Chem.* **92**, 1488 (1988).
³E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
⁴T. J. Wallington, J. C. Ball, O. J. Nielsen, and E. Bartkiewicz, *J. Phys. Chem.* **96**, 1241 (1992).
⁵NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -9.8 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.3 \times 10^{-11} \exp(-1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 233\text{--}322 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

At 298 K, the absolute rate coefficients of Clyne and Walker¹ and Manning and Kurylo² and the relative rate coefficient of Wallington *et al.*³ are in good agreement. However, the temperature dependencies measured by Clyne and Walker¹ and Manning and Kurylo² do not agree. The preferred 298 K rate coefficient is the average of those of Manning and Kurylo² and Wallington *et al.*,³ and the temperature dependence is that of Manning and Kurylo.² The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹M. A. A. Clyne and R. F. Walker, J. Chem. Soc. Faraday Trans. 1, **69**, 1547 (1973).
²R. G. Manning and M. J. Kurylo, J. Phys. Chem. **81**, 291 (1977).
³T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 0.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$1.5 \times 10^{-11} \exp(-1580/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985 ¹	(a)
7.3×10^{-14}	298		
<i>Reviews and Evaluations</i>			
$1.7 \times 10^{-11} \exp(-1630/T)$	281–368	NASA, 1994 ²	(b)

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
 (b) Based on the results of Tschuikow-Roux *et al.*¹

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Tschuikow-Roux *et al.*,¹ normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in this evaluation.

Preferred Values

$$k = 7.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.5 \times 10^{-11} \exp(-1580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 281\text{--}368 \text{ K.}$$

References

- ¹E. Tschuikow-Roux, T. Yano, and J. Niedzielski, J. Chem. Phys. **82**, 65 (1985).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$1.8 \times 10^{-11} \exp(-1340/T)$	273–368	Tschuikow-Roux <i>et al.</i> , 1988 ¹	(a)
2.0×10^{-13}	298		
$(1.10 \pm 0.25) \times 10^{-13}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
$1.2 \times 10^{-11} \exp(-1390/T)$	273–368	NASA, 1994 ³	(c)

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC, and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Relative rate technique. Cl atoms were generated by photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the room temperature results of Tuazon *et al.*² and the temperature dependent results of Tschuikow-Roux *et al.*¹

$k = 1.0 \times 10^{-11} \exp(-1340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 273–368 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The recommended value is based on the room temperature results of Tuazon *et al.*² and the temperature dependence reported by Tschuikow-Roux *et al.*,¹ normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in this evaluation.

References

¹E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, *J. Phys. Chem.* **92**, 1488 (1988).

²E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$\Delta H^\circ = -19.9 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$2.70 \times 10^{-11} \exp[-(1301 \pm 2)/T]$	273–368	Tschuikow-Roux <i>et al.</i> , 1988 ¹	(a)
3.43×10^{-13}	298		
<i>Reviews and Evaluations</i>			
$8.7 \times 10^{-12} \exp(-910/T)$	270–330	IUPAC, 1992 ²	(b)
$3.1 \times 10^{-11} \exp(-1350/T)$	273–368	NASA, 1994 ³	(c)

Comments

- (a) Relative rate method. Cl atoms were generated by the photolysis of Cl_2 at 424 nm, and the concentrations of CH_2Cl_2 and CH_4 measured by GC. The measured rate coefficient ratio of $k(\text{Cl} + \text{CH}_2\text{Cl}_2)/k(\text{Cl} + \text{CH}_4)$

$= (2.81 \pm 0.02) \exp[-(49 \pm 2)/T]$ is placed on an absolute basis by using the rate coefficient of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (b) The 298 K rate coefficient was based on the relative rate coefficients of Knox⁴ and Niki *et al.*,⁵ and the temperature dependence was derived from the study of Knox.⁴
- (c) Based on the relative rate coefficients of Tschuikow-Roux *et al.*¹

Preferred Values

$$k = 3.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

$$k = 2.8 \times 10^{-11} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 270–370 K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at 298 K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The reported rate coefficient data^{1,4–7} exhibit appreciable scatter in both the room temperature rate coefficients as well as in the temperature dependencies. At room temperature, the rate coefficients derived from the most recent relative

rate studies of Niki *et al.*⁵ and Tschuikow-Roux *et al.*¹ are in good agreement. Accordingly, the preferred 298 K rate coefficient is the average of those of Niki *et al.*⁵ and Tschuikow-Roux *et al.*,¹ with the temperature dependence being that derived from the data of Tschuikow-Roux *et al.*¹ Analogous to the Cl + CH₄ reaction, the room temperature rate coefficients of Davis *et al.*⁶ and Clyne and Walker⁷ are higher than the preferred values.

References

- ¹E. Tschuikow-Roux, F. Faraji, S. Paddison, J. Niedzielski, and K. Miyokawa, *J. Phys. Chem.* **92**, 1488 (1988).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA, Evaluation No. 11, 1994 (see references in Introduction).
- ⁴J. H. Knox, *Trans. Faraday Soc.* **58**, 275 (1962).
- ⁵H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Int. J. Chem. Kinet.* **12**, 1001 (1980).
- ⁶D. D. Davis, W. Braun, and A. M. Bass, *Int. J. Chem. Kinet.* **2**, 101 (1970).
- ⁷M. A. A. Clyne and R. F. Walker, *J. Chem. Soc. Faraday Trans. 1*, **69**, 1547 (1973).

Cl + CHF₂Cl (HCFC-22) → HCl + CF₂Cl

$$\Delta H^\circ = -9.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.7 \pm 0.2) \times 10^{-15}$	297	Sawerysyn <i>et al.</i> , 1992 ¹	(a)
<i>Relative Rate Coefficients</i>			
$(2.0 \pm 0.4) \times 10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
1.9×10^{-15}	298	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow system with MS monitoring of pseudo-first-order decay of the haloalkane in the presence of excess Cl atoms.
- (b) Relative rate technique. Cl atoms were generated by photolysis of Cl₂. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the results of Sawerysyn *et al.*¹ and Tuazon *et al.*²

Preferred Values

$$k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at 298 K.}$$

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Sawerysyn *et al.*¹ and Tuazon *et al.*,² which are in good agreement. Since the only studies carried out have been at room temperature, only a room temperature value is recommended.

References

- ¹J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, *Chem. Phys. Lett.* **198**, 197 (1992).
- ²E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -17.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(1.0 \pm 0.2) \times 10^{-14}$	294	Glavas and Heicklen, 1985 ¹	(a)
$(2.1 \pm 0.4) \times 10^{-14}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
2.1×10^{-14}	298	NASA, 1994 ³	(c)

Comments

- (a) Relative rate technique employing steady-state photolysis of $\text{Cl}_2\text{-CHFCl}_2\text{-O}_2\text{-NO-NO}_2\text{-N}_2$ mixtures. The measured rate coefficient ratio is placed on absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{NO} + \text{M}) = 1.0 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the results of Tuazon *et al.*²

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Tuazon *et al.*² These results are preferred over the earlier, less direct results of Glavas and Heicklen.¹ Since the only studies carried out have been at room temperature, only a room temperature value is recommended.

References

- ¹S. Glavas and J. Heicklen, *J. Photochem.* **31**, 21 (1985).
²E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
³NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$$k = 2.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$\Delta H^\circ = -39.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 7.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.9 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}330 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 400 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the relative rate study of Knox,¹ with the uncertainty limits being sufficient to encompass the data of Clyne and Walker.² The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹J. H. Knox, *Trans. Faraday Soc.* **58**, 275 (1962).
²M. A. A. Clyne and R. F. Walker, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1547 (1973).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$k_1=1.5\times 10^{-11} \exp(-240/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985 ¹	(a)
$k_1=6.7\times 10^{-12}$	298		
$k_2=1.2\times 10^{-11} \exp(-830/T)$	281–368		
$k_2=7.3\times 10^{-13}$	298		
<i>Reviews and Evaluations</i>			
$k_1=1.8\times 10^{-11} \exp(-290/T)$	281–368	NASA, 1994 ²	(b)
$k_2=1.4\times 10^{-11} \exp(-880/T)$	281–368		

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Based on the results of Tschuikow-Roux *et al.*¹

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \Delta(E_2/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended values are based on the results of the relative rate study of Tschuikow-Roux *et al.*,¹ normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in this evaluation.

Preferred Values

$$k_1 = 6.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 1.5 \times 10^{-11} \exp(-240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 281\text{--}368 \text{ K.}$$

$$k_2 = 7.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 1.2 \times 10^{-11} \exp(-830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 281\text{--}368 \text{ K.}$$

References

- ¹E. Tschuikow-Roux, T. Yano, and J. Niedzielski, *J. Chem. Phys.* **82**, 65 (1985).
- ²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$k_1 = 6.8 \times 10^{-12} \exp(-960/T)$	280–360	Yano and Tschuikow-Roux, 1986 ¹	(a)
$k_1 = 2.7 \times 10^{-13}$	298		
$k_2 = 7.6 \times 10^{-12} \exp(-2394/T)$	280–360		
$k_2 = 2.5 \times 10^{-15}$	298		
$(2.4 \pm 0.7) \times 10^{-13}$	295	Wallington and Hurley, 1992 ²	(b)
$(2.4 \pm 0.5) \times 10^{-13}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ³	(c)
<i>Reviews and Evaluations</i>			
$k_1 = 6.4 \times 10^{-12} \exp(-950/T)$	280–360	NASA, 1994 ⁴	(d)
$k_2 = 7.2 \times 10^{-12} \exp(-2390/T)$	280–360		

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl₂. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.1 \times 10^{-11} \exp(-95/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl₂. The decays of the reactant and reference organic measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate technique. Cl atoms were generated by the photolysis of Cl₂. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Based on the results of Yano and Tschuikow-Roux.¹ The room temperature values of Refs. 2 and 3 are in good agreement.

Preferred Values

$$k_1 = 2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 6.8 \times 10^{-12} \exp(-960/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 280\text{--}360 \text{ K.}$$

$$k_2 = 2.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 7.6 \times 10^{-12} \exp(-2395/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 280\text{--}360 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta \log k_2 = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \Delta(E_2/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended values for the two reaction channels are based on the results of the relative rate study of Yano and Tschuikow-Roux,¹ normalized to the value of the rate constant for the reference reaction (Cl + C₂H₆) recommended in this evaluation. The overall rate coefficient is in good agreement with the room temperature relative rate coefficient studies of Wallington and Hurley² and Tuazon *et al.*³

References

- ¹T. Yano and E. Tschuikow-Roux, J. Photochem. **32**, 25 (1986).
²T. J. Wallington and M. D. Hurley, Chem. Phys. Lett. **189**, 437 (1992).
³E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, Int. J. Chem. Kinet. **24**, 639 (1992).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$2.7 \times 10^{-11} \exp(-1060/T)$	280–360	Yano and Tschuikow-Roux, 1986 ¹	(a)
7.7×10^{-13}	298		
<i>Reviews and Evaluations</i>			
$2.6 \times 10^{-11} \exp(-1060/T)$	280–360	NASA, 1994 ²	(b)

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl₂. Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.1 \times 10^{-11} \exp(-95/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Based on the results of Yano and Tschuikow-Roux.¹

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Yano and Tschuikow-Roux,¹ normalized to the value of the rate constant for the reference reaction (Cl + C₂H₆) recommended in this evaluation.

Preferred Values

$$k = 7.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.7 \times 10^{-11} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 280\text{--}360 \text{ K.}$$

References

- ¹T. Yano and E. Tschuikow-Roux, J. Photochem. **32**, 25 (1986).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = 18.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$1.0 \times 10^{-11} \exp(-3830/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985 ¹	(a)
2.6×10^{-17}	298		
<i>Reviews and Evaluations</i>			
$1.2 \times 10^{-11} \exp(-3880/T)$	281–368	NASA, 1994 ²	(b)

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC and the measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Based on the results of Tschuikow-Roux *et al.*¹

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended value is based on the results of the relative rate study of Tschuikow-Roux *et al.*,¹ normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in this evaluation.

Preferred Values

$$k = 2.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.0 \times 10^{-11} \exp(-3830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 281\text{--}368 \text{ K.}$$

References

¹E. Tschuikow-Roux, T. Yano, and J. Niedzielski, *J. Chem. Phys.* **82**, 65 (1985).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$k_1=4.8\times 10^{-12} \exp(-1560/T)$	281–368	Tschuikow-Roux, Yano, and Niedzielski, 1985 ¹	(a)
$k_1=2.5\times 10^{-14}$	298		
$k_2=6.7\times 10^{-12} \exp(-1670/T)$	281–368		
$k_2=2.5\times 10^{-14}$	298		
<i>Reviews and Evaluations</i>			
$k_1=5.5\times 10^{-12} \exp(-1610/T)$	281–368	NASA, 1994 ²	(b)
$k_2=7.7\times 10^{-12} \exp(-1720/T)$	281–368		

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC and the measured rate coefficient ratios are placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 9.6 \times 10^{-12} \exp(-1350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (b) Based on the results of Tschuikow-Roux *et al.*¹

Preferred Values

$$k_1 = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 4.8 \times 10^{-12} \exp(-1560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 281\text{--}368 \text{ K.}$$

$$k_2 = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$k_2 = 6.7 \times 10^{-12} \exp(-1670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 281–368 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.5$ at 298 K.

$\Delta(E/R)_1 = \Delta(E/R)_2 = \pm 500$ K.

Comments on Preferred Values

The recommended values are based on the results of the relative rate study of Tschuikow-Roux *et al.*,¹ normalized to

the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in this evaluation.

References

¹E. Tschuikow-Roux, T. Yano, and J. Niedzielski, *J. Chem. Phys.* **82**, 65 (1985).

²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(5.6 \pm 2.0) \times 10^{-16}$	297	Sawerysyn <i>et al.</i> , 1992 ¹	(a)
Relative Rate Coefficients			
$(3.90 \pm 0.52) \times 10^{-16}$	295	Wallington and Hurley, 1992 ²	(b)
$(3.7 \pm 0.8) \times 10^{-16}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ³	(c)
Reviews and Evaluations			
4.0×10^{-16}	298	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with MS monitoring of the pseudo-first-order decays of the haloalkane in the presence of excess Cl atoms.
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Based on the results of Sawerysyn *et al.*,¹ Wallington and Hurley,² and Tuazon *et al.*³

Preferred Values

$k = 4.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–3, which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

¹J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, *Chem. Phys. Lett.* **198**, 197 (1992).

²T. J. Wallington and M. D. Hurley, *Chem. Phys. Lett.* **189**, 437 (1992).

³E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).

⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.2) \times 10^{-15}$	297	Sawerysyn <i>et al.</i> , 1992 ¹	(a)
$1.0 \times 10^{-12} \exp[-(1800 \pm 500)/T]$	298–376	Warren and Ravishankara, 1993 ²	(b)
$(2.4 \pm 0.4) \times 10^{-15}$	298		
<i>Relative Rate Coefficients</i>			
$(2.0 \pm 0.2) \times 10^{-15}$	295	Wallington and Hurley, 1992 ³	(c)
$(2.4 \pm 0.5) \times 10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ⁴	(d)
<i>Reviews and Evaluations</i>			
$1.0 \times 10^{-12} \exp(-1800/T)$	298–376	NASA, 1994 ⁵	(e)

Comments

- (a) Discharge flow system with MS monitoring of the pseudo-first-order decays of the haloalkane in the presence of excess Cl atoms.
- (b) Cl atoms were generated by laser flash photolysis of CCl_4 at 222 nm. The pseudo-first-order decays of Cl atoms in excess HCFC were monitored by resonance fluorescence.
- (c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (e) Based on the results of Refs. 1–4.

Preferred Values

$k = 2.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.0 \times 10^{-12} \exp(-1800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 298–376 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–4, which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara,² the only study carried out over a range of temperatures. The reported *A* factor is lower than expected.

References

- ¹J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, *Chem. Phys. Lett.* **198**, 197 (1992).
²R. F. Warren and A. R. Ravishankara, *Int. J. Chem. Kinet.* **25**, 833 (1993).
³T. J. Wallington and M. D. Hurley, *Chem. Phys. Lett.* **189**, 437 (1992).
⁴E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
⁵NASA Evaluation No. 11, 1994 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k < 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred value is based on the study of Wine *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.²

This reaction is too slow to be of importance in atmospheric chemistry.

References

- ¹P. H. Wine, D. H. Semmes, and A. R. Ravishankara, *Chem. Phys. Lett.* **90**, 128 (1982).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.3) \times 10^{-15}$	297	Sawerysyn <i>et al.</i> , 1992 ¹	(a)
Relative Rate Coefficients			
$(1.38 \pm 0.18) \times 10^{-15}$	295	Wallington and Hurley, 1992 ²	(b)
$(1.6 \pm 0.3) \times 10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ³	(c)
Reviews and Evaluations			
1.5×10^{-15}	298	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system with MS monitoring of the pseudo-first-order decays of the haloalkane in the presence of excess Cl atoms.
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Based on the results of Sawerysyn *et al.*,¹ Wallington and Hurley,² and Tuazon *et al.*³

Preferred Values

$k = 1.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–3, which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

- ¹J. P. Sawerysyn, A. Talhaoui, B. Meriaux, and P. Devolder, *Chem. Phys. Lett.* **198**, 197 (1992).
- ²T. J. Wallington and M. D. Hurley, *Chem. Phys. Lett.* **189**, 437 (1992).
- ³E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Relative Rate Coefficients			
$8.7 \times 10^{-12} \exp(-2439/T)$	280–360	Yano and Tschuikow-Roux, 1986 ¹	(a)
2.4×10^{-15}	298		
1.9×10^{-15}	298	Nielsen <i>et al.</i> , 1992 ²	(b)
Reviews and Evaluations			
$7.5 \times 10^{-12} \exp(-2430/T)$	280–360	NASA, 1994 ³	(c)

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC. The measured rate coefficient ratio is

placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.1 \times 10^{-11} \exp(-95/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and

reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (c) Based on the results of Yano and Tschuikow-Roux *et al.*¹ and Nielsen *et al.*²

Preferred Values

$k = 2.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 7.9 \times 10^{-12} \exp(-2440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 280–360 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The recommended value is based on results of the relative rate studies of Nielsen *et al.*² and Yano and Tschuikow-Roux *et al.*¹ (the latter data being normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{C}_2\text{H}_6$) recommended in this evaluation).

References

¹T. Yano and E. Tschuikow-Roux, *J. Photochem.* **32**, 25 (1986).

²O. J. Nielsen, T. Ellermann, J. Sehested, and T. J. Wallington, *J. Phys. Chem.* **96**, 10875 (1992).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(2.4 \pm 0.5) \times 10^{-16}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ¹	(a)
$(2.5 \pm 0.6) \times 10^{-16}$	295	Sehested <i>et al.</i> , 1993 ²	(b)
<i>Reviews and Evaluations</i>			
2.4×10^{-16}	298	NASA, 1994 ³	(c)

Comments

- (a) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is ratio placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_3\text{CF}_2\text{Cl}) = 4.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the results of Tuazon *et al.*¹ and Sehested *et al.*²

Preferred Values

$k = 2.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred value at 298 K is based on the results of the relative rate studies of Tuazon *et al.*¹ and Sehested *et al.*² which are in good agreement. Since studies have only been carried out at room temperature, no temperature dependence is recommended.

References

¹E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).

²J. Sehested, T. Ellermann, O. J. Nielsen, T. J. Wallington, and M. D. Hurley, *Int. J. Chem. Kinet.* **25**, 701 (1993).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.16 \times 10^{-12} \exp[-(1800 \pm 150)/T]$ $(2.62 \pm 0.50) \times 10^{-15}$	276–376 298	Warren and Ravishankara, 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$(2.7 \pm 0.6) \times 10^{-15}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ²	(b)
<i>Reviews and Evaluations</i>			
$1.1 \times 10^{-12} \exp(-1800/T)$	280–380	NASA, 1994 ³	(c)

Comments

- (a) Cl atoms were generated by laser flash photolysis of CCl_4 at 222 nm. The pseudo-first-order decays of Cl atoms in excess HCFC were monitored by resonance fluorescence.
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the results of Warren and Ravishankara¹ and Tuazon *et al.*²

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results reported by Warren and Ravishankara¹ and Tuazon *et al.*,² which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara,¹ the only study carried out over a range of temperatures.

Preferred Values

$k = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.1 \times 10^{-12} \exp(-1800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 276–376 K.

References

- ¹R. F. Warren and A. R. Ravishankara, *Int. J. Chem. Kinet.* **25**, 833 (1993).
²E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
³NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$3.94 \times 10^{-12} \exp[-(1740 \pm 100)/T]$ $(1.15 \pm 0.30) \times 10^{-14}$	276–382 298	Warren and Ravishankara, 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$(1.22 \pm 0.18) \times 10^{-14}$	295	Wallington and Hurley, 1992 ²	(b)
$(1.4 \pm 0.3) \times 10^{-14}$	298	Tuazon, Atkinson, and Corchnoy, 1992 ³	(c)
<i>Reviews and Evaluations</i>			
$4.4 \times 10^{-12} \exp(-1750/T)$	298	NASA, 1994 ⁴	(d)

Comments

- (a) Cl atoms were generated by laser flash photolysis of CCl_4 at 222 nm. The pseudo-first-order decays of Cl atoms in excess HCFC were monitored by resonance fluorescence.
- (b) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Relative rate technique. Cl atoms were generated by the photolysis of Cl_2 . The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient is placed on an absolute basis by use of a rate coefficient of $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Based on the results of Warren and Ravishankara,¹ Wallington and Hurley,² and Tuazon *et al.*³

Preferred Values

$$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.4 \times 10^{-12} \exp(-1750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 276\text{--}382 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred value at 298 K is based on the results reported in Refs. 1–3, which are in good agreement. The recommended temperature dependence is that reported by Warren and Ravishankara,¹ the only study carried out over a range of temperatures.

References

- ¹R. F. Warren and A. R. Ravishankara, *Int. J. Chem. Kinet.* **25**, 833 (1993).
²T. J. Wallington and M. D. Hurley, *Chem. Phys. Lett.* **189**, 437 (1992).
³E. C. Tuazon, R. Atkinson, and S. B. Corchnoy, *Int. J. Chem. Kinet.* **24**, 639 (1992).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Cl + OCS → SCI + CO

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 1.1 \times 10^{-16}$	298	Eibling and Kaufman, 1983 ¹	(a)
$< 4 \times 10^{-15}$	298	Clyne <i>et al.</i> , 1984 ²	(b)
$< 1 \times 10^{-14}$	298	Nava, Brobst, and Stief, 1985 ³	(c)
<i>Reviews and Evaluations</i>			
$< 1.0 \times 10^{-16}$	298	NASA, 1994 ⁴	(d)

Comments

- (a) Fast-flow discharge system with mass-spectrometric detection used. $[\text{Cl}]$ monitored and from minimum observable change in $[\text{Cl}]$ in presence of OCS upper limit to k obtained. SCI_2^+ was observed in small concentrations and if it is assumed to be due solely to the reaction of Cl with OCS, a lower limit of $k > 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ can be derived.
- (b) Discharge flow study of OCS removal in excess Cl. $[\text{OCS}^+]$ monitored by mass spectrometry. No consumption of OCS detectable, leading to upper limit to k .
- (c) Flash photolysis of CCl_4 to produce Cl atoms in excess OCS. $[\text{Cl}]$ monitored by resonance fluorescence. No consumption of Cl detected with OCS in range 100–300 Torr, leading to upper limit to k .
- (d) Accepted upper limit obtained by Eibling and Kaufman.¹

Preferred Values

$$k < 1.0 \times 10^{-16} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The reaction of Cl atoms with OCS is extremely slow and only upper limits to the rate coefficient have been obtained. The lowest of these¹ is preferred.

References

- ¹R. E. Eibling and M. Kaufman, *Atmos. Environ.* **17**, 429 (1983).
²M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, *J. Chem. Soc. Faraday Trans. 2*, **80**, 877 (1984).
³D. F. Nava, W. D. Brobst, and L. J. Stief, *J. Phys. Chem.* **89**, 4703 (1985).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$<5 \times 10^{-15}$ (Air, 300 Torr)	293	Nicovich, Shackelford, and Wine, 1990 ¹	(a)
Relative Rate Coefficients			
$(0.83 \pm 0.17) \times 10^{-13}$ (Air, 760 Torr)	298	Martin, Barnes, and Becker, 1987 ²	(b)
$<4 \times 10^{-15}$ (Air, 700 Torr)	298	Wallington, Andino, and Potts, 1991 ³	(c)
Reviews and Evaluations			
$<4 \times 10^{-15}$	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) Pulsed laser photolysis of Cl_2 in CS_2 , N_2 , O_2 mixtures over the pressure range of 30–300 Torr and the temperature range of 193–258 K. $[\text{Cl}]$ monitored by resonance fluorescence. Experiments in absence of O_2 reveal reversible adduct formation and establishment of equilibrium between Cl , CS_2 , and CS_2Cl . Thermodynamic parameters for equilibrium derived. Upper limit tabulated for overall removal of CS_2 in presence of O_2 is for all channels of $\text{CS}_2\text{Cl} + \text{O}_2$ reaction which do not lead to Cl atom formation.
- (b) Steady state photolysis of Cl_2 in presence of CS_2 , N_2 , O_2 , and reference compound (CH_4 or CH_3Cl). $[\text{CS}_2]$ and $[\text{CH}_4]$ or $[\text{CH}_3\text{Cl}]$ monitored by quadrupole mass spectrometry. Constant total pressure of 760 Torr. $[\text{N}_2]/[\text{O}_2]$ varied. $k(\text{Cl} + \text{CH}_3\text{Cl}) = 5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ used.⁵
- (c) Steady state photolysis of Cl_2 in the presence of CS_2 , N_2 , O_2 , and the reference compound (CH_4 , CH_3Cl , or CHF_2Cl). $[\text{CS}_2]$ and concentration of reference compound monitored by FTIR. CH_4 and CH_3Cl shown to be unsuitable as reference compounds. Results suggest CHF_2Cl to be suitable. Value of $k(\text{Cl} + \text{CHF}_2\text{Cl})/k(\text{Cl} + \text{CH}_4) < 0.04$ measured in same study and combined with $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Ref. 6) and measured $k(\text{Cl} + \text{CS}_2)/k(\text{Cl} + \text{CHF}_2\text{Cl})$ in presence of O_2 to give tabulated upper limit to k .

- (d) Accepted the value of Wallington *et al.*³

Preferred Values

$$k \leq 4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K in air at } 1 \text{ bar.}$$

Comments on Preferred Values

The overall reaction of Cl with CS_2 appears to be too slow to be of importance in the atmosphere. Nicovich *et al.*¹ have shown that it proceeds initially by rapid formation of the ClCS_2 adduct, as suggested earlier by Martin *et al.*,² but the subsequent reaction of the adduct with O_2 appears to be slow.

The recommended upper limit is that of Wallington *et al.*³ which agrees with the work of Nicovich *et al.*¹ Wallington *et al.*³ have suggested that the value obtained by Martin *et al.*² was erroneously high due to complexities in their system arising from HO radical production from the reference compounds which were chosen.

References

- ¹J. M. Nicovich, C. J. Shackelford, and P. H. Wine, *J. Phys. Chem.* **94**, 2896 (1990).
- ²D. Martin, I. Barnes, and K. H. Becker, *Chem. Phys. Lett.* **140**, 195 (1987).
- ³T. J. Wallington, J. M. Andino, and A. R. Potts, *Chem. Phys. Lett.* **176**, 103 (1991).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵NASA Evaluation No. 7, 1985 (see references in Introduction).
- ⁶NASA Evaluation No. 8, 1987 (see references in Introduction).

Cl + CH₃SCH₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-10} (3 Torr N ₂)	297	Stickel <i>et al.</i> , 1992 ¹	(a)
$(3.3 \pm 0.5) \times 10^{-10}$ (700 Torr N ₂)	297		
<i>Relative Rate Coefficients</i>			
$(3.2 \pm 0.3) \times 10^{-10}$ (740 Torr N ₂)	295	Nielsen <i>et al.</i> , 1990 ²	(b)

Comments

- (a) Rate coefficient measurements used pulsed laser photolysis of COCl₂-CH₃SCH₃-N₂ mixtures at 266 nm. [Cl] was monitored by resonance fluorescence. Some experiments were carried out with CD₃SCD₃ and C₂H₅SC₂H₅. Yield of HCl studied by 248 nm pulsed laser photolysis of COCl₂-CH₃SCH₃-CO₂-N₂ mixtures over the pressure range 0.6–203 Torr. [HCl] monitored by tunable diode laser spectroscopy. Reaction studied over the temperature range 240–421 K.
- (b) Photolysis of mixtures of COCl₂-CH₃SCH₃-cyclohexane-N₂ in a Teflon chamber. [Cyclohexane] and [CH₃SCH₃] measured at intervals by GC. $k(\text{Cl} + \text{cyclohexane}) = 3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ used.³

Preferred Values

$k = 3.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar N₂.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K and 1 bar N₂.

Comments on Preferred Values

The most recent study of this reaction by Stickel *et al.*¹ shows the reaction kinetics to have a complex dependency on temperature and pressure. The overall reaction rate is

close to collisional and increases with decreasing temperature and with increasing pressure. The HCl yield approaches unity as the pressure tends to zero but decreases to a value of ~ 0.5 at 203 Torr N₂ and 297 K.

These findings are interpreted in terms of the occurrence of two reaction channels, Cl abstraction and adduct formation. At low pressures the abstraction channel is dominant but with increasing pressure the adduct can be stabilized leading to an increase in the total k as pressure increases and temperature decreases.

Until the reaction is studied in more detail and a complete analysis of the temperature and pressure dependence can be made our recommendations are limited to high pressures and 298 K. They are based on the results of Stickel *et al.*¹ and Nielsen *et al.*² which are in excellent agreement. There is also a value of $2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 760 Torr N₂ reported by Barnes *et al.*,⁴ but no experimental details are given.

References

- ¹R. E. Stickel, J. M. Nicovich, S. Wang, Z. Zhao, and P. H. Wine, *J. Phys. Chem.* **96**, 9875 (1992).
- ²O. J. Nielsen, H. W. Sidebottom, L. Nelson, O. Rattigan, J. Treacy, and D. J. O'Farrell, *Int. J. Chem. Kinet.* **22**, 603 (1990).
- ³R. Atkinson and S. Aschmann, *Int. J. Chem. Kinet.* **17**, 33 (1985).
- ⁴I. Barnes, V. Bastian, K. H. Becker, and D. Martin, *Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series 393, p. 476 (1989).

$$\Delta H^\circ = 4.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(5.5 \pm 0.3) \times 10^{-14}$	298	Leu and Lin, 1979 ¹	(a)
7.4×10^{-14}	298	Ravishankara, Eisele, and Wine, 1983 ²	(a)
$(6.7 \pm 0.7) \times 10^{-14}$	298	Loewenstein and Anderson, 1984 ³	(a)
$1.7 \times 10^{-12} \exp[-(911 \pm 373)/T]$	253–333	Boodaghians <i>et al.</i> , 1987 ⁴	(a)
$(6.8 \pm 1.0) \times 10^{-14}$	293		
<i>Reviews and Evaluations</i>			
$1.4 \times 10^{-12} \exp(-900/T)$	250–330	NASA, 1994 ⁵	(b)

Comments

- (a) Discharge flow system with resonance fluorescence detection of HO.
- (b) Based on the results of Leu and Lin,¹ Ravishankara *et al.*,² Loewenstein and Anderson,³ and Boodaghians *et al.*⁴

Preferred Values

$k = 6.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.4 \times 10^{-12} \exp(-900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–330 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The preferred room temperature value is the average of the values reported by Leu and Lin,¹ Ravishankara *et al.*,² Loewenstein and Anderson,³ and Boodaghians *et al.*⁴ All of these studies were carried out in a discharge flow system with resonance fluorescence detection of HO radicals. The temperature dependence is from the study of Boodaghians *et al.*⁴ Loewenstein and Anderson³ determined that the exclusive products are $\text{Cl} + \text{HOCl}$.

References

- ¹M. T. Leu and C. L. Lin, *Geophys. Res. Lett.* **6**, 425 (1979).
²A. R. Ravishankara, F. L. Eisele, and P. H. Wine, *J. Chem. Phys.* **78**, 1140 (1983).
³L. M. Loewenstein and J. G. Anderson, *J. Phys. Chem.* **88**, 6277 (1984).
⁴R. B. Boodaghians, I. W. Hall, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **83**, 529 (1987).
⁵NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -67.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(7.8 \pm 0.3) \times 10^{-13}$	298	Sharkey and Smith, 1993 ¹	(a)
$(5.4 \pm 0.25) \times 10^{-13}$	216		
$(5.6 \pm 0.45) \times 10^{-13}$	178		
$(5.2 \pm 0.3) \times 10^{-13}$	138		
<i>Reviews and Evaluations</i>			
$2.4 \times 10^{-12} \exp(-330/T)$	200–300	IUPAC, 1992 ²	(b)
$2.6 \times 10^{-12} \exp(-350/T)$	200–300	NASA, 1994 ³	(b)

Comments

- (a) Pulsed laser photolysis of HNO_3 at 266 nm with LIF detection of HO radical decay in excess HCl.
- (b) Based on the data of Molina *et al.*,⁴ Keyser,⁵ and Rav-

ishankara *et al.*,⁶ which gave higher room temperature values than earlier data.

Preferred Values

$k = 8.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.4 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The recommendation is unchanged from our previous evaluation, IUPAC, 1992.² The studies of Molina *et al.*,⁴ Keyser,⁵ and Ravishankara *et al.*,⁶ which paid careful attention to the [HCl] present in the experiments, all show room temperature values higher by about 20–25% than other studies.^{7–14} Ravishankara *et al.*⁶ showed that HCl losses can be a problem, leading to low k values, and this is a plausible cause of these discrepancies. The higher value, $k(298) = 8.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (average of the 3 studies^{4–6}) is the most reliable value. The preferred temperature-dependent expression for the range 200–300 K is obtained by weighted linear least squares fit to the data from these three studies.^{4–6} Results of the recent low temperature study of Sharkey and Smith¹ are in good agreement with this recommendation down to 216 K but are significantly higher at 178 K and 138 K. Ravishankara *et al.*⁶ reported the three parameter expres-

sion $k = 4.5 \times 10^{-17} T^{1.65} \exp(112/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the temperature range 240–1055 K.

References

- ¹P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **89**, 631 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴M. J. Molina, L. T. Molina, and C. A. Smith, Int. J. Chem. Kinet. **16**, 1151 (1984).
- ⁵L. Keyser, J. Phys. Chem. **88**, 4750 (1984).
- ⁶A. R. Ravishankara, P. H. Wine, J. R. Wells, and R. L. Thompson, Int. J. Chem. Kinet. **17**, 1281 (1985).
- ⁷B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).
- ⁸D. Husain, J. M. C. Plane, and C. C. Xiang, J. Chem. Soc. Faraday Trans. 2, **80**, 713 (1984).
- ⁹G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1948 (1973).
- ¹⁰M. S. Zahniser, F. Kaufman, and J. G. Anderson, Chem. Phys. Lett. **27**, 507 (1974).
- ¹¹I. W. M. Smith and R. Zellner, J. Chem. Soc. Faraday Trans. 2, **70**, 1045 (1974).
- ¹²A. R. Ravishankara, G. Smith, R. T. Watson, and D. D. Davis, J. Phys. Chem. **81**, 2220 (1977).
- ¹³W. Hack, G. Mex, and H.-Gg. Wagner, Ber. Bunsenges. Phys. Chem. **81**, 677 (1977).
- ¹⁴D. Husain, J. M. C. Plane, and N. K. H. Slater, J. Chem. Soc. Faraday Trans. 2, **77**, 1949 (1981).

$$\Delta H^\circ = -101.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.0 \times 10^{-12} \exp(-500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The only reported experimental value¹ has a large uncertainty. The preferred value is based on the midrange value of $5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K from this study and an A factor of $3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, i.e., equal to that for the HO + H₂O₂ reaction. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

- ¹C. A. Ennis and J. W. Birks, J. Phys. Chem. **92**, 1119 (1988).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -5.2 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -233.2 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.1 \times 10^{-11} \exp(120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the
 temperature range 200–373 K.
 $k_1/k = 0.98$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 150 \text{ K}$.
 $\Delta(k_1/k) = {}^{+0.02}_{-0.12}$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient k is based on the three studies^{1–3} in which [ClO] was measured directly. The uncer-

tainty reflects the differences in the 298 K values and the reported temperature coefficients. The measurement of the branching ratio for HCl formation based on measurement of the HCl stable product,³ $k_1/k = 0.98 \pm 0.12$, is more accurate since this is clearly the minor channel. However, the uncertainties do not allow the occurrence of this HCl channel to be eliminated completely. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

- ¹A. J. Hills and C. J. Howard, *J. Chem. Phys.* **81**, 4458 (1984).
²J. P. Burrows, T. J. Wallington, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **80**, 957 (1984).
³G. Poulet, G. Laverdet, and G. Le Bras, *J. Phys. Chem.* **90**, 159 (1986).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ(1) = -213 \text{ kJ} \cdot \text{mol}^{-1}$
 $\Delta H^\circ(2) = -18.7 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$k = 7.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.5 \times 10^{-13} \exp(800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the
 temperature range 290–480 K.
 $k_2/k = 0$.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the single experimental study of Poulet *et al.*¹ in a discharge flow system with EPR

and LIF detection of HO radical decay and molecular beam mass spectrometry detection of the product HOCl. Indication of curvature in the Arrhenius plot dictates caution in extrapolation beyond the experimental range. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

- ¹G. Poulet, H. Zagogianni, and G. Le Bras, *Int. J. Chem. Kinet.* **18**, 847 (1986).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -97 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.4 \times 10^{-12} \exp[-(1250 \pm 155)/T]$	259–348	Ganske <i>et al.</i> , 1992 ¹	(a)
$(3.6 \pm 0.2) \times 10^{-14}$	298		
<i>Reviews and Evaluations</i>			
3.5×10^{-14}	298	IUPAC, 1992 ²	(b)
$2.4 \times 10^{-12} \exp(-1250/T)$	260–350	NASA, 1994 ³	(c)

Comments

- (a) Fast-flow discharge system. Pseudo-first-order decays of HO radicals in excess ClNO₂ were monitored by resonance fluorescence. Two different flow tube wall coatings, halocarbon wax and phosphoric acid, were used to check for possible heterogeneous reactions. Mass spectrometry showed HOCl to be the sole chlorine-containing product.
- (b) Based on the room temperature results of Ganske *et al.*⁴
- (c) Based on the results of Ganske *et al.*¹

Preferred Values

$k = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.4 \times 10^{-12} \exp(-1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the results of the temperature-dependent study of Ganske *et al.*¹ Mass spectrometric studies showed HOCl to be the sole chlorine-containing product, with no evidence for production of HONO₂ or Cl₂, thereby showing that the only reaction pathway is that yielding HOCl + NO₂.

References

- ¹J. A. Ganske, H. N. Berko, M. J. Ezell, and B. J. Finlayson-Pitts, *J. Phys. Chem.* **96**, 2568 (1992).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³NASA Evaluation No. 11, 1994 (see references in Introduction).
⁴J. A. Ganske, M. J. Ezell, H. N. Berko, and B. J. Finlayson-Pitts, *Chem. Phys. Lett.* **179**, 204 (1991).

$$\Delta H^\circ(1) = -66 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = 8.4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = -95.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 3.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.2 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 246–387 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The results of the only two reported studies of Ravishankara *et al.*¹ and Zahniser *et al.*² are in good agreement at 245

K (within 25%), considering the difficulties associated with handling ClONO₂. The preferred value is that of Zahniser *et al.*² Neither study reported any data on the reaction products. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, *Geophys. Res. Lett.* **4**, 7 (1977).
²M. S. Zahniser, J. S. Chang, and F. Kaufman, *J. Chem. Phys.* **67**, 997 (1977).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -77.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.90 \times 10^{-14} T^{0.89} \exp[-(1447 \pm 75)/T]$	295–955	Taylor <i>et al.</i> , 1993 ¹	(a)
$(4.9 \pm 0.6) \times 10^{-14}$	295		
<i>Relative Rate Coefficients</i>			
$3.78 \times 10^{-18} T^2 \exp[-(655 \pm 74)/T]$	293–358	Hsu and DeMore, 1994 ²	(b)
3.53×10^{-14}	298		
<i>Reviews and Evaluations</i>			
$1.8 \times 10^{-12} \exp(-1115/T)$	240–300	IUPAC, 1992 ³	(c)
$7.33 \times 10^{-18} T^2 \exp(-809/T)$	247–955	Atkinson, 1994 ⁴	(d)
$4.0 \times 10^{-12} \exp(-1400/T)$	247–400	NASA, 1994 ⁵	(e)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals. Rate coefficients were measured at 742, 775, 875, 925, and 955 K, and combined with rate coefficients from a previous study⁶ to obtain the cited temperature-dependent expression and 295 K rate coefficient.
- (b) Relative rate method. HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. The concentrations of CH₃Cl and CH₃CHF₂ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{Cl})/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (1.91 \pm 0.45) \exp[-(195 \pm 74)/T]$ is placed on an absolute base by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Derived from the rate coefficient data of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ and Jeong and Kaufman.¹¹
- (d) Derived from the absolute rate coefficient data of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman,¹¹ and those listed by Taylor *et al.*,¹ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (e) Derived from the absolute rate coefficient data of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman,¹¹ and Taylor *et al.*,^{1,6} at temperatures <400 K and the relative rate coefficients of Hsu and DeMore.²

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

At room temperature and below, the absolute rate coefficients of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman,¹¹ and Taylor *et al.*⁶ are in good agreement. The rate coefficients determined by Taylor *et al.*⁶ at temperatures of ~428–485 K are significantly higher than those of Perry *et al.*⁸ and Jeong and Kaufman,¹¹ and use of the rate data of Taylor *et al.*^{1,6} leads to a rate expression which predicts rate coefficients at ~250 K which are 10–25% lower than those reported by Davis *et al.*⁹ and Jeong and Kaufman.¹¹ The room temperature rate coefficient of Brown *et al.*¹² is ~20–25% higher than other absolute data,^{6–11} and is not used in the evaluation. The rate coefficients of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Paraskevopoulos *et al.*,¹⁰ Jeong and Kaufman,¹¹ and Taylor *et al.*¹ and those of Taylor *et al.*⁶ as listed by Taylor *et al.*¹ (with the rate coefficients of Taylor *et al.*⁶ being averaged at 473 and 475 K, 524 and 525 K, 667 K, and 695 K, and the rate coefficient at 735 K being omitted¹) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 7.33 \times 10^{-18} T^2 \times \exp(-809/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 247–955 K. The preferred Arrhenius expression, $k = A \times \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2 T^2$ and $B = D + 2T$. The rate coefficients obtained from the relative rate study of Hsu and DeMore² are lower than the preferred values over the temperature range studied by Hsu and DeMore² (295–358 K), and the temperature-dependent expression of Hsu and DeMore² cited in the table leads to calculated rate coefficients at 240 K and 300 K which are 2% and 14% lower, respectively, than predicted from the three parameter equation.

Preferred Values

$$k = 4.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.8 \times 10^{-12} \exp(-1340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}300 \text{ K.}$$

References

- ¹P. H. Taylor, Z. Jiang, and B. Dellinger, *Int. J. Chem. Kinet.* **25**, 9 (1993).
- ²K.-J. Hsu and W. B. DeMore, *Geophys. Res. Lett.* **21**, 805 (1994).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶P. H. Taylor, J. A. D'Angelo, M. C. Martin, J. H. Kasner, and B. Dellinger, *Int. J. Chem. Kinet.* **21**, 829 (1989).
- ⁷C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 197 (1976).
- ⁸R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.* **64**, 1618 (1976).
- ⁹D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. Watson, *J. Chem. Phys.* **65**, 1268 (1976).
- ¹⁰G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, *J. Phys. Chem.* **85**, 561 (1981).
- ¹¹K.-M. Jeong and F. Kaufman, *J. Phys. Chem.* **86**, 1808 (1982).
- ¹²A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, *Atmos. Environ.* **24A**, 361 (1990).

No new data have been published since our last evaluation.

Preferred Values

$k = 4.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.0 \times 10^{-12} \exp(-1135/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The rate coefficients measured by Howard and Evenson,¹ Watson *et al.*,² Handwerk and Zellner,³ Paraskevopoulos *et al.*,⁴ and Jeong and Kaufman⁵ are in reasonably good agreement at temperatures $> \sim 290 \text{ K}$, although there is a significant discrepancy between the rate coefficients of Watson *et al.*² and Jeong and Kaufman⁵ at $\sim 250 \text{ K}$. The data from all five studies^{1–5} have been fitted to the three param-

eter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 3.77 \times 10^{-18} T^2 \exp(-604/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 245–486 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2 T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.⁶

References

- ¹C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 197 (1976).
- ²R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, *J. Phys. Chem.* **81**, 256 (1977).
- ³V. Handwerk and R. Zellner, *Ber. Bunsenges. Phys. Chem.* **82**, 1161 (1978).
- ⁴G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, *J. Phys. Chem.* **85**, 561 (1981).
- ⁵K.-M. Jeong and F. Kaufman, *J. Phys. Chem.* **86**, 1808 (1982).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -87.4 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.01 \times 10^{-15} T^{1.09} \exp[-(771 \pm 48)/T]$	295–955	Taylor <i>et al.</i> , 1993 ¹	(a)
$(1.47 \pm 0.18) \times 10^{-13}$	295		
<i>Relative Rate Coefficients</i>			
$1.92 \times 10^{-18} T^2 \exp[-(166 \pm 29)/T]$	293–360	Hsu and DeMore, 1994 ²	(b)
9.34×10^{-14}	298		
$1.51 \times 10^{-18} T^2 \exp[-(60 \pm 20)/T]$	298–368	Hsu and DeMore, 1994 ²	(b)
1.13×10^{-13}	298		
<i>Reviews and Evaluations</i>			
$4.4 \times 10^{-12} \exp(-1030/T)$	240–300	IUPAC, 1992 ³	(c)
$6.14 \times 10^{-18} T^2 \exp(-389/T)$	245–955	Atkinson, 1994 ⁴	(d)
$3.8 \times 10^{-12} \exp(-1050/T)$	245–400	NASA, 1994 ⁵	(e)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals. These data supersede the earlier data from this group.⁶
- (b) Relative rate method. HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. CH₂Cl₂ and CH₃CHF₂ (or CH₃CH₂F) concentrations were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_2\text{Cl}_2)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.97 \pm 0.09) \exp[(294 \pm 29)/T]$ and $k(\text{HO} + \text{CH}_2\text{Cl}_2)/k(\text{HO} + \text{CH}_3\text{CH}_2\text{F}) = (0.32 \pm 0.02) \exp[(171 \pm 20)/T]$ are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{CH}_3\text{CH}_2\text{F}) = 4.72 \times 10^{-18} T^2 \exp(-213/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Derived from the absolute rate coefficients of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ and Jeong and Kaufman.¹⁰
- (d) Derived from the absolute rate coefficient data of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Jeong and Kaufman,¹⁰ and Taylor *et al.*,¹ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (e) Derived from the absolute rate coefficient data of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Jeong and Kaufman,¹⁰ and Taylor *et al.*,¹ using only the rate coefficients obtained at temperatures <400 K, and the relative rate coefficients of Hsu and DeMore.²

Preferred Values

$k = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.7 \times 10^{-12} \exp(-920/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The relative rate coefficients of Hsu and DeMore² at 298 K are in reasonable agreement with the absolute rate coefficient of Davis *et al.*,⁹ but are ~20–35% lower than the absolute rate coefficients of Howard and Evenson,⁷ Perry *et al.*,⁸ Jeong and Kaufman,¹⁰ and Taylor *et al.*¹ A fit of the absolute rate coefficients of Howard and Evenson,⁷ Perry *et al.*,⁸ Davis *et al.*,⁹ Jeong and Kaufman,¹⁰ and Taylor *et al.*¹ to the three parameter equation $k = CT^2 \exp(-D/T)$ leads to $k = 6.14 \times 10^{-18} T^2 \exp(-389/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 245–955 K, with a 298 K rate coefficient of $1.48 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The 298 K rate coefficients measured by Hsu and DeMore² relative to the reactions of the HO radical with CH₃CH₂F and CH₃CHF₂ are ~30% lower than this value obtained from the absolute rate data, and the value of *C* in the three parameter equation is lowered by 15% to $C = 5.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, resulting in the three parameter equation $k = 5.2 \times 10^{-18} T^2 \exp(-390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 245–955 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = Ce^2 T^2$ and $B = D + 2T$. The uncertainty limits have been increased to take into account the discrepancies between the various studies.

References

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$$\Delta H^\circ = -76.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$8.1 \times 10^{-13} \exp[-(1516 \pm 53)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(4.9 \pm 0.45) \times 10^{-15}$	298		
$1.74 \times 10^{-12} \exp[-(1701 \pm 39)/T]$	302–382	Yujing <i>et al.</i> , 1993 ²	(b)
5.99×10^{-15}	302		
<i>Relative Rate Coefficients</i>			
$2.32 \times 10^{-20} T^{2.58} \exp[-(740 \pm 45)/T]$	298–366	Hsu and DeMore, 1995 ³	(c)
4.69×10^{-15}	298		
<i>Reviews and Evaluations</i>			
$7.8 \times 10^{-13} \exp(-1530/T)$	240–300	IUPAC, 1992 ⁴	(d)
$1.51 \times 10^{-18} T^2 \exp(-1000/T)$	250–482	Atkinson, 1989, ⁵ 1994 ⁶	(e)
$1.0 \times 10^{-12} \exp(-1600/T)$	250–400	NASA, 1994 ⁷	(f)

Comments

- (a) Discharge flow system with EPR detection of HO radicals.
- (b) Discharge flow system with resonance fluorescence detection of HO radicals.
- (c) Relative rate method. HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. The concentrations of CHF₂Cl and CH₄ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{Cl})/k(\text{HO} + \text{CH}_4) = (0.24 \pm 0.03) \exp[(342 \pm 45)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Derived from the absolute rate coefficients of Atkinson *et al.*,⁸ Howard and Evenson,⁹ Watson *et al.*,¹⁰ Chang and Kaufman,¹¹ Handwerk and Zellner,¹² Paraskevopoulos *et al.*,¹³ and Jeong and Kaufman.¹⁴
- (e) Derived from the absolute rate coefficients of Atkinson *et al.*,⁸ Howard and Evenson,⁹ Watson *et al.*,¹⁰ Chang and Kaufman,¹¹ Handwerk and Zellner,¹² Paraskevopoulos *et al.*,¹³ and Jeong and Kaufman,¹⁴ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (f) Derived from the rate coefficients of Atkinson *et al.*,⁸ Howard and Evenson,⁹ Watson *et al.*,¹⁰ Chang and Kaufman,¹¹ Handwerk and Zellner,¹² Paraskevopoulos *et al.*,¹³ Jeong and Kaufman,¹⁴ Orkin and Khamaganov,¹ and Hsu and DeMore.³

Preferred Values

$$k = 4.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.8 \times 10^{-13} \exp(-1530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 240\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The absolute rate coefficients of Orkin and Khamaganov¹ and the relative rate coefficients of Hsu and DeMore³ are in good agreement with previous absolute rate coefficients^{8–14} and with our previous evaluation, IUPAC, 1992⁴ (to within 12% of our previous evaluation⁴ from 298–370 K and 21% at 460 K for the data of Orkin and Khamaganov¹ and to within 7% of our previous evaluation⁴ for the data of Hsu and DeMore³). However, the absolute rate coefficients of Yujing *et al.*² are ~25% higher than our previous evaluation.⁴ The absolute rate coefficients of Atkinson *et al.*,⁸ Howard and Evenson,⁹ Watson *et al.*,¹⁰ Chang and Kaufman,¹¹ Handwerk and Zellner,¹² Paraskevopoulos *et al.*,¹³ and Jeong and Kaufman¹⁴ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.51 \times 10^{-18} T^2 \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–482 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2 T^2$ and $B = D + 2T$. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

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- ⁹C. J. Howard and K. M. Evenson, J. Chem. Phys. **64**, 197 (1976).
¹⁰R. T. Watson, E. Machado, B. C. Conaway, S. Wagner, and D. D. Davis, J. Phys. Chem. **81**, 256 (1977).
¹¹J. S. Chang and F. Kaufman, J. Chem. Phys. **66**, 4989 (1977).

- ¹²Handwerk and R. Zellner, Ber. Bunsenges Phys. Chem. **82**, 1161 (1978).
¹³G. Paraskevopoulos, D. L. Singleton, and R. S. Irwin, J. Phys. Chem. **85**, 561 (1981).
¹⁴K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).

$$\Delta H^\circ = -85.3 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.8 \times 10^{-13} \exp(-1010/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Howard and Evenson,¹ Perry *et al.*,² Watson *et al.*,³ Chang and Kaufman,⁴ Paraskevopoulos *et al.*,⁵ and Jeong and Kaufman⁶ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.70 \times 10^{-18} T^2 \exp(-479/T) \text{ cm}^3$

$\text{molecule}^{-1} \text{ s}^{-1}$ over the temperature range 241–483 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = Ce^2 T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.⁷

References

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²R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., J. Chem. Phys. **64**, 1618 (1976).
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⁶K.-M. Jeong and F. Kaufman, J. Phys. Chem. **86**, 1808 (1982).
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$$\Delta H^\circ = -106.7 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.65 \times 10^{-17} T^{1.52} \exp[-(261 \pm 42)/T]$	295–775	Taylor <i>et al.</i> , 1993 ¹	(a)
$(1.12 \pm 0.10) \times 10^{-13}$	295		
<i>Relative Rate Coefficients</i>			
$1.03 \times 10^{-18} T^2 \exp[(35 \pm 64)/T]$	288–357	Hsu and DeMore, 1994 ²	(b)
9.37×10^{-14}	298		
<i>Reviews and Evaluations</i>			
$3.3 \times 10^{-12} \exp(-1030/T)$	240–300	IUPAC, 1992 ³	(c)
$1.80 \times 10^{-18} T^2 \exp(-129/T)$	245–775	Atkinson, 1994 ⁴	(d)
$2.0 \times 10^{-12} \exp(-900/T)$	245–400	NASA, 1994 ⁵	(e)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals. These data supersede previous measurements from this group.⁶
 (b) Relative rate method. HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor. The concentrations of CHCl₃ and CH₃CHF₂ were

measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHCl}_3)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.52 \pm 0.11) \exp[(495 \pm 64)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

- (c) Derived using the absolute rate coefficients of Howard and Evenson,⁷ Davis *et al.*,⁸ and Jeong and Kaufman.⁹

- (d) Derived using the absolute rate coefficient data of Howard and Evenson,⁷ Davis *et al.*,⁸ and Taylor *et al.*,¹ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (e) Derived from the absolute rate coefficients of Howard and Evenson,⁷ Davis *et al.*,⁸ Jeong and Kaufman,⁹ and Taylor *et al.*,¹ using only rate coefficients obtained at temperatures < 400 K, and the relative rate coefficients of Hsu and DeMore.²

Preferred Values

$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 9.3 \times 10^{-13} \exp(-660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Taylor *et al.*¹ (which supersede those of Taylor *et al.*⁶) at temperatures of 360–480 K are significantly lower than the rate coefficients of Jeong and Kaufman,⁹ by up to a factor of ~ 1.7 . The relative rate

coefficients of Hsu and DeMore² are in good agreement with the absolute rate coefficient data^{1,7–9} at 298 K, but have a lower temperature dependence than measured in the absolute rate studies.^{1,7–9} The absolute rate coefficients of Howard and Evenson,⁷ Davis *et al.*,⁸ and Taylor *et al.*¹ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.80 \times 10^{-18} T^2 \exp(-129/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 245–775. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

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- ⁸D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, *J. Chem. Phys.* **65**, 1268 (1976).
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$$\Delta H^\circ = 97 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k < 7 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k < 1 \times 10^{-12} \exp(-3540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–478 K.

Comments on Preferred Values

The preferred values are based upon an estimated Arrhenius preexponential factor of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the upper limit to the rate coefficient determined at 478 K in the absolute rate study of Chang and Kaufman.¹ This

yields $k < 1 \times 10^{-12} \exp(-3540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and is consistent with the lack of reaction observed by Cox *et al.*² in their relative rate study. The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹J. S. Chang and F. Kaufman, *Geophys. Res. Lett.* **4**, 192 (1977).
- ²R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, *Atmos. Environ.* **10**, 305 (1976).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 78.5 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k < 1 \times 10^{-12} \exp(-3650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–480 K.

Comments on Preferred Values

The preferred values are based upon an estimated Arrhenius preexponential factor of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the upper limit to the rate coefficient determined at 480 K in the absolute rate study of Chang and Kaufman.¹ This

yields $k < 1 \times 10^{-12} \exp(-3650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and is consistent with the lack of reaction observed by Cox *et al.*² in their relative rate study. The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹J. S. Chang and F. Kaufman, *Geophys. Res. Lett.* **4**, 192 (1977).
²R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, *Atmos. Environ.* **10**, 305 (1976).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 49.6 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k < 1 \times 10^{-12} \exp(-2260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range $\sim 250\text{--}300 \text{ K}$.

of 5. Assuming an Arrhenius preexponential factor of $1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, this leads to the upper limit to the Arrhenius expression given. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹R. A. Cox, R. G. Derwent, A. E. J. Eggleton, and J. E. Lovelock, *Atmos. Environ.* **10**, 305 (1976).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the relative rate study of Cox *et al.*,¹ with their upper limit to the rate coefficient being increased by a factor

No new data have been published since our last evaluation.

Preferred Values

$k = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.0 \times 10^{-13} \exp(445/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–420 K.

Kirchner,³ Edney *et al.*,⁴ Klöpffer *et al.*,⁵ and Kirchner *et al.*,⁶ which are not used in the derivation of the preferred values, are in general agreement with the preferred values, which are identical to our previous evaluation, IUPAC, 1992.⁷

References

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²J. S. Chang and F. Kaufman, *J. Chem. Phys.* **66**, 4989 (1977).
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⁶K. Kirchner, D. Helf, P. Ott, and S. Vogt, *Ber. Bunsenges. Phys. Chem.* **94**, 77 (1990).
⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is derived from the mean of the values of Howard¹ and Chang and Kaufman.² The Arrhenius parameters are those of Chang and Kaufman,² with the A-factor reduced to yield the preferred value at 298 K. The room temperature rate coefficients reported by

No new data have been published since our last evaluation.

Preferred Values

$k = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 9.4 \times 10^{-12} \exp(-1200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
 the temperature range 300–420 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred 298 K value is derived from the mean of the values of Howard¹ and Chang and Kaufman.² The Arrhenius parameters are those of Chang and Kaufman.² The Arrhenius

expression and 305 K rate coefficient reported by Kirchner,³ and Kirchner *et al.*,⁴ which are not used in the derivation of the preferred values, are in reasonable agreement with the preferred values, which are identical to our previous evaluation, IUPAC, 1992.⁵

References

- ¹C. J. Howard, *J. Chem. Phys.* **65**, 4771 (1976).
- ²J. S. Chang and F. Kaufman, *J. Chem. Phys.* **66**, 4989 (1977).
- ³K. Kirchner, *Chimia* **37**, 1 (1983).
- ⁴K. Kirchner, D. Helf, P. Ott, and S. Vogt, *Ber. Bunsenges. Phys. Chem.* **94**, 77 (1990).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CH₃CF₂Cl (HCFC-142b) → H₂O + CH₂CF₂Cl

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.45 \pm 0.31) \times 10^{-15}$	270	Zhang, Huie, and Kurylo, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
$9.2 \times 10^{-13} \exp(-1705/T)$	240–300	IUPAC, 1992 ²	(b)
$1.77 \times 10^{-18} T^2 \exp(-1174/T)$	223–427	Atkinson, 1994 ³	(c)
$1.3 \times 10^{-12} \exp(-1800/T)$	223–427	NASA, 1994 ⁴	(d)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO.
- (b) Derived from the rate coefficient data of Howard and Evenson,⁵ Watson *et al.*,⁶ and Gierczak *et al.*⁷
- (c) Derived from the absolute rate coefficient data of Howard and Evenson,⁵ Watson *et al.*,⁶ and Gierczak *et al.*,⁷ using the three parameter equation $k = CT^2 \times \exp(-D/T)$.
- (d) Derived from the absolute rate coefficients of Howard and Evenson,⁵ Watson *et al.*,⁶ Handwerk and Zellner,⁸ Paraskevopoulos *et al.*,⁹ Liu *et al.*,¹⁰ Gierczak *et al.*,⁷ Zhang *et al.*,¹ and Zellner *et al.* (unpublished data, 1993).

Preferred Values

$k = 3.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
 $k = 9.2 \times 10^{-13} \exp(-1705/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
 the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The rate coefficients obtained^{1,5–12} exhibit a large degree of scatter, especially at temperatures $\leq 300 \text{ K}$. In particular, the rate coefficients measured by Clyne and Holt,¹¹ Brown *et al.*,¹² and, to a lesser extent, Handwerk and Zellner,⁸ Paraskevopoulos *et al.*,⁹ Liu *et al.*,¹⁰ and Zhang *et al.*¹ are higher than those of Howard and Evenson,⁵ Watson *et al.*,⁶ and Gierczak *et al.*⁷ Accordingly, the rate coefficient data of Howard and Evenson,⁵ Watson *et al.*,⁶ and Gierczak *et al.*⁷ have been fitted to the three parameter equation $k = CT^2 \times \exp(-D/T)$, resulting in $k = 1.77 \times 10^{-18} T^2 \exp(-1174/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 223–427 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.²

References

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- ⁶R. T. Watson, G. Machado, B. Conaway, S. Wagner, and D. D. Davis, *J. Phys. Chem.* **81**, 256 (1977).
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¹⁰R. Liu, R. E. Huie, and M. J. Kurylo, J. Phys. Chem. **94**, 3247 (1990).

¹¹M. A. A. Clyne and P. M. Holt, J. Chem. Soc. Faraday Trans. 2, **75**, 582 (1979).

¹²A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.82 \pm 0.65) \times 10^{-15}$	250	Zhang, Huie, and Kurylo, 1992 ¹	(a)
$(2.01 \pm 0.90) \times 10^{-15}$	250		
$(3.39 \pm 0.82) \times 10^{-15}$	270		
$(4.80 \pm 1.46) \times 10^{-15}$	297		
$2.4 \times 10^{-12} \exp[-(1790 \pm 100)/T]$	298–479	Lancar, Le Bras, and Poulet, 1993 ²	(b)
$(5.7 \pm 1.5) \times 10^{-15}$	298		
Relative Rate Coefficients			
$4.73 \times 10^{-20} T^{2.58} \exp[-(893 \pm 105)/T]$	298–358	Huder and DeMore, 1993 ³	(c,d)
5.73×10^{-15}	298		
$1.78 \times 10^{-18} T^2 \exp[-(984 \pm 28)/T]$	298–358	Huder and DeMore, 1993 ³	(c,e)
5.85×10^{-15}	298		
Reviews and Evaluations			
$7.0 \times 10^{-13} \exp(-1425/T)$	240–300	IUPAC, 1992 ⁴	(f)
$1.35 \times 10^{-18} T^2 \exp(-893/T)$	233–393	Atkinson, 1994 ⁵	(g)
$1.7 \times 10^{-13} \exp(-1700/T)$	250–479	NASA, 1994 ⁶	(h)

Comments

- (a) Flash photolysis system with resonance fluorescence detection of HO radicals. Experiments carried out with reduced flash energies or water vapor concentrations (resulting in lower initial HO radical concentrations) led to the lower measured rate coefficients cited in the table. These data supersede those of Liu *et al.*⁷ at 243–298 K.
- (b) Discharge flow system with EPR detection of HO radicals.
- (c) Relative rate method. HO radicals were generated by the photolysis of $\text{H}_2\text{O}-\text{O}_3$ mixtures at 254 nm in $\text{H}_2\text{O}-\text{O}_3-\text{CH}_3\text{CFCl}_2-\text{CH}_4$ (or CH_3CCl_3)-Ar- O_2 mixtures. The concentrations of CH_3CFCl_2 and CH_4 (or CH_3CCl_3) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{CFCl}_2)/k(\text{HO} + \text{CH}_4) = (0.49 \pm 0.16) \times \exp[(189 \pm 105)/T]$ and $k(\text{HO} + \text{CH}_3\text{CFCl}_2)/k(\text{HO} + \text{CH}_3\text{CCl}_3) = (0.79 \pm 0.07) \exp[-(74 \pm 28)/T]$ are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (d) Relative to $k(\text{HO} + \text{CH}_4)$.
- (e) Relative to $k(\text{HO} + \text{CH}_3\text{CCl}_3)$.
- (f) Based on the absolute rate coefficients of Talukdar *et al.*⁸
- (g) Derived from the absolute rate coefficients of Talukdar *et al.*,⁸ using the three parameter equation $k = CT^2 \times \exp(-D/T)$.
- (h) Derived from the rate coefficients of Liu *et al.*⁷ (at temperatures ≥ 330 K), Talukdar *et al.*⁸ (at temperatures ≥ 253 K), Zhang *et al.*,¹ Lancar *et al.*,² and Hsu and DeMore.³

Preferred Values

$k = 5.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.0 \times 10^{-13} \exp(-1425/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Brown *et al.*⁹ are higher than those from the absolute rate studies of Liu *et al.*,⁷ Talukdar *et al.*,⁸ Zhang *et al.*,¹ and Lancar *et al.*² at all temperatures studied,⁹ and the rate coefficients of Liu *et al.*⁷ at temperatures ≤ 298 K are significantly higher than those of Talukdar *et al.*,⁸ Zhang *et al.*,¹ and Lancar *et al.*² The measurements of Zhang *et al.*¹ show that the earlier lower tem-

perature (≤ 298 K) data of Liu *et al.*⁷ were in error due to the occurrence of secondary reactions of OH radicals with reaction products. The rate coefficients of Talukdar *et al.*,⁸ Zhang *et al.*¹ (obtained at low flash energies and/or low water vapor concentrations and with high associated uncertainties), Lancar *et al.*,² and Huder and DeMore³ are in good agreement, as are those of Talukdar *et al.*⁸ and Liu *et al.*⁷ at temperatures ≥ 330 K.

The rate coefficients of Talukdar *et al.*⁸ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.35 \times 10^{-18} T^2 \exp(-893/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 233–393 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.⁴

The rate coefficients of Huder and DeMore,³ obtained relative to the reactions of the HO radical with CH_4 and CH_3CCl_3 , are within 5% of those calculated from the preferred three parameter equation over the temperature range 298–358 K studied.³

References

- ¹Z. Zhang, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.* **96**, 1533 (1992).
- ²I. Lancar, G. Le Bras, and G. Poulet, *J. Chim. Phys.* **90**, 1897 (1993).
- ³K. Huder and W. B. DeMore, *Geophys. Res. Lett.* **20**, 1575 (1993).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁵R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁶NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁷R. Liu, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.* **94**, 3247 (1990).
- ⁸R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, *J. Phys. Chem.* **95**, 5815 (1991).
- ⁹A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, *Atmos. Environ.* **24A**, 2499 (1990).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.78 \times 10^{-18} T^{2.08} \exp[-(1068 \pm 108)/T]$	298–761	Jiang, Taylor, and Dellinger, 1992 ¹	(a)
$(1.1 \pm 0.1) \times 10^{-14}$	298		
$(1.2 \pm 0.2) \times 10^{-14}$	298	Lancar, Le Bras, and Poulet, 1993 ²	(b)
<i>Reviews and Evaluations</i>			
$1.2 \times 10^{-12} \exp(-1440/T)$	240–300	IUPAC, 1992 ³	(c)
$2.25 \times 10^{-18} T^2 \exp(-910/T)$	243–379	Atkinson, 1994 ⁴	(d)
$1.8 \times 10^{-12} \exp(-1550/T)$	243–379	NASA, 1994 ⁵	(e)

Comments

- Laser photolysis system with LIF detection of HO radicals.
- Discharge flow system with EPR detection of HO radicals.
- Derived from the absolute rate coefficients of Finlayson-Pitts *et al.*⁶ and the 243–379 K absolute rate coefficients of Talukdar *et al.*⁷
- Derived from the absolute rate coefficients of Finlayson-Pitts *et al.*⁶ and the 243–379 K absolute rate coefficients of Talukdar *et al.*⁷ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- The 298 K rate coefficient was derived from the absolute rate coefficients of Finlayson-Pitts *et al.*⁶ and Talukdar *et al.*⁷ and the relative rate coefficient of DeMore.⁸ The temperature dependence was that of Talukdar *et al.*⁷

Preferred Values

$k = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.2 \times 10^{-12} \exp(-1440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Jiang *et al.*¹ and Lancar *et al.*² are somewhat higher than those of Finlayson-Pitts *et al.*⁶ and Talukdar *et al.*,⁷ with the discrepancy between the rate coefficients of Jiang *et al.*¹ and those of Finlayson-Pitts *et al.*⁶ and Talukdar *et al.*⁷ increasing with increasing temperature. A unit-weighted least-squares analysis of the absolute rate coefficients of Finlayson-Pitts *et al.*⁶ and Talukdar *et al.*⁷ using the expression $k = CT^2 \exp(-D/T)$, leads to $k = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 243–379 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. This recommendation is identical to our previous evaluation, IUPAC, 1992.³

The relative rate coefficients of DeMore,⁸ when placed on an absolute basis by use of the present recommendation for the reaction of the HO radical with CH_4 , lead to $k(\text{HO} + \text{CH}_3\text{CCl}_3) = 4.92 \times 10^{-20} T^{2.58} \exp(-728/T) \text{ cm}^3$

molecule⁻¹ s⁻¹ over the temperature range 277–356 K, equivalent to an Arrhenius expression of $k = 1.16 \times 10^{-12} \times \exp(-1412/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ centered at 265 K and a 298 K rate coefficient of $1.02 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in excellent agreement with our recommendation.

References

- ¹Z. Jiang, P. H. Taylor, and B. Dellinger, *J. Phys. Chem.* **96**, 8961 (1992).
²I. Lancar, G. Le Bras, and G. Poulet, *J. Chim. Phys.* **90**, 1897 (1993).

- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
⁴R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1, (1994).
⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
⁶B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko, and C. C. Lai, *Geophys. Res. Lett.* **19**, 1371 (1992).
⁷R. K. Talukdar, A. Mellouki, A.-M. Schmoltner, T. Watson, S. Montzka, and A. R. Ravishankara, *Science* **257**, 227 (1992).
⁸W. B. DeMore, *Geophys. Res. Lett.* **19**, 1367 (1992).

No new data have been published since our last evaluation.

Preferred Values

$k = 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.2 \times 10^{-13} \exp(-1100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 250 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Howard and Evenson¹ and Handwerk and Zellner² (corrected to 298 K), and the temperature dependence is that

obtained from a unit-weighted least-squares analysis of the data of Handwerk and Zellner.² The rate coefficients of Clyne and Holt³ are in serious disagreement with those of Handwerk and Zellner,² and are not used in the evaluation. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 197 (1976).
²V. Handwerk and R. Zellner, *Ber. Bunsenges. Phys. Chem.* **82**, 1161 (1978).
³M. A. A. Clyne and P. M. Holt, *J. Chem. Soc. Faraday Trans. 2*, **75**, 582 (1979).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.2 \times 10^{-12} \exp(-1580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The corrected data of Watson *et al.*¹ are accepted, assuming that the observed C₂ haloalkene impurities present in the CH₂ClCF₂Cl sample react with the OH radical with a rate

coefficient of $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature. The rate coefficients of Jeong *et al.*² are higher, especially at <300 K, suggesting the presence of reactive impurities in the CH₂ClCF₂Cl sample used. The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, *Int. J. Chem. Kinet.* **11**, 187 (1979).
²K.-M. Jeong, K.-J. Hsu, J. B. Jeffries, and F. Kaufman, *J. Phys. Chem.* **88**, 1222 (1984).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$3.38 \times 10^{-20} T^{2.58} \exp[-(715 \pm 40)/T]$	298–366	Hsu and DeMore, 1995 ¹	(a,b)
7.38×10^{-15}	298		
$6.44 \times 10^{-13} \exp[-(1330 \pm 52)/T]$	298–356	Hsu and DeMore, 1995 ¹	(a,c)
7.36×10^{-15}	298		
<i>Reviews and Evaluations</i>			
$5.4 \times 10^{-13} \exp(-1205/T)$	240–300	IUPAC, 1992 ²	(d)
$1.03 \times 10^{-18} T^2 \exp(-675/T)$	210–425	Atkinson, 1994 ³	(e)
$8.0 \times 10^{-13} \exp(-1350/T)$	210–425	NASA, 1994 ⁴	(f)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or from O_3 - H_2O mixtures in the UV, in H_2O (or H_2O - O_3)- CHFClCF_3 - CH_4 (or CHF_2CHF_2)- O_2 - N_2 mixtures. The concentrations of CHFClCF_3 and CH_4 (or CHF_2CHF_2) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CHFClCF}_3)/k(\text{HO} + \text{CH}_4) = (0.35 \pm 0.04) \exp[(367 \pm 40)/T]$ and $k(\text{HO} + \text{CHFClCF}_3)/k(\text{HO} + \text{CHF}_2\text{CHF}_2) = (0.46 \pm 0.07) \times \exp[(300 \pm 52)/T]$ are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation) and $k(\text{HO} + \text{CHF}_2\text{CHF}_2) = 1.4 \times 10^{-12} \times \exp(-1630/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (b) Relative to $k(\text{HO} + \text{CH}_4)$.
- (c) Relative to $k(\text{HO} + \text{CHF}_2\text{CHF}_2)$.
- (d) Derived from the absolute rate coefficients of Watson *et al.*⁵ and Gierczak *et al.*⁶
- (e) Derived from the absolute rate coefficients of Watson *et al.*⁵ and Gierczak *et al.*⁶ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (f) Derived from the absolute rate coefficients of Howard and Evenson,⁷ Watson *et al.*,⁵ and Gierczak *et al.*⁶ and the relative rate coefficients of Hsu and DeMore.¹

Preferred Values

$k = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.4 \times 10^{-13} \exp(-1205/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

At room temperature, the absolute and relative rate coefficients^{1,5–7} range over a factor of ~ 1.7 , with the absolute rate coefficient of Howard and Evenson⁷ being the highest, and the relative rate coefficients of Hsu and DeMore¹ being the lowest. The rate coefficients of Watson *et al.*⁵ and Gierczak *et al.*⁶ are in excellent agreement, and the rate coefficients from these two studies^{5,6} have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.03 \times 10^{-18} T^2 \exp(-675/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210–425 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.² The uncertainty limits have been increased to overlap the relative rate coefficient data of Hsu and DeMore.¹

References

- ¹K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1994).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵R. T. Watson, A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis, *Int. J. Chem. Kinet.* **11**, 187 (1979).
- ⁶T. Gierczak, R. Talukdar, G. L. Vaghjiani, E. R. Lovejoy, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5001 (1991).
- ⁷C. J. Howard and K. M. Evenson, *J. Chem. Phys.* **64**, 4303 (1976).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.1 \times 10^{-12} \exp[-(940 \pm 200)/T]$ $(4.3 \pm 1.0) \times 10^{-14}$	295–385 295	Nielsen, 1991 ¹	(a)
<i>Relative Rate Coefficients</i>			
$5.5 \times 10^{-19} T^2 \exp[-(95 \pm 36)/T]$ 3.45×10^{-14}	298–359 298	Hsu and DeMore, 1995 ²	(b)
<i>Reviews and Evaluations</i>			
$5.5 \times 10^{-13} \exp(-815/T)$	240–300	IUPAC, 1992 ³	(c)
$1.06 \times 10^{-18} T^2 \exp(-283/T)$	213–400	Atkinson, 1994 ⁴	(d)
$7.0 \times 10^{-13} \exp(-900/T)$	213–400	NASA, 1994 ⁵	(e)

Comments

- (a) Pulsed radiolysis system with resonance absorption detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of H₂O at 185 nm or from O₃-H₂O mixtures in the UV, in H₂O (or H₂O-O₃)-CHCl₂CF₃-CH₃CHF₂-O₂-N₂ mixtures. The concentrations of CHCl₂CF₃ and CH₃CHF₂ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHCl}_2\text{CF}_3)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.28 \pm 0.03) \exp[(365 \pm 36)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Derived from the absolute rate coefficients of Howard and Evenson,⁶ Watson *et al.*,⁷ Liu *et al.*,⁸ and Gierczak *et al.*⁹
- (d) Derived from the absolute rate coefficients of Howard and Evenson,⁶ Watson *et al.*,⁷ Liu *et al.*,⁸ and Gierczak *et al.*,⁹ using the three parameter equation $k = CT^2 \times \exp(-D/T)$.
- (e) Derived from the rate coefficients of Howard and Evenson,⁶ Watson *et al.*,⁷ Liu *et al.*,⁸ Gierczak *et al.*,⁹ Nielsen,¹ Hsu and DeMore,² and Zellner *et al.* (unpublished data, 1993).

Preferred Values

$k = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.5 \times 10^{-13} \exp(-815/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The measured absolute rate coefficients of Howard and Evenson,⁶ Watson *et al.*,⁷ Liu *et al.*,⁸ and Gierczak *et al.*⁹ are in reasonable agreement, but are significantly lower than those of Brown *et al.*¹⁰ and Nielsen.¹ The rate coefficients of Howard and Evenson,⁶ Watson *et al.*,⁷ Liu *et al.*,⁸ and Gierczak *et al.*⁹ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.06 \times 10^{-18} T^2 \times \exp(-283/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 213–400 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$, and is identical to our previous evaluation, IUPAC, 1992.³

The relative rate constants of Hsu and DeMore² are within 12% of those predicted from the recommended three parameter equation over the temperature range studied² (298–359 K).

References

- O. J. Nielsen, Chem. Phys. Lett. **187**, 286 (1991).
- K.-J. Hsu and W. B. DeMore, J. Phys. Chem. **99**, 1235 (1995).
- IUPAC, Supplement IV, 1992 (see references in Introduction).
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- A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$9.2 \times 10^{-13} \exp[-(1281 \pm 85)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(1.23 \pm 0.10) \times 10^{-14}$	298		

Comments

- (a) Discharge flow system with EPR detection of HO radicals.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Orkin and Khamaganov.¹

Preferred Values

$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.4 \times 10^{-13} \exp(-1255/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 298–460 K.

References

- ¹ V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 157 (1993).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.13 \times 10^{-12} \exp[-(918 \pm 52)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(5.30 \pm 0.41) \times 10^{-14}$	298		

Comments

- (a) Discharge flow system with EPR detection of HO radicals.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred Arrhenius expression is obtained from a unit-weighted least-squares analysis of the absolute rate coefficients of Orkin and Khamaganov.¹

Preferred Values

$k = 5.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.2 \times 10^{-12} \exp(-940/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 298–460 K.

References

- ¹ V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 157 (1993).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$6.14 \times 10^{-18} T^2 \exp[-(343 \pm 42)/T]$	294–362	Hsu and DeMore, 1995 ¹	(a)
1.73×10^{-14}	298		

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of H_2O at 185 nm or from the photolysis of O_3 - H_2O mixtures in the UV, in H_2O (or H_2O - O_3)- CHFClCFCl_2 - CH_3CHF_2 - O_2 - N_2 mixtures. The concentrations of CHFClCFCl_2 and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHFClCFCl}_2)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.31 \pm 0.04) \exp[(117 \pm 42)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).

$k = 4.1 \times 10^{-12} \exp(-945/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the relative rate coefficients of Hsu and DeMore.¹ The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered at 300 K and is derived from the cited three parameter expression, $k = CT^2 \exp(-D/T)$, with $A = C e^2 T^2$ and $B = D + 2T$.

Preferred Values

$k = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

References

¹K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).

No new data have been published since our last evaluation.

Preferred Values

$k = 2.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-12} \exp(-1130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–400 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The rate coefficients measured by Zhang *et al.*¹ and Nelson *et al.*² over the temperature range 295–365 K are in good agreement within the experimental uncertainties. The rate coefficients measured by Brown *et al.*³ at 251 K and 300 K are significantly higher, and are not used in the evaluation. The preferred 298 K rate coefficient is the average of those

calculated from the Arrhenius expressions of Zhang *et al.*¹ and Nelson *et al.*,² and the preferred temperature dependence is the mean of those of Zhang *et al.*¹ and Nelson *et al.*² [a least-squares analysis of these data^{1,2} yields $k = 1.56 \times 10^{-12} \exp(-1239/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, largely weighted by the 270 K and 400 K rate coefficients of Zhang *et al.*¹]. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

¹Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, *Geophys. Res. Lett.* **18**, 5 (1991).

²D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, *J. Phys. Chem.* **96**, 249 (1992).

³A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, *Nature* **347**, 541 (1990).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k = 8.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.5 \times 10^{-13} \exp(-1230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
 the temperature range 290–400 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are derived from a least-squares analysis of the rate coefficients of Zhang *et al.*¹ and Nelson *et al.*,² which are in excellent agreement. The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹Z. Zhang, R. Liu, R. E. Huie, and M. J. Kurylo, *Geophys. Res. Lett.* **18**, 5 (1991).
- ²D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, *J. Phys. Chem.* **96**, 249 (1992).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k = 2.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.0 \times 10^{-13} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
 the temperature range 290–370 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the sole study of Nelson *et al.*,¹ and are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, *J. Phys. Chem.* **96**, 249 (1992).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limit to the rate coefficient reported by Libuda *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.²

References

- ¹H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, *J. Phys. Chem.* **94**, 5860 (1990).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred upper limit to the 298 K rate coefficient is based on the sole reported study of Nelson *et al.*,¹ with the preferred upper limit being increased by a factor of 5 over

that cited by Nelson *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.²

References

¹L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 577 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(3.1 \pm 0.2) \times 10^{-12}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
3.0×10^{-12}	298	IUPAC, 1992 ²	(b)
3.1×10^{-12}	298	Atkinson, 1994 ³	(c)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or $\text{C}_2\text{H}_5\text{ONO}$ in CH_3ONO (or $\text{C}_2\text{H}_5\text{ONO}$)-NO- CH_2ClCHO - $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$ -air mixtures at atmospheric pressure. The concentrations of CH_2ClCHO and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_2\text{ClCHO})/k(\text{HO} + 2\text{-butanone})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-butanone}) = 1.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³
- (b) Based on the absolute rate coefficient of Balestra-Garcia *et al.*⁴
- (c) Based on the rate coefficients of Balestra-Garcia *et al.*,⁴ Starcke *et al.*,⁵ and Scollard *et al.*¹

Preferred Values

$k = 3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Balestra-Garcia *et al.*⁴ and Scollard *et al.*,¹ which are in excellent agreement. The reaction is expected to proceed essentially totally by channel (1) at 298 K.

References

¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

⁴C. Balestra-Garcia, G. Le Bras and H. Mac Leod, *J. Phys. Chem.* **96**, 3312 (1992).

⁵J. Starcke, F. Zabel, L. Elsen, W. Nelsen, I. Barnes, and K. H. Becker, *Proceedings of the 5th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Kluwer Academic, Dordrecht, The Netherlands, 1990), pp. 172–176.

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.2) \times 10^{-12}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(a)
<i>Relative Rate Coefficients</i>			
$(2.0 \pm 0.3) \times 10^{-12}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(b)

Comments

- (a) Laser photolysis system with resonance fluorescence detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or $\text{C}_2\text{H}_5\text{ONO}$ in CH_3ONO (or $\text{C}_2\text{H}_5\text{ONO}$)- CHFCICHO -toluene-air mixtures. The concentrations of CHFCICHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHFCICHO})/k(\text{HO} + \text{toluene})$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²

Preferred Values

$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard *et al.*,¹ which are in good agreement. The reaction is expected to proceed by channel (1) at room temperature.¹

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).
- ²R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$(2.3 \pm 0.1) \times 10^{-12}$	298 $\pm$ 2	Scollard <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
2.4×10^{-12}	298	IUPAC, 1992 ²	(b)
2.5×10^{-12}	298	Atkinson, 1994 ³	(c)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of CH_3ONO or $\text{C}_2\text{H}_5\text{ONO}$ in CH_3ONO (or $\text{C}_2\text{H}_5\text{ONO}$)- $\text{NO-CHCl}_2\text{CHO-CH}_3\text{C(O)CH}_2\text{CH}_3$ -air mixtures at atmospheric pressure. The concentrations of CHCl_2CHO and 2-butanone were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHCl}_2\text{CHO})/k(\text{HO} + 2$ -

butanone) is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-butanone}) = 1.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³

- (b) Based on the absolute rate coefficient of Balestra-Garcia *et al.*⁴
- (c) Based on the rate coefficients of Balestra-Garcia *et al.*,⁴ Starcke *et al.*,⁵ and Scollard *et al.*¹

Preferred Values

$k = 2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of those of Balestra-Garcia *et al.*⁴ and Scollard *et al.*,¹ which are in excellent agreement. The reaction is expected to proceed essentially totally by channel (1) at 298 K.¹

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
⁴C. Balestra-Garcia, G. Le Bras and H. Mac Leod, *J. Phys. Chem.* **96**, 3312 (1992).
⁵J. Starcke, F. Zabel, L. Elsen, W. Nelsen, I. Barnes, and K. H. Becker, *Proceedings of the 5th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Kluwer Academic, Dordrecht, The Netherlands, 1990), pp. 172–176.

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(9.5 \pm 0.5) \times 10^{-13}$	298 ± 2	Scollard <i>et al.</i> , 1993 ¹	(a)
Relative Rate Coefficients			
$(7.0 \pm 0.5) \times 10^{-13}$	298 ± 2	Scollard <i>et al.</i> , 1993 ¹	(b)

Comments

- (a) Laser photolysis system with resonance fluorescence detection of HO radicals.
 (b) Relative rate method. HO radicals were generated by the photolysis of CH₃ONO or C₂H₅ONO in CH₃ONO (or C₂H₅ONO)-CF₂ClCHO-ethanol-air mixtures. The concentrations of CF₂ClCHO and ethanol were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CF}_2\text{ClCHO})/k(\text{HO} + \text{ethanol})$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{ethanol}) = 3.27 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard *et al.*,¹ which are in reasonable agreement.

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).
²R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

Preferred Values

$k = 8.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.1) \times 10^{-12}$	298 ± 2	Scollard <i>et al.</i> , 1993 ¹	(a)
Relative Rate Coefficients			
$(1.1 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard <i>et al.</i> , 1993 ¹	(b)

Comments

- (a) Laser photolysis system with resonance fluorescence detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the photolysis of CH₃ONO or C₂H₅ONO in CH₃ONO (or C₂H₅ONO)-CFCl₂CHO-toluene-air mixtures. The concentrations of CFCl₂CHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CFCl}_2\text{CHO})/k(\text{HO} + \text{toluene})$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.²

Preferred Values

$$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.20 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Scollard *et al.*,¹ which are in good agreement.

References

- ¹D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).
- ²R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.28 \pm 0.25) \times 10^{-12}$	298 ± 2	Barry <i>et al.</i> , 1994 ¹	(a)
$(8.9 \pm 1.5) \times 10^{-13}$	298 ± 2	Barry <i>et al.</i> , 1994 ¹	(b)
<i>Relative Rate Coefficients</i>			
$(1.6 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard <i>et al.</i> , 1993 ²	(c)
$(1.05 \pm 0.18) \times 10^{-12}$	298 ± 2	Barry <i>et al.</i> , 1994 ¹	(d)
<i>Reviews and Evaluations</i>			
1.4×10^{-12}	298	IUPAC, 1992 ³	(e)
1.3×10^{-12}	298	Atkinson, 1994 ⁴	(f)
$8.2 \times 10^{-12} \exp(-600/T)$	298–520	NASA, 1994 ⁵	(g)

Comments

- (a) Discharge flow system with resonance fluorescence detection of HO radicals.
- (b) Discharge flow system with EPR detection of HO radicals.
- (c) Relative rate method. HO radicals were generated by the photolysis of CH₃ONO or C₂H₅ONO in CH₃ONO (or C₂H₅ONO)-CCl₃CHO-toluene-air mixtures. The concentrations of CCl₃CHO and toluene were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CCl}_3\text{CHO})/k(\text{HO} + \text{toluene})$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{toluene}) = 5.96 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴
- (d) Relative rate method. HO radicals were generated by the photolysis of O₃ in the presence of water vapor in O₃-H₂O-CCl₃CHO-2-methylpropane-air mixtures at atmospheric pressure. The concentrations of CCl₃CHO and 2-methylpropane were measured by GC. The measured rate coefficient ratio $k(\text{HO} + \text{CCl}_3\text{CHO})/k(\text{HO}$

+2-methylpropane)=0.45 ± 0.01 is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{2-methylpropane}) = 2.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁴

- (e) Based on the room temperature rate coefficients of Dóbé *et al.*,⁶ Nelson *et al.*,⁷ and Balestra-Garcia *et al.*⁸
- (f) Based on the room temperature rate coefficients of Starcke *et al.*,⁹ Nelson *et al.*,⁷ Balestra-Garcia *et al.*,⁸ and Scollard *et al.*²
- (g) The 298 K rate coefficient was the average of the three determinations of Barry *et al.*¹ The temperature dependence was that of Dóbé *et al.*⁶

Preferred Values

$$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The most recent absolute and relative rate study of Barry *et al.*¹ supersedes previous measurements of Nelson *et al.*,⁷ Balestra-Garcia *et al.*,⁸ and Scollard *et al.*² The average of the three independent determinations of the rate coefficient by Barry *et al.*,¹ [$k = (1.1 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$], is ~ 30 lower than the absolute 298 K rate coefficient of Dóbé *et al.*,⁶ but is in agreement with the value of Starcke *et al.*⁹

The preferred 298 K rate coefficient is the average value reported by Barry *et al.*¹ No temperature dependence is recommended.

References

- ¹J. Barry, D. J. Scollard, J. J. Treacy, H. W. Sidebottom, G. Le Bras, G. Poulet, S. Téton, A. Chichinin, C. E. Canosa-Mas, D. J. Kinnison, R. P.

Wayne, and O. J. Nielsen, *Chem. Phys. Lett.* **221**, 353 (1994).

²D. J. Scollard, J. J. Treacy, H. W. Sidebottom, C. Balestra-Garcia, G. Laverdet, G. Le Bras, H. Mac Leod, and S. Téton, *J. Phys. Chem.* **97**, 4683 (1993).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

⁴R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

⁵NASA Evaluation No. 11, 1994 (see references in Introduction).

⁶S. Dóbé, L. A. Khachatryan, and T. Bérces, *Ber. Bunsenges. Phys. Chem.* **93**, 847 (1989).

⁷L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 577 (1990).

⁸C. Balestra-Garcia, G. Le Bras, and H. Mac Leod, *J. Phys. Chem.* **96**, 3312 (1992).

⁹J. Starcke, F. Zabel, L. Elsen, W. Nelsen, I. Barnes, and K. H. Becker, *Proceedings of the 5th European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants* (Kluwer Academic, Dordrecht, The Netherlands, 1990), pp. 172–176.

No new data have been published since our last evaluation.

Preferred Values

$$k = 9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 1.0 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the relative rate coefficient study of Nelson *et al.*¹ and is identical to our previous evaluation, IUPAC, 1992.² However, the data presented in Figure 5 of Nelson *et al.*¹ and in the earlier presentation of Nelson *et al.*³ yields a rate coefficient for the

reaction of HO radicals with $\text{CH}_3\text{C(O)Cl}$ of $k = 6.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $298 \pm 3 \text{ K}$, a factor of ~ 7.5 higher than cited in Nelson *et al.*¹ This apparent discrepancy requires clarification.

References

¹L. Nelson, I. Shanahan, H. W. Sidebottom, J. Treacy, and O. J. Nielsen, *Int. J. Chem. Kinet.* **22**, 577 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³L. Nelson, J. J. Treacy, and H. W. Sidebottom, *Proceedings of the 3rd European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*, 1984 (Riedel, Dordrecht, Holland, 1984), pp. 258–263.

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i>			
$< 3 \times 10^{-13}$	300 ± 3	McLoughlin, Kane, and Shanahan, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
2.1×10^{-14}	298	IUPAC, 1992 ²	(b)

Comments

- (a) Relative rate method. HO radicals generated by the photolysis of $\text{CH}_3\text{ONO-NO-CHF}_2\text{OCHClCF}_3$ -diethyl

ether-air mixtures at atmospheric pressure. The concentrations of $\text{CHF}_2\text{OCHClCF}_3$ and diethyl ether were measured by GC. The upper limit to the rate coefficient

ratio of $k(\text{HO} + \text{CHF}_2\text{OCHClCF}_3)/k(\text{HO} + \text{diethyl ether})$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{diethyl ether}) = 1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³

- (b) Based on the absolute rate coefficient of Brown *et al.*⁴

Preferred Values

$k = 2.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$.

Comments on Preferred Values

The preferred value is based on the absolute rate coefficient of Brown *et al.*,⁴ with expanded uncertainty limits, and is identical to our previous evaluation, IUPAC, 1992.² The upper limit to the rate coefficient measured by McLoughlin *et al.*¹ is consistent with the preferred value.

References

- ¹P. McLoughlin, R. Kane, and I. Shanahan, *Int. J. Chem. Kinet.* **25**, 137 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁴A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, *Atmos. Environ.* **24A**, 2499 (1990).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Relative Rate Coefficients</i> $< 3 \times 10^{-13}$	300 ± 3	McLoughlin, Kane, and Shanahan, 1993 ¹	(a)
<i>Reviews and Evaluations</i> $6.1 \times 10^{-13} \exp(-1080/T)$	300–430	IUPAC, 1992 ²	(b)

Comments

- (a) Relative rate method. HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO-CHF}_2\text{OCF}_2\text{CHFCl}$ -diethyl ether-air mixtures at atmospheric pressure. The concentrations of $\text{CHF}_2\text{OCF}_2\text{CHFCl}$ and diethyl ether were measured by GC. The measured upper limit to the rate coefficient ratio $k(\text{HO} + \text{CHF}_2\text{OCF}_2\text{CHFCl})/k(\text{HO} + \text{diethyl ether})$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{diethyl ether}) = 1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.³
- (b) Based on the absolute rate coefficients of Brown *et al.*⁴

Preferred Values

$k = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.1 \times 10^{-13} \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–430 K.

Reliability

$\Delta \log k = \pm 0.5$.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the absolute rate study of Brown *et al.*,⁴ and are identical to our previous evaluation, IUPAC, 1992.² The upper limit to the rate coefficient measured by McLoughlin *et al.*¹ is consistent with the preferred values.

References

- ¹P. McLoughlin, R. Kane and I. Shanahan, *Int. J. Chem. Kinet.* **25**, 137 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁴A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, *Atmos. Environ.* **24A**, 2499 (1990).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(1.9 \pm 0.7) \times 10^{-12}$	298	Hayman <i>et al.</i> , 1994 ¹	(a)

Comments

- (a) Laser flash photolysis-UV absorption study of $\text{CF}_3\text{CCl}_3\text{-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures. The kinetic data were obtained by analyzing two sets of transient decays for $\text{CF}_3\text{CCl}_2\text{O}_2$ and HO_2 radicals on the basis of a mechanism consisting of 10 reactions.

Preferred Values

$$k = 1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

While the above value of the rate coefficient seems reasonable, it has been derived from the analysis of a complex chemical system and requires independent verification to reduce the recommended error limits. It is interesting to note, by comparison with data for analogous halogenated RO_2 radicals, that while the α -substitution of Cl appears to reduce the rate coefficient slightly, the presence of the CF_3 group causes a much larger reduction in the value of k .

References

- ¹G. D. Haymann, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, *Atmos. Environ.* **28A**, 421 (1994).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $3.26 \times 10^{-13} \exp[(822 \pm 63)/T]$ $(4.9 \pm 0.6) \times 10^{-12}$	251–600 298	Catoire <i>et al.</i> , 1994 ¹	(a)

Comments

- (a) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-CH}_3\text{Cl-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures at a total pressure of 760 Torr. Kinetic data were obtained by analyzing pairs of decay curves for CH_2ClO_2 and HO_2 radicals.

Preferred Values

$$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 3.2 \times 10^{-13} \exp(820/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}600 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The data of Catoire *et al.*¹ indicate that the rate coefficients of the reactions of CH_2ClO_2 and CH_3O_2 radicals with

the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self reactions of CH_2ClO_2 and CH_3O_2 radicals where chlorine substitution greatly enhances the rate coefficient. Confirmation of the above data is required.

The products of the reaction are not well characterized. The results^{2,3} from the Cl atom-initiated photo-oxidation of CH_3Cl indicate the possible formation of the hydroperoxide, CH_2ClOOH . At the same time the observation in these earlier steady-state experiments^{2,3} of an excess of H_2O over H_2O_2 formation has given rise to the suggestion of an alternative pathway, $\text{HO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HCOCl}$. More information from product studies is needed.

References

- ¹V. Catoire, R. Lesclaux, P. D. Lightfoot, and M.-T. Rayez, *J. Phys. Chem.* **98**, 2899 (1994).
²E. Sanhueza and J. Heicklen, *J. Phys. Chem.* **79**, 7 (1975).
³H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Int. J. Chem. Kinet.* **12**, 1001 (1980).

$$\Delta H^\circ = 4.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 7 \times 10^{-18}$	298	Cantrell <i>et al.</i> , 1987 ¹	(a)
$< 5 \times 10^{-17}$	298	Mellouki <i>et al.</i> , 1989 ²	(b)
$< 2.4 \times 10^{-17}$	298	Canosa-Mas <i>et al.</i> , 1989 ³	(c)
<i>Reviews and Evaluations</i>			
$< 5 \times 10^{-17}$	298	NASA, 1994 ⁴	(d)

Comments

- (a) Value derived from computer fits of time-concentration data for reactants and products monitored by FTIR absorption spectrometry.
- (b) Discharge flow-EPR technique. Value derived from fitting to a complex mechanism.
- (c) Discharge flow-multipath absorption technique. No reaction observed at room temperature. At higher temperatures (333–473 K), values derived from fitting to a complex mechanism yielded the Arrhenius expression of $k = 4 \times 10^{-12} \exp(-3330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Based on the results of Mellouki *et al.*²

Preferred Values

$$k < 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is the upper limit to the rate coefficient reported by Mellouki *et al.*² in a study using the discharge flow-EPR technique. Somewhat lower upper limits have been reported by Cantrell *et al.*¹ and by Canosa-Mas *et al.*³ Canosa-Mas *et al.*³ also reported Arrhenius parameters at higher temperatures (over the range 333–473 K). The preferred value indicates that this reaction is not important in the chemistry of the atmosphere.

References

- ¹C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, *J. Phys. Chem.* **91**, 6017 (1987).
- ²A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, *J. Phys. Chem.* **93**, 8017 (1989).
- ³C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **85**, 709 (1989).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.²

References

- ¹R. Atkinson, S. M. Aschmann, and M. A. Goodman, *Int. J. Chem. Kinet.* **19**, 299 (1987).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred value is derived from the relative rate coefficients measured by Atkinson *et al.*,¹ and is identical to our previous evaluation, IUPAC, 1992.² The upper limit to the

rate coefficient has been increased over that derived from the relative rate coefficient data.¹

References

¹R. Atkinson, S. M. Aschmann, and M. A. Goodman, *Int. J. Chem. Kinet.* **19**, 299 (1987).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -194 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -66 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.6 \times 10^{-13} \exp(710/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

$$k_2/k < 0.003 \text{ at } 298 \text{ K.}$$

$\times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 298 K.⁵ The preferred value at room temperature is based on the results reported in Refs. 1–5, and the recommended temperature dependence is from Ref. 3. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁶

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The data of Cattell and Cox¹ are in good agreement with the earlier measurements,^{2–5} and the absence of a pressure dependence excludes a possible addition channel. The lowest upper limit for HCl formation via channel (2) is $k_2 \leq 1.5$

References

¹F. C. Cattell and R. A. Cox, *J. Chem. Soc. Faraday Trans. 2*, **82**, 1413 (1986).

²B. Reimann and F. Kaufman, *J. Chem. Phys.* **69**, 2925 (1978).

³R. M. Stimpfle, R. A. Perry, and C. J. Howard, *J. Chem. Phys.* **71**, 5183 (1979).

⁴T. J. Leck, J. E. Cook, and J. W. Birks, *J. Chem. Phys.* **72**, 2364 (1980).

⁵J. P. Burrows and R. A. Cox, *J. Chem. Soc. Faraday Trans. 1*, **77**, 2465 (1981).

⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -146.8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -148.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k_1 < 1.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 < 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

can be combined with their measured rate coefficient at 413 K to derive $A = 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E/R > 3600 \text{ K}$. For k_2 one can estimate $A = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and derive $E/R > 4000 \text{ K}$.

Comments on Preferred Values

The preferred upper limit for k_1 is based on the results of the study of Stevens and Anderson.¹ The preferred upper limit for k_2 is based on the data of DeMore *et al.*² and Wongdontri-Stuper *et al.*³ These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴ The upper limit of Stevens and Anderson¹ at room temperature

References

¹P. S. Stevens and J. G. Anderson, *Geophys. Res. Lett.* **17**, 1287 (1990).

²W. B. DeMore, C. L. Lin, and S. Jaffe, presented at ACS National Meeting, Philadelphia, PA, 1975.

³W. Wongdontri-Stuper, R. Jayanty, R. Simonaitis, and J. Heicklen, *J. Photochem.* **10**, 163 (1979).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -37.4 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 6.2 \times 10^{-12} \exp(294/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 202–415 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The room temperature rate coefficients reported by Clyne and MacRobert,¹ Lee *et al.*,² Clyne and Watson,³ Leu and DeMore,⁴ and Ray and Watson⁵ are in very good agreement and are averaged to yield the 298 K preferred value. The value reported by Zahniser and Kaufman⁶ from a competi-

tive study is about 30% higher. The Arrhenius expression is derived from a least squares fit to the data reported in Refs. 1–5. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

- ¹M. A. A. Clyne and A. J. MacRobert, *Int. J. Chem. Kinet.* **12**, 79 (1980).
- ²Y.-P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, *Int. J. Chem. Kinet.* **14**, 711 (1982).
- ³M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **70**, 2250 (1974).
- ⁴M. T. Leu and W. B. DeMore, *J. Phys. Chem.* **82**, 2049 (1978).
- ⁵G. W. Ray and R. T. Watson, *J. Phys. Chem.* **85**, 2955 (1981).
- ⁶M. S. Zahniser and F. Kaufman, *J. Chem. Phys.* **66**, 3673 (1977).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -111.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients**Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Reviews and Evaluations</i>			
$1.6 \times 10^{-31} (T/300)^{-3.4} [\text{N}_2]$	200–300	IUPAC, 1992 ¹	(a)
$1.8 \times 10^{-31} (T/300)^{-3.4} [\text{air}]$	200–300	NASA, 1994 ²	(b)
$1.8 \times 10^{-31} [\text{N}_2]$	300	Rayez and Destriau, 1993 ³	(c)

Comments

- (a) There is excellent agreement between various studies. The preferred value is the average of eleven different studies evaluated earlier.^{4–6} The falloff curve is evaluated with $F_c = 0.5$ at 298 K.
- (b) Several independent low-pressure determinations are in excellent agreement.^{7–10}
- (c) Theoretical evaluation following Ref. 11. Using $\Delta H^\circ_0 = 105 \text{ kJ mol}^{-1}$, $\beta_c = 0.71$ is obtained; if a value $\Delta H^\circ_0 = 110 \text{ kJ mol}^{-1}$ is employed, $\beta_c = 0.54$ results.

Preferred Values

$k_0 = 1.6 \times 10^{-31} (T/300)^{-3.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

No new experimental measurements have been reported since our last evaluation, and the preferred values are identical to our previous evaluation, IUPAC, 1992.¹

High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Reviews and Evaluations</i>			
2×10^{-11}	200–300	IUPAC, 1992 ¹	(a)
$1.5 \times 10^{-11} (T/300)^{-1.9}$	200–300	NASA, 1994 ²	(b)
4.0×10^{-12}	300	Rayez and Destriau, 1993 ³	(c)

Comments

- (a) Since there are no direct measurements of k at pressures above 1 bar, k_{∞} cannot be established with certainty, and theoretical predictions are no better than about a factor of 2. However, if the falloff curves below 1 atm are fitted with the given k_0 , k_{∞} , and F_c values, this uncertainty does not influence the representation of the falloff curve.
- (b) The high-pressure rate coefficient and the temperature dependence were from the model of Smith and Golden.¹² This modeling fits the data of Refs. 13 and 14.
- (c) Theoretical calculations based on the method of Ref. 15. Estimations with $\Delta H_0^\circ = 105$ or 110 kJ mol^{-1} lead to identical k_{∞} values.

Preferred Values

$k_{\infty} = 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred values are identical to those in our previous evaluation, IUPAC, 1992.¹

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
- ²NASA Evaluation No. 11, 1994 (see references in Introduction).
- ³M. T. Rayez and M. Destriau, Chem. Phys. Lett. **206**, 278 (1993).
- ⁴CODATA, Supplement II, 1984 (see references in Introduction).
- ⁵IUPAC, Supplement III, 1989 (see references in Introduction).
- ⁶NASA Evaluation No. 9, 1990 (see references in Introduction).
- ⁷M. S. Zahniser, J. S. Chang, and F. Kaufman, J. Chem. Phys. **67**, 997 (1977).
- ⁸J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. H. Hart, J. Chem. Phys. **66**, 4591 (1977).
- ⁹M. T. Leu, C. L. Lin, and W. B. DeMore, J. Phys. Chem. **81**, 190 (1977).
- ¹⁰Y.-P. Lee, R. M. Stimpfle, R. A. Perry, J. A. Mucha, K. M. Evenson, D. A. Jennings, and C. J. Howard, Int. J. Chem. Kinet. **14**, 711 (1982).
- ¹¹J. Troe, J. Chem. Phys. **66**, 4758 (1977), J. Phys. Chem. **83**, 114 (1979).
- ¹²G. P. Smith and D. M. Golden, Int. J. Chem. Kinet. **10**, 489 (1978).
- ¹³R. A. Cox and R. Lewis, J. Chem. Soc. Faraday Trans. 1, **75**, 2649 (1979).
- ¹⁴W. Dasch, K.-H. Sternberg, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **85**, 611 (1981).
- ¹⁵J. Troe, J. Phys. Chem. NF **161**, 209 (1989).

$$\Delta H^\circ(1) = -44.6 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -46.5 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(5.0 \pm 1.4) \times 10^{-13}$	210–353	Biggs <i>et al.</i> , 1991 ¹	(a)
$k_1 < 1 \times 10^{-13}$	298	Becker <i>et al.</i> , 1991 ²	(b)
$k_2 = (4.3 \pm 1.0) \times 10^{-13}$	298		
<i>Branching Ratios</i>			
$k_1/k = 0.80 \pm 0.10$	297	Biggs <i>et al.</i> , 1991 ¹	(a)
$k_1/k < 0.20$	298	Becker <i>et al.</i> , 1991 ²	(b)
<i>Reviews and Evaluations</i>			
4.0×10^{-13}	298	IUPAC, 1992 ³	(c)
4.7×10^{-13}	210–350	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow apparatus. Pseudo-first-order decay of NO₃ in excess ClO determined by optical absorption at 662 nm. Product branching ratios were measured with a quadrupole mass spectrometer. The ratio k_2/k was determined to be 0.20 ± 0.10 at 297 K, decreasing with decreasing temperature to a value of 0.035 at 216 K.
- (b) Discharge flow-mass spectrometric technique. Rate constants were derived from numerical simulation of the ClO and OClO concentration profiles.
- (c) Based on the results of Cox *et al.*^{5,6}
- (d) Based on the results of Biggs *et al.*,¹ Becker *et al.*,² and Cox *et al.*^{5,6}

Preferred Values

$k = 4.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 210–350 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the results reported by Cox *et al.*,^{5,6} Biggs *et al.*,¹ and Becker *et al.*² Biggs *et al.*¹ report the rate constant to be independent of temperature, consistent with the results of Cox *et al.*⁶ There is a significant discrepancy in the reported values for the branching ratio. Biggs *et al.*¹ report the major reaction channel to be that forming ClOO + NO₂ (channel 1), consistent with the results of Cox *et al.*⁶ In contrast, Becker *et al.*² report the major channel to be that forming OClO + NO₂ (channel 2). From a study of the OClO-NO₃ system, Friedl *et al.*⁷ conclude that at 220 K the major reaction channel is channel 1, in general agreement with the conclusions of Biggs *et al.*¹

References

- ¹P. Biggs, M. H. Harwood, A. D. Parr, and R. P. Wayne, *J. Phys. Chem.* **95**, 7746 (1991).
- ²E. Becker, U. Wille, M. M. Rahman, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.* **95**, 1173 (1991).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵R. A. Cox, R. A. Barton, E. Ljungstrom, and D. W. Stocker, *Chem. Phys. Lett.* **108**, 228 (1984).
- ⁶R. A. Cox, M. Fowles, D. Moulton, and R. P. Wayne, *J. Phys. Chem.* **91**, 3361 (1987).
- ⁷R. R. Friedl, S. P. Sander, and Y. L. Yung, *J. Phys. Chem.* **96**, 7490 (1992).

$$\Delta H^\circ(1) = -203.2 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = 15.6 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = 13.7 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 1.01 \times 10^{-12} \exp[-(1590 \pm 100)/T]$	260–390	Nickolaisen, Friedl, and Sander, 1994 ¹	(a)
$k_2 = 2.98 \times 10^{-11} \exp[-(2450 \pm 330)/T]$	260–390		
$k_3 = 3.50 \times 10^{-13} \exp[-(1370 \pm 150)/T]$	260–390		
<i>Branching Ratios</i>			
$k_1/k = 0.40 \pm 0.08$	298	Horowitz <i>et al.</i> , 1993 ²	(b)
$k_2/k = 0.42 \pm 0.08$	298		
$k_3/k = 0.18 \pm 0.02$	298		
<i>Reviews and Evaluations</i>			
$k_1 = 4.9 \times 10^{-15}$	298	IUPAC, 1992 ³	(c)
$k_2 = 3.4 \times 10^{-15}$	298		
$k_3 = 1.7 \times 10^{-15}$	298		
$k_1 = 1.0 \times 10^{-12} \exp(-1590/T)$	260–390	NASA, 1994 ⁴	(d)
$k_2 = 3.0 \times 10^{-11} \exp(-2450/T)$	260–390		
$k_3 = 3.5 \times 10^{-13} \exp(-1370/T)$	260–390		

Comments

- (a) Flash photolysis/long path ultraviolet absorption technique. Cl₂-Cl₂O mixtures were photolyzed at wavelengths longer than 300 nm. The UV absorption of ClO and OClO were monitored with an optical multichannel analyzer. The reaction was studied over a wide range of temperature, pressure, and initial reactant stoichiometry.
- (b) Cl₂ sensitized continuous photolysis of Cl₂-O₃ mixtures in excess O₂. Decay of O₃ and formation of OClO monitored by UV absorption.
- (c) Based on results of Clyne *et al.*⁵ and Cox and Derwent.⁶
- (d) Based on results of Nickolaisen *et al.*¹

Preferred Values

$$k_1 = 4.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 8.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_3 = 3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 1.0 \times 10^{-12} \exp(-1590/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

$$k_2 = 3.0 \times 10^{-11} \exp(-2450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

$$k_3 = 3.5 \times 10^{-13} \exp(-1370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \Delta(E_3/R) = \pm 300 \text{ K; } \Delta(E_2/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The recommended values for the individual reaction channels are those from the recent study of Nickolaisen *et al.*¹ This study using a flash photolysis/long path ultraviolet absorption technique is the most comprehensive study of this system, covering a wide range of temperature, initial reactant stoichiometry, and pressure. These results¹ are preferred over the results of earlier studies of the total bimolecular rate coefficient at low pressures by Clyne and co-workers⁵ as discussed in reviews of Watson,^{7,8} and those of other studies reported by Hayman *et al.*,⁹ Cox and Derwent,⁶ Simon *et al.*,¹⁰ and Horowitz *et al.*² The room temperature branching ratios are $k_1:k_2:k_3=0.29:0.50:0.21$. The reaction exhibits both bimolecular and termolecular reaction channels. The termolecular reaction dominates at pressures higher than about 0.013 bar.

References

- ¹S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, *J. Phys. Chem.* **98**, 155 (1994).
- ²A. Horowitz, D. Bauer, J. N. Crowley, and G. K. Moortgat, *Geophys. Res. Lett.* **20**, 1423 (1993).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵M. A. A. Clyne, D. J. McKenney, and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **71**, 322 (1975).
- ⁶R. A. Cox and R. G. Derwent, *J. Chem. Soc. Faraday Trans. 1*, **75**, 1635 (1979).
- ⁷R. T. Watson, *J. Phys. Chem. Ref. Data* **6**, 871 (1977).
- ⁸R. T. Watson, Proceedings of the NATO Advanced Study Institute on Atmospheric Ozone, Report FAA-EE-80-20, FAA, Washington, DC (1980).
- ⁹G. D. Hayman, J. M. Davies, and R. A. Cox, *Geophys. Res. Lett.* **13**, 1347 (1986).
- ¹⁰F. G. Simon, W. Schneider, G. K. Moortgat, and J. P. Burrows, *J. Photochem. Photobiol. A* **55**, 1 (1990).

$$\Delta H^\circ = -75.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.22 \times 10^{-33} \exp[(833 \pm 34)/T] [\text{N}_2]$	195-390	Nickolaisen, Friedl, and Sander, 1994 ¹	(a)
$(0.99 \pm 0.05) \times 10^{-32} [\text{He}]$	300		
$(1.24 \pm 0.09) \times 10^{-32} [\text{O}_2]$	300		
$(1.71 \pm 0.06) \times 10^{-32} [\text{Ar}]$	300		
$(2.60 \pm 0.17) \times 10^{-32} [\text{CF}_4]$	300		
$(3.15 \pm 0.14) \times 10^{-32} [\text{SF}_6]$	300		
$(6.7 \pm 3.6) \times 10^{-32} [\text{Cl}_2]$	300		
<i>Reviews and Evaluations</i>			
$1.7 \times 10^{-32} (T/300)^{-4} [\text{N}_2]$	200-260	IUPAC, 1992 ²	(b)
$2.2 \times 10^{-32} (T/300)^{-3.1} [\text{N}_2]$	200-300	NASA, 1994 ³	(c)

Comments

- (a) Flash photolysis of Cl_2 at $\lambda > 300$ nm in the presence of Cl_2O . ClO radicals were generated by the reaction $\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{ClO} + \text{Cl}_2$ and monitored by UV absorption spectroscopy using either a photomultiplier for detection at 275.5 nm or an optical multichannel analyzer for detection over the wavelength range 270–280 nm. Below 250 K, the reaction is in the falloff regime. From a third-law analysis the value of ΔH° of $-(75.7 \pm 0.9)$ kJ mol $^{-1}$ was derived.
- (b) The recommended values are an average of the rate data of Refs. 4 and 5.
- (c) Based on data in Refs. 1, 4, and 5.

Preferred Values

$$k_0 = 1.7 \times 10^{-32} (T/300)^{-4} [\text{N}_2] \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.1 \text{ at 298 K.}$$

$$\Delta n = \pm 1.5.$$

Comments on Preferred Values

For temperatures relevant in atmospheric chemistry the recent experiments by Nickolaissen *et al.*¹ and our previously recommended values² are in very good agreement. Thus, the preferred values are identical to our previous evaluation, IUPAC, 1992.²

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(6 \pm 2) \times 10^{-12}$	195–390	Nickolaissen, Friedl, and Sander, 1994 ¹	(a)
<i>Reviews and Evaluations</i>			
5.4×10^{-12}	200–300	IUPAC, 1992 ²	(b)
$3.5 \times 10^{-12} (T/300)^{-1.0}$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 . The k_∞ value was obtained from falloff data measured below 250 K.
- (b) See comment (b) for k_0 .
- (c) See comment (c) for k_0 .

Preferred Values

$$k_\infty = 5.4 \times 10^{-12} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ at 298 K.}$$

Comments on Preferred Values

Our earlier recommended values² are consistent with the recent data from Ref. 1, and the preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹ S. L. Nickolaissen, R. R. Friedl, and S. P. Sander, *J. Phys. Chem.* **98**, 155 (1994).
- ² IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³ NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴ S. P. Sander, R. R. Friedl, and Y. L. Yung, *Science* **245**, 1095 (1989).
- ⁵ M. Troler, R. L. Mauldin III, and A. R. Ravishankara, *J. Phys. Chem.* **94**, 4896 (1990).

$$\Delta H^\circ = 75.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$9.81 \times 10^{-7} \exp[-(7980 \pm 320)/T] [\text{N}_2]$	260–310	Nickolaisen, Friedl, and Sander, 1994 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.35 \times 10^{-5} (T/300)^{-5} \exp(-8720/T) [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$1.7 \times 10^{-5} (T/300)^{-3.1} \exp(-8744/T) [\text{N}_2]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Flash photolysis of Cl_2 at $\lambda > 300$ nm in the presence of Cl_2O . ClO radicals were monitored with an optical multichannel analyzer at 270–280 nm; the pressure range was 25–650 Torr. From a third-law analysis, the value of $\Delta H^\circ = 75.7 \pm 0.9 \text{ kJ mol}^{-1}$ was derived.
- (b) The preferred values were calculated from $k_0 = 1.7 \times 10^{-32} (T/300)^{-4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reverse reaction (Ref. 2) and the equilibrium constant from Cox and Hayman.⁴ The preferred values correspond to falloff curves with $F_c = 0.6$.
- (c) Calculated with the recommended k_0 value for the reverse reaction and the value of K_c from Table 3 of the NASA evaluation.

Preferred Values

$$k_0 = 2.2 \times 10^{-18} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1 \times 10^{-6} \exp(-8000/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 260\text{--}310 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 900 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the results of Ref. 1 and is in good agreement with the values from our previous evaluation.²

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{15} \exp(-8820/T)$	260–310	Nickolaisen, Friedl, and Sander, 1994 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.8 \times 10^{15} \exp(-8450/T)$	200–300	IUPAC, 1992 ²	(b)
$2.7 \times 10^{15} (T/300)^{-1.0} \exp(-8744/T)$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 . This value is based on the rate coefficient $k_\infty = 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reverse reaction and the equilibrium constant $K_c = 1.24 \times 10^{-27} \exp(8820/T) \text{ cm}^3 \text{ molecule}^{-1}$, both from Ref. 1.
- (b) Based on the preferred value $k_\infty = 5.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reverse reaction and K_c from Cox and Hayman.⁴
- (c) Calculated with the recommended k_∞ value for the reverse reaction and the value of K_c from Table 3.³

Preferred Values

$$k_\infty = 6.7 \times 10^2 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_\infty = 4.8 \times 10^{15} \exp(-8820/T) \text{ s}^{-1} \text{ over the temperature range } 260\text{--}310 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3.$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The values of Nickolaisen *et al.*¹ are adopted here.

References

¹S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, *J. Phys. Chem.* **98**, 155 (1994).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴R. A. Cox and G. D. Hayman, *Nature* **332**, 796 (1988).

$$\Delta H^\circ = -44 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(6.2 \pm 1.0) \times 10^{-32} (T/300)^{-4.7} [\text{N}_2]$	200–260	Burkholder <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.8 \times 10^{-31} [\text{N}_2]$	226	IUPAC, 1992 ²	(b)

Comments

(a) Flash photolysis study of mixtures of $\text{N}_2\text{O}-\text{Cl}_2-\text{OCIO}-\text{He}$ or $\text{CF}_2\text{Cl}_2-\text{OCIO}-\text{N}_2$ at 193 nm. From the first mixture, rate data were obtained while from the second mixture equilibrium constants and the absorption spectra of Cl_2O_3 between 220 and 320 nm were derived. From a second-law analysis of the data, together with those of Hayman and Cox,³ $\Delta H^\circ = -(46.4 \pm 5.1) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -(88.7 \pm 18.9) \text{ J mol}^{-1} \text{ K}^{-1}$ were derived. The kinetic data were obtained from a fit of the falloff curves between 25–250 Torr total pressure using $F_c = 0.6$.

(b) Based on the measurements of Parr *et al.*⁴

Preferred Values

$k_0 = 6.2 \times 10^{-32} (T/300)^{-4.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The values of the extensive study of Burkholder *et al.*¹ are adopted here. At 226 K the rate coefficient of Ref. 1 is in reasonable agreement with that recommended previously.²

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.4 \pm 1.2) \times 10^{-11}$	200–260	Burkholder <i>et al.</i> , 1993 ¹	(a)

Comments

(a) See comment (a) for k_0 .

Comments on Preferred Values

The preferred values are from Ref. 1.

Preferred Values

$k_\infty = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

References

¹J. B. Burkholder, R. L. Mauldin III, R. J. Yokelson, S. Solomon, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 7597 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³G. D. Hayman and R. A. Cox, *Chem. Phys. Lett.* **155**, 1 (1989).

⁴A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, *Geophys. Res. Lett.* **17**, 2357 (1990).

$$\Delta H^\circ = 44 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No direct measurements are available.

Preferred Values

$$k_0 = 2.8 \times 10^{-18} [\text{N}_2] \text{ s}^{-1} \text{ at } 226 \text{ K.}$$

$= 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$ at 226 K from Ref. 2. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 226 \text{ K.}$$

Comments on Preferred Values

This value is calculated from the rate coefficient of the reverse reaction, $k_0 = 2.8 \times 10^{-31} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 226 K from Ref. 1, and the equilibrium constant K_c

References

- ¹A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, *Geophys. Res. Lett.* **17**, 2357 (1990).
²G. D. Hayman and R. A. Cox, *Chem. Phys. Lett.* **155**, 1 (1989).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = 3.1 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(3) = 1.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$3.25 \times 10^{-12} \exp[-(114 \pm 38)/T]$	225–355	Helleis, Crowley, and Moortgat, 1993 ¹	(a)
2.22×10^{-12}	295		
$(1.9 \pm 0.4) \times 10^{-12}$	293	Kenner, Ryan, and Plumb, 1993 ²	(b)
<i>Branching Ratios</i>			
$k_1/k = 1.51 \exp[-(218 \pm 93)/T]$	225–355	Helleis, Crowley, and Moortgat, 1993 ¹	(a)
$k_2/k = 0.08 \exp[(377 \pm 178)/T]$	225–355		
<i>Reviews and Evaluations</i>			
$k_1 < 4 \times 10^{-12}$	200	IUPAC, 1992 ³	(c)
$k_3 < 1 \times 10^{-15}$	200		
$k_1 = 4.9 \times 10^{-12} \exp(-330/T)$	200–355	NASA, 1994 ⁴	(d)
$k_2 = 2.6 \times 10^{-13} \exp(260/T)$	200–355		

Comments

- (a) Discharge flow-mass spectrometer technique. Pseudo-first-order decay of CH_3O_2 radicals in excess ClO monitored at $m/e=47$. Overall rate constant and branching ratios were found to be independent of pressure.
- (b) Flow reactor with quadrupole mass spectrometer sampling. Decays of CH_3O_2 radicals were monitored at $m/e=47$.
- (c) Upper limits based on the results of DeMore.⁵
- (d) Based on the results of Helleis *et al.*¹

Preferred Values

$$k_1 = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$= 4.9 \times 10^{-12} \exp(-330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 225\text{--}355 \text{ K.}$$

$$k_2 = 6.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$= 2.6 \times 10^{-13} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 225\text{--}355 \text{ K.}$$

$$k_3 < 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 200 \text{ K.}$$

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \pm 0.3$ at 298 K.

$\Delta(E_1/R) = \pm 200$ K.

$\Delta(E_2/R) = \pm 250$ K.

Comments on Preferred Values

The recommended expressions for the individual reaction channels are derived from the temperature dependent expressions for the overall rate constant and the branching ratios reported by Helleis *et al.*¹ These results are consistent with the overall rate constant measurements of Kenner *et al.*² and Simon *et al.*⁶ at room temperature and with the upper limit for k_1 at 200 K reported by DeMore.⁵ The upper limit for k_3 is based on the results of DeMore⁵ and is consistent with the

observations of Helleis *et al.*¹ that only reaction channels (1) and (2) are important. The recommended Arrhenius expressions yield approximately equal rate constants of 1×10^{-12} cm³ molecule⁻¹ s⁻¹ for k_1 and k_2 at 200 K.

References

- ¹F. Helleis, J. N. Crowley, and G. K. Moortgat, *J. Phys. Chem.* **97**, 11464 (1993).
- ²R. D. Kenner, K. R. Ryan, and I. C. Plumb, *Geophys. Res. Lett.* **20**, 1571 (1993).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵W. B. DeMore, *J. Geophys. Res.* **96**, 4995 (1991).
- ⁶F. G. Simon, J. P. Burrows, W. Schneider, G. K. Moortgat, and P. J. Crutzen, *J. Phys. Chem.* **93**, 7807 (1989).

ClO + CH₃SCH₃ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.9 \pm 0.5) \times 10^{-14}$	298	Barnes <i>et al.</i> , 1989 ¹	(a)
$(9.5 \pm 2.0) \times 10^{-15}$	298	Barnes <i>et al.</i> , 1991 ²	(a)
<i>Reviews and Evaluations</i>			
9.5×10^{-15}	298	NASA, 1994 ³	(b)

Comments

- (a) Fast flow discharge system used. ClO radicals were produced by the reaction $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$. [ClO] was monitored by mass spectrometry.
- (b) Based on the rate coefficient of Barnes *et al.*²

Preferred Values

$k = 9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The two available measurements^{1,2} of this rate coefficient come from the same laboratory using basically the same

technique. In the earlier study,¹ wall effects were evident and it was recognized that the value of k obtained was likely to be an upper limit. Better control of wall effects was obtained in the later study,² and the value found there is taken as the preferred value but with substantial error limits.

The reaction is usually assumed to produce $\text{CH}_3\text{S(O)CH}_3 + \text{Cl}$ but, although the sulfoxide has been detected,¹ no yields have been measured.

References

- ¹I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393, p. 464 (1989).
- ²I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.* **23**, 579 (1991).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).

OCIO + O₃ → ClO₃ + O₂

$\Delta H^\circ = -5.7 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.1 \times 10^{-12} \exp(-4700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
 the temperature range 262–298 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.
 $\Delta(E/R) = \pm 1000 \text{ K}$.

Comments on Preferred Values

The preferred value is based on the results reported in the study of Wongdontri-Stuper *et al.*¹ Within the indicated un-

certainty limits, the preferred values encompass the lower room temperature value reported by Birks *et al.*² The preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹W. Wongdontri-Stuper, R. K. M. Jayanty, R. Simonaitis, and J. Hecklen, *J. Photochem.* **10**, 163 (1979).
²J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, *J. Chem. Phys.* **66**, 4591 (1977).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -51.1 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the only direct study of this reaction reported by Bemand *et al.*¹ In the absence of

experimental data no recommendation is given for the temperature dependence. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.²

References

- ¹P. P. Bemand, M. A. A. Clyne, and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **69**, 1356 (1973).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -75 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients**Rate coefficient data**

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $1 \times 10^{-31} [\text{He}]$	220	Friedl, Sander, and Yung, 1992 ¹	(a)

Comments

- (a) The experiments were carried out in a long-path absorption flow reactor. NO_3 radicals were generated by the reaction of F atoms with HNO_3 or of Cl atoms with ClONO_2 . The products were analyzed by IR and UV absorption measurements. At $T < 230 \text{ K}$ the formation of O_2ClONO_2 dominated while at higher temperatures ClO and NO_2 were also observed, indicating the presence of secondary reactions. The k_0 value was derived from a measured rate constant of $2 \times 10^{-14} \text{ cm}^3 \text{ mol-}$

$\text{ecule}^{-1} \text{ s}^{-1}$ at 4 Torr of He. Using unimolecular rate theory² and the experimental parameters, the bond dissociation energy given above was derived ($\pm 13 \text{ kJ mol}^{-1}$).

Preferred Values

$k_0 = 1 \times 10^{-31} [\text{He}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 220 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 220 K.

Comments on Preferred Values

The recommended values are based on the measurements of Friedl *et al.*¹

References

¹R. R. Friedl, S. P. Sander, and Y. L. Yung, *J. Phys. Chem.* **96**, 7490 (1992).

²J. Troe, *J. Phys. Chem.* **83**, 114 (1979).

$$\Delta H^\circ = -71.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k < 1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 200 \text{ K.}$$

Comments on Preferred Values

The recommended upper limit is that determined by DeMore and Tschuikow-Roux¹ from measurement of the quantum yield of O₃ loss in the photolysis of Cl₂-O₃ mixtures at λ > 300 nm. The experiments were very sensitive to this reaction. Reaction at a rate greater than this upper limit would have had a marked effect on the quantum yield of ozone loss and also would have resulted in a dependence of the quan-

tum yield on the ozone concentration; however, neither effect was observed.¹ These measurements refer to a temperature of about 200 K; the value of this rate coefficient at higher temperatures would be of no atmospheric significance because of the thermal decomposition of the Cl₂O₂ dimer. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.²

References

¹W. B. DeMore and E. Tschuikow-Roux, *J. Phys. Chem.* **94**, 5856 (1990).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -127.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.4 \times 10^{-29} (T/300)^{-5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 2.$$

Comments on Preferred Values

There are no measurements for this reaction, but theoretical modeling of the complete series¹ CX₃ + O₂ + M (X = F, Cl) provides a reliable basis for interpolating rate data between members of this series.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Comments on Preferred Values

We prefer a slightly higher value than estimated in Ref. 1. These preferred values are chosen as for the related reaction $\text{CFCl}_2 + \text{O}_2 + \text{M}$ (see this evaluation), based on data from Ref. 2. $F_c=0.6$ is recommended as for $\text{CFCl}_2 + \text{O}_2 + \text{M}$. ΔH° is estimated following Ref. 1. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

- ¹W. Forst and F. Caralp, J. Chem. Soc. Faraday Trans. **87**, 2307 (1991).
²F. Danis, Ph.D. Thesis, Bordeaux, 1990, cited in Ref. 1.
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -124.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 5.5 \times 10^{-30} (T/300)^{-6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Comments on Preferred Values

The preferred values are based on Ref. 1. The data appear consistent with other results for the series $\text{CX}_3 + \text{O}_2 + \text{M}$ (X=Cl, F) (see this evaluation).

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 2.$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

sure limit remains relatively uncertain. The more recent value from Ref. 1 is preferred because it is close to the k_∞ value for the reaction $\text{CF}_3 + \text{O}_2 + \text{M}$ (see this evaluation). The preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ at 298 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

Experiments have been limited to the lower part of the falloff curve. Therefore, the extrapolation to the high pres-

References

- ¹F. Danis, Ph.D. Thesis, Bordeaux, 1990, cited in Ref. 2.
²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -82.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(6.5 \pm 0.2) \times 10^{-31} (T/300)^{-6.1 \pm 0.2} [\text{He}]$	298–333	Fenter <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.6 \times 10^{-30} (T/300)^{-6} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$6.9 \times 10^{-31} (T/300)^{-6.4} [\text{N}_2]$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Photolysis of CCl_3Br at 248 nm with detection of CCl_3 either by mass spectrometry or by UV absorption at 215 nm. In the first case, N_2 pressures were varied between 1–12 Torr and in the second case between 20–760 Torr N_2 . The derived k_0 values at 298 and 333 were obtained from a falloff fit using $F_c=0.6$.
- (b) The preferred values are based on Ref. 4, and are consistent with the data for $\text{M}=\text{He}$ from Ref. 5. The falloff curves are extrapolated with $F_c=0.6$.
- (c) Based on the data from Refs. 1 and 4.

Preferred Values

$$k_0 = 9 \times 10^{-31} (T/300)^{-6} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The preferred values are based on the data of Refs. 1, 4, and 5. The values of k_0 in Refs. 1 and 5 were determined using $F_c=0.6$.

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.2) \times 10^{-12} (T/300)^{-1.1 \pm 0.6}$	298–333	Fenter <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
3.6×10^{-12}	200–300	IUPAC, 1992 ²	(b)
$2.4 \times 10^{-12} (T/300)^{-2.1}$	200–300	NASA, 1994 ³	(c)

Comments

- (a) See comment (a) for k_0 .
- (b) The preferred values are an average of the data from Refs. 4–6.
- (c) See comment (c) for k_0 .

Comments on Preferred Values

Preferred values are based on the results of Refs. 1 and 4–6.

References

Preferred Values

$$k_\infty = 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.4 \text{ over the temperature range 200–300 K.}$$

¹F. F. Fenter, P. D. Lightfoot, J. T. Niiranen, and D. Gutman, *J. Phys. Chem.* **97**, 5313 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴F. Danis, F. Caralp, M. T. Rayez, and R. Lesclaux, *J. Phys. Chem.* **95**, 7300 (1991).

⁵K. R. Ryan and I. C. Plumb, *Int. J. Chem. Kinet.* **16**, 591 (1984).

⁶R. Cooper, J. B. Cumming, S. Gordon, and W. A. Mulac, *Rad. Phys. Chem.* **16**, 169 (1980).

$$\Delta H^\circ = -107 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.4 \times 10^{-28} (T/300)^{-6.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 200–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at 298 K.}$$

$$\Delta n = \pm 2.$$

Comments on Preferred Values

The preferred values are from Ref. 1, and are consistent with data for the reactions $\text{CCl}_3\text{O}_2 + \text{NO}_2$ and $\text{CFCl}_2\text{O}_2 + \text{NO}_2$. These values are sensitive to the chosen value of F_c , for which a value of 0.26 was calculated¹ over the range 220–300 K. The values from Ref. 2 in part are lower because of the larger value of F_c used.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range 200–300 K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ over the temperature range 200–300 K.}$$

independent of the temperature. The large negative temperature coefficient of k_∞ reported in Ref. 2 appears to be an artifact from the falloff extrapolations used. The preferred values of k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.³

References

Comments on Preferred Values

The preferred values are from the fit in Ref. 1 using identical k_∞ values for all $\text{CX}_3\text{O}_2 + \text{NO}_2$ reactions (X=F, Cl),

¹M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).

²F. Wu and R. W. Carr, *Int. J. Chem. Kinet.* **23**, 701 (1991).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 107 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 9.0 \times 10^{-19} [\text{N}_2] \text{ s}^{-1} \text{ at 298 K.}$$

$$k_0 = 1.8 \times 10^{-3} \exp(-10500/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range 260–300 K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The data from the experiments of Ref. 1 are preferred here. The calculations of F_c (0.3 at 280 K from Ref. 1 and 0.26 over the range 250–300 K from Ref. 2) are in agreement.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_{\infty} = 5.4 \times 10^{-2} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_{\infty} = 1.6 \times 10^{16} \exp(-11990/T) \text{ s}^{-1} \text{ over the temperature range } 260\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta \log (E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

See comments on k_0 . The preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

¹D. Köppenkaströf and F. Zabel, *Int. J. Chem. Kinet.* **23**, 1 (1991).

²M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -106 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.7 \times 10^{-28} (T/300)^{-6.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 2.$$

Comments on Preferred Values

The preferred values are from the analysis of Ref. 1 on the basis of $F_c = 0.23$. The falloff data from Ref. 2 show some anomalies for $T = 233 \text{ K}$. The best fit is obtained for 298 K .

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_{\infty} = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ independent of temperature over the range } 250\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_{\infty} = \pm 0.3 \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Comments on Preferred Values

See comments on k_0 . The preferred values are identical to those in our previous evaluation, IUPAC, 1992.³

References

¹M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).

²F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, *J. Chem. Soc. Faraday Trans. 2*, **84**, 569 (1988).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 106 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 1.5 \times 10^{-18} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.0 \times 10^{-2} \exp(-10860/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Comments on Preferred Values

The data from the experiments of Ref. 1 are preferred. The calculation of $F_c = 0.28$ is consistent with the analysis of Ref. 2, leading to $F_c = 0.23$.

Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_\infty = 9.6 \times 10^{-2} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_\infty = 6.6 \times 10^{16} \exp(-12240/T) \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

Comments on Preferred Values

See comments on k_0 . The agreement between Refs. 1 and 3 at 1 atm ($\Delta \log k = 0.17$) appears satisfactory. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

¹D. Köppenkastrup and F. Zabel, Int. J. Chem. Kinet. **23**, 1 (1991).

²M. Destriau and J. Troe, Int. J. Chem. Kinet. **22**, 915 (1990).

³R. Simonaitis, S. Glavas, and J. Heicklen, Geophys. Res. Lett. **6**, 385 (1979).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -105.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$$k_0 = 3.2 \times 10^{-28} (T/300)^{-7.7} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}300 \text{ K.}$$

Comments on Preferred Values

The preferred values are from the theoretical analysis of Ref. 1. The experimental data from Ref. 2 for $T = 233 \text{ K}$ apparently are inconsistent with this analysis. $F_c = 0.21$ is used for falloff extrapolations.

Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 3.$$

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–300 K.

consistent set of falloff curves. The preferred values of k_0 and k_{∞} are identical to those in our previous evaluation, IUPAC, 1992.³

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the temperature range 250–300 K.

Comments on Preferred Values

The value of k_{∞} in Ref. 1 was chosen identical for all reactions $\text{CX}_3\text{O}_2 + \text{NO}_2 + \text{M}$ (X=F, Cl), which leads to a

References

¹M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).

²F. Caralp, R. Lesclaux, M. T. Rayez, J. C. Rayez, and W. Forst, *J. Chem. Soc. Faraday Trans. 2*, **84**, 569 (1988).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = 105.6 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 7.6 \times 10^{-18} [\text{N}_2] \text{ s}^{-1}$ at 298 K.
 $k_0 = 6.3 \times 10^{-3} \exp(-10235/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 250–300 K.

Comments on Preferred Values

The experimental data of Ref. 1 are recommended. The calculation of $F_c = 0.22$ is consistent with the analysis of Ref. 2, which gave $F_c = 0.20$ with only a weak temperature dependence.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_{\infty} = 0.29 \text{ s}^{-1}$ at 298 K.
 $k_{\infty} = 4.8 \times 10^{16} \exp(-11820/T) \text{ s}^{-1}$ over the temperature range 250–300 K.

Comments on Preferred Values

See comments on k_0 . The agreement between Refs. 1 and 3 for 1 atm total pressure ($\Delta \log k = 0.11$) appears satisfactory. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

¹D. Köppenkaströf and F. Zabel, *Int. J. Chem. Kinet.* **23**, 1 (1991).

²M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).

³R. Simonaitis and J. Heicklen, *Chem. Phys. Lett.* **62**, 473 (1979); **68**, 245 (1979).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (3.6 \pm 0.5) \times 10^{-12}$	298	Hayman <i>et al.</i> , 1994 ¹	(a)
$k_2 = (9_{-5}^{+6}) \times 10^{-13}$	298		

Comments

- (a) Laser flash photolysis-UV absorption study of $\text{CF}_3\text{CCl}_3\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures. Kinetic data were obtained by analyzing two sets of transient decays on the basis of a mechanism consisting of 13 reactions.

Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

$\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

While the above values of the rate coefficients¹ appear reasonable, they have been derived from the analysis of a complex chemical system and require independent verification to reduce the recommended error limits.

Preferred Values

$k_1 = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

References

- ¹G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, *Atmos. Environ.* **28A**, 421 (1994).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 4.1 \times 10^{-12}$	298	Wallington and Nielsen, 1991 ¹	(a,b)
<i>Reviews and Evaluations</i>			
$\leq 4.1 \times 10^{-12}$	298	Lightfoot <i>et al.</i> , 1992 ²	(c)

Comments

- (a) k is defined by $-\text{d}[\text{CF}_2\text{ClCH}_2\text{O}_2]/\text{dt} = 2k[\text{CF}_2\text{ClCH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CF}_2\text{ClCH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CF}_2\text{ClCH}_3\text{-O}_2\text{-SF}_6$ mixtures over the pressure range 114–760 Torr. $\text{CF}_2\text{ClCH}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{250} = (3.38 \pm 0.68) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of $k_{\text{obs}} = (4.1 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k (see Comments on Preferred Values).
- (c) Based on the data of Wallington and Nielsen.¹

Preferred Values

$k \leq 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient at 298 K as determined by Wallington and Nielsen.¹ It has been noted² that this system has also been studied by Jemi-Alade *et al.*,³ using a flash photolysis-UV absorption technique. Although no rate coefficients were obtained, a strong residual absorption was observed, indicating a complex chemical system with the probability of secondary removal of $\text{CF}_2\text{ClCH}_2\text{O}_2$ radicals. No product studies have been reported on this reaction and consequently the branching ratio is unknown.

References

- ¹T. J. Wallington and O. J. Nielsen, *Int. J. Chem. Kinet.* **23**, 785 (1991).
²P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
³A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, *Chem. Phys. Lett.* **179**, 119 (1991).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $\leq 4.4 \times 10^{-12}$	298	Wallington and Nielsen, 1991 ¹	(a,b)
<i>Reviews and Evaluations</i> $\leq 4.1 \times 10^{-12}$	298	Lightfoot <i>et al.</i> , 1992 ²	(c)

Comments

- (a) k is defined by $-d[\text{CFCl}_2\text{CH}_2\text{O}_2]/dt = 2k[\text{CFCl}_2\text{CH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CFCl}_2\text{CH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CFCl}_2\text{CH}_3\text{-O}_2\text{-SF}_6$ mixtures over the pressure range 114–760 Torr. $\text{CFCl}_2\text{CH}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{230} = (3.38 \pm 0.68) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of $k_{\text{obs}} = (4.36 \pm 0.64) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k (see Comments on Preferred Values).
- (c) Based on the data of Wallington and Nielsen,¹ but scaled to an evaluated value² of σ_{230} ($\text{CFCl}_2\text{CH}_2\text{O}_2$).

Preferred Values

$k \leq 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

We have recommended a rounded-off upper limit for the rate coefficient at 298 K as determined by Wallington and Nielsen.¹ It has been noted² that this system has also been studied by Jemi-Alade *et al.*,³ using a flash photolysis-UV absorption technique. Although no rate coefficients were obtained, a strong residual absorption was observed, indicating a complex chemical system with the probability of secondary removal of $\text{CFCl}_2\text{CH}_2\text{O}_2$ radicals. No product studies have been reported on this reaction and consequently the branching ratio is unknown.

References

- ¹T. J. Wallington and O. J. Nielsen, *Int. J. Chem. Kinet.* **23**, 785 (1991).
²P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
³A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, *Chem. Phys. Lett.* **179**, 119 (1991).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $\leq 3.3 \times 10^{-12}$	295	Wallington, Ellermann, and Nielsen, 1994 ¹	(a,b)
<i>Branching Ratios</i> $k_2/k \approx 1.0$	296	Edney, Gay, and Driscoll, 1991 ²	(c)
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1993 ³	(d)
$k_2/k \approx 1.0$	298	Hayman <i>et al.</i> , 1994 ⁴	(e)

Comments

- (a) k is defined by $-d[\text{CF}_3\text{CCl}_2\text{O}_2]/dt = 2k[\text{CF}_3\text{CCl}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals (k_{obs}).
- (b) Pulse radiolysis study of $\text{CF}_3\text{CHCl}_2\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 760 Torr. $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{250} = (1.70 \pm 0.26) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of $k_{\text{obs}} = (3.33 \pm 0.53) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is an upper limit to k (see Comments on Preferred Values).
- (c) Steady-state photolysis of Cl_2 in the presence of $\text{CF}_3\text{CHCl}_2\text{-air}$ mixtures with FTIR absorption spectroscopic analysis. $\sim 100\%$ conversion of CF_3CHCl_2 to CF_3COCl was observed, consistent with channel (2) as the sole route for the self-reaction of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals.
- (d) Similar experiments to those of Comment (c), with 98% conversion of CF_3CHCl_2 to CF_3COCl being observed.
- (e) Similar experiments to those of Comment (c), with analysis by multichannel UV absorption spectroscopy. $\sim 100\%$ conversion of CF_3CHCl_2 to CF_3COCl was observed.

Preferred Values

$k_2 \leq 3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 1.0$ at 298 K.

Reliability

$\Delta(k_2/k) = \pm 0.05$ at 298 K.

Comments on Preferred Values

The product studies²⁻⁴ have confirmed the absence of the formation of any $\text{CF}_3\text{CCl}_2\text{OOC}_2\text{CF}_3$ product and are consistent with reaction (2) being the sole pathway for the self-reaction of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals.

We have recommended a rounded-off upper limit for the rate coefficient at 298 K, as determined by Wallington *et al.*¹ A study of $\text{CF}_3\text{CCl}_2\text{O}_2$ reactions by Jemi-Alade *et al.*,⁵ involving flash photolysis-UV absorption of Cl_2 in the presence of CF_3CHCl_2 and O_2 , showed no decay in the absorption curves of $\text{CF}_3\text{CCl}_2\text{O}_2$ over the time scale 0–40 min. This was attributed to the regeneration of $\text{CF}_3\text{CCl}_2\text{O}_2$ via Cl atom reactions. In the Wallington *et al.*¹ study which involved concentrations of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals an order of magnitude higher than the Jemi-Alade *et al.*² system, the UV absorptions of the radical showed significant decays over the time scale 0–1000 ms. Until the chemistry of both these systems is better understood the k_{obs} value from the second-order decay of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals observed by Wallington *et al.*¹ must be taken as an upper limit.

References

- ¹T. J. Wallington, T. Ellermann, and O. J. Nielsen, *Res. Chem. Intermed.* **20**, 265 (1994).
²E. O. Edney, B. W. Gay, Jr., and D. J. Driscoll, *J. Atmos. Chem.* **12**, 105 (1991).
³E. C. Tuazon and R. Atkinson, *J. Atmos. Chem.* **17**, 179 (1993).
⁴G. D. Hayman, M. E. Jenkin, T. P. Murrells, and C. E. Johnson, *Atmos. Environ.* **28A**, 421 (1994).
⁵A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, *Chem. Phys. Lett.* **179**, 119 (1991).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$k_2 \leq 3.1 \times 10^{-13} \exp(735/T)$	228–380	Dagaut, Wallington, and Kurylo, 1988 ¹	(a,b)
$k_2 \leq 3.8 \times 10^{-12}$	298		
$k_2 = 1.95 \times 10^{-13} \exp[(874 \pm 26)/T]$	251–600	Catoire <i>et al.</i> , 1994 ²	(a,c)
$k_2 = (4.2 \pm 0.4) \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	305	Sanhueza and Heicklen, 1975 ³	(d)
$k_2/k \approx 1.0$	298	Niki <i>et al.</i> , 1980 ⁴	(e)
<i>Reviews and Evaluations</i>			
$k_{\text{obs}} = 3.9 \times 10^{-13} \exp(735/T)$	228–380	Lightfoot <i>et al.</i> , 1992 ⁵	(f)

Comments

- (a) k is defined by $-d[\text{CH}_2\text{ClO}_2]/dt = 2k[\text{CH}_2\text{ClO}_2]^2$ and has been derived from the measured overall second-order decay of CH_2ClO_2 radicals (k_{obs}).
- (b) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{Cl-O}_2\text{-N}_2$ mixtures at total pressures of 25–400 Torr at 298 K and of 100 Torr (N_2) from 228–380 K. The peroxy radicals were monitored by UV absorption with $\sigma_{250} = (3.14 \pm 0.45) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of k_{obs} is an upper limit to k_2 , because of the possibility of secondary reactions producing an enhanced decay of CH_2ClO_2 radicals (see Comments on Preferred Values).
- (c) Similar experiments to those in Comment (b) at a total pressure of 760 Torr and with peroxy radical concentrations being monitored by UV absorption spectrometry from 205 to 290 nm. Values of k_{obs} were found to be markedly dependent on the monitoring wavelength, since the $\text{RO}_2 + \text{HO}_2$ reaction is not much faster than that for $\text{RO}_2 + \text{RO}_2$, leading to significant concentrations of HO_2 radicals. Values of k_2 were obtained by an iterative process.
- (d) Photolysis of Cl_2 in the presence of $\text{CH}_3\text{Cl-O}_2$ mixtures. *In situ* monitoring of products by IR showed exclusive formation of HCl and HCOCl as the initial products.
- (e) Photolysis of Cl_2 in the presence of $\text{CH}_3\text{Cl-air}$ mixtures. *In situ* monitoring of reactants and products by FTIR spectroscopy showed 90–95% conversion of CH_3Cl to HCOCl .
- (f) Based on the data of Dagaut *et al.*,¹ but scaled to an amended value of $\sigma_{250} = 3.91 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ for the CH_2ClO_2 radical.

Preferred Values

$$k_2 = 3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 2.0 \times 10^{-13} \exp(870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}600 \text{ K.}$$

Reliability

$$\Delta \log k_2 = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The product studies^{3,4} have shown that the radical forming reaction (2) is the only important channel for the self-reaction of CH_2ClO_2 radicals.

The above recommendations are based on the more comprehensive study of Catoire *et al.*² This showed excellent agreement with the earlier data of Dagaut *et al.*¹ when both sets of data were analyzed by a simple second-order treatment from results derived at $\lambda = 250 \text{ nm}$. Catoire *et al.*² have also shown that the rate coefficient of the $\text{CH}_2\text{ClO}_2 + \text{HO}_2$ reaction is of similar magnitude to that of k_2 . This leads to the presence of significant concentrations of HO_2 radicals in the system, shown by variation of k_{obs} with monitoring λ , and means that the value of k_2 cannot be obtained simply from k_{obs} and a knowledge of the branching ratio. The rate coefficients of Catoire *et al.*,² obtained by numerical modeling of the system, are consequently preferred.

References

- ¹ P. Dagaut, T. J. Wallington, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 815 (1988).
- ² V. Catoire, R. Lesclaux, P. D. Lightfoot, and M.-T. Rayez, *J. Phys. Chem.* **98**, 2889 (1994).
- ³ E. Sanhueza and J. Heicklen, *J. Phys. Chem.* **79**, 7 (1975).
- ⁴ H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Int. J. Chem. Kinet.* **12**, 1001 (1980).
- ⁵ P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.6 \times 10^{-12} (T/298)^{-3.0}$	253–333	Russell <i>et al.</i> , 1990 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k = 1.0$	298	Jayanty, Simonaitis, and Heicklen, 1975 ²	(c)
$k_2/k = 1.0$	296	Ohta and Mizoguchi, 1980 ³	(d)
<i>Reviews and Evaluations</i>			
$8.9 \times 10^{-14} \exp(859/T)$	253–333	Lightfoot <i>et al.</i> , 1992 ⁴	(e)

Comments

- (a) k is defined by $-d[\text{CCl}_3\text{O}_2]/dt = 2k[\text{CCl}_3\text{O}_2]$.²
- (b) Flash photolysis of Cl_2 in the presence of CHCl_3 - O_2 - N_2 mixtures at 760 Torr total pressure. k was determined from the measurement of COCl_2 by UV absorption spectroscopy at 240 nm, assumed to be formed in a long chain, involving the reactions $\text{Cl} + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_3$; $\text{CCl}_3 + \text{O}_2 (+\text{M}) \rightarrow \text{CCl}_3\text{O}_2 (+\text{M})$; $2\text{CCl}_3\text{O}_2 \rightarrow 2\text{CCl}_3\text{O} + \text{O}_2$; $\text{CCl}_3\text{O} \rightarrow \text{COCl}_2 + \text{Cl}$.
- (c) Photolysis of CCl_4 in the presence of O_2 with GC or IR analysis of COCl_2 , formed in 100% yield.
- (d) Photolysis of CCl_3CHO in the presence of O_2 with IR analysis of COCl_2 , formed in 100% yield.
- (e) Based on the data of Russell *et al.*¹

Preferred Values

$k = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.9 \times 10^{-14} \exp(860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–430 K.
 $k_2/k = 1.0$.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.
 $\Delta(k_2/k) = \pm 0.05$.

Comments on Preferred Values

The preferred data are from the study of Russell *et al.*,¹ which is based on the rate of formation of COCl_2 from the decomposition reaction $\text{CCl}_3\text{O} \rightarrow \text{COCl}_2 + \text{Cl}$, following the interaction of CCl_3O_2 radicals. Additional evidence that the self-reaction of CCl_3O_2 proceeds exclusively through the radical-forming channel [reaction (2)] is derived from the earlier product studies of Jayanty *et al.*² and Ohta and Mizoguchi.³

References

- ¹J. J. Russell, J. A. Seetula, D. Gutman, F. Danis, F. Caralp, P. D. Lightfoot, R. Lesclaux, C. F. Melius, and S. M. Senkan, *J. Phys. Chem.* **94**, 3277 (1990).
²R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, *J. Photochem.* **4**, 203 (1975).
³T. Ohta and I. Mizoguchi, *Int. J. Chem. Kinet.* **12**, 717 (1980).
⁴P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(5.2 \pm 1.3) \times 10^{-12}$	295	Maricq <i>et al.</i> , 1993 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k = 0.95 \pm 0.05$	295	Maricq <i>et al.</i> , 1993 ¹	(b)

Comments

- (a) k is defined by $-d[\text{CH}_3\text{CHClO}_2]/dt = 2k[\text{CH}_3\text{CHClO}_2]$.²
- (b) Pulsed photolysis of Cl_2 in the presence of $\text{C}_2\text{H}_5\text{Cl}$ - O_2 - N_2 mixtures with time-resolved IR spectral photography and transient diode laser absorption measurements. The above rate coefficient and branching ratio were obtained from the time-dependence and magnitude of the secondary HCl rise, by computer simulations involving a mechanism of 24 reactions.

Preferred Values

$k_2 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 0.95$ at 298 K.

Reliability

$\Delta \log k_2 = \pm 0.3$ at 298 K.
 $\Delta(k_2/k) = \pm 0.05$ at 298 K.

Comments on Preferred Values

While the data of Maricq *et al.*¹ for the room temperature rate coefficient seem reasonable in relation to the values of other related halogen-containing peroxy radicals, they have been obtained from very indirect measurements. Confirmation by independent measurements is required to lower the recommended error limits.

References

- ¹M. M. Maricq, J. Shi, J. J. Szente, L. Rimai, and E. W. Kaiser, *J. Phys. Chem.* **97**, 9686 (1993).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 1.1 \times 10^{-13} \exp(1020/T)$	228–380	Dagaut, Wallington, and Kurylo, 1988 ¹	(a,b)
$\leq 3.6 \times 10^{-12}$	298		
$\leq 6.0 \times 10^{-12}$	295	Maricq <i>et al.</i> , 1993 ¹	(c)
<i>Branching Ratios</i>			
$k_2/k=0.69$	295	Wallington, Andino, and Japar, 1990 ³	(d)
$k_1/k=0.31$	295		
<i>Reviews and Evaluations</i>			
$k_{\text{obs}} = 1.1 \times 10^{-13} \exp(1020/T)$	228–380	Lightfoot <i>et al.</i> , 1992 ⁴	(e)
2.1×10^{-12}	298	Wallington, Dagaut, and Kurylo, 1992 ⁵	(f)

Comments

- (a) k is defined by $-\text{d}[\text{CH}_2\text{ClCH}_2\text{O}_2]/\text{dt} = 2k[\text{CH}_2\text{ClCH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CH}_2\text{ClCH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Flash photolysis of Cl_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures over the pressure range 25–400 Torr with UV absorption measurements of $[\text{CH}_2\text{ClCH}_2\text{O}_2]$ using $\sigma_{250} = (3.64 \pm 0.39) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of k_{obs} is an upper limit to k , because of the possibility of secondary reactions producing an enhanced decay of $\text{CH}_2\text{ClCH}_2\text{O}_2$ radicals (see Comments on Preferred Values).
- (c) Pulsed photolysis of Cl_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at 760 Torr pressure. Time-resolved UV absorption spectra of $(\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{HO}_2)$. The values of $\sigma(\text{CH}_2\text{ClCH}_2\text{O}_2)$ obtained are $\sim 13\%$ larger than those reported by Dagaut *et al.*¹ [see Comment (b)].
- (d) Steady-state photolysis of $\text{Cl}_2\text{-C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at total pressures of 700 Torr with FTIR spectroscopic monitoring of the decay of C_2H_4 and the formation of CH_2ClCHO , $\text{CH}_2\text{ClCH}_2\text{OOH}$, and $\text{CH}_2\text{ClCH}_2\text{OH}$. The listed branching ratios were derived from the yields of $\text{CH}_2\text{ClCH}_2\text{OH}$ and CH_2ClCHO relative to the decay of C_2H_4 .
- (e) Based on the data of Dagaut *et al.*¹
- (f) Calculated from the value $k_{\text{obs}} = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Dagaut *et al.*¹) and $k_2/k=0.69$ (Wallington *et al.*³) at 295 K.

Preferred Values

$k \leq 4.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k \leq 1.6 \times 10^{-13} \exp(1020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–380 K.
 $k_2/k=0.7$ at 298 K.

Reliability

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The upper limits to the overall rate coefficient from the studies of Dagaut *et al.*¹ and Maricq *et al.*² differ by 67%. A small part of this discrepancy is accounted for by the different absorption cross sections for the $\text{CH}_2\text{ClCH}_2\text{O}_2$ radical observed by these authors, but a large part of the difference is still unresolved. In addition, there is the difficulty of correcting the observed rate coefficients of the second-order decay of $\text{CH}_2\text{ClCH}_2\text{O}_2$ radicals for the secondary chemistry. The rate coefficient for the self-reaction of $\text{CH}_2\text{ClCH}_2\text{O}_2$ radicals is quite large and it is not certain that the rate of the reaction $\text{HO}_2 + \text{CH}_2\text{ClCH}_2\text{O}_2$ will be large enough to compete with the self-reaction of $\text{CH}_2\text{ClCH}_2\text{O}_2$ radicals.

We have averaged the results of Dagaut *et al.*¹ and Maricq *et al.*² to obtain an upper limit of the overall rate coefficient at 298 K. This value was then used to adjust the A-factor from the temperature-dependent data of Dagaut *et al.*¹ to obtain the recommended Arrhenius equation.

References

- ¹P. Dagaut, T. J. Wallington, and M. J. Kurylo, *Chem. Phys. Lett.* **146**, 589 (1988).
- ²M. M. Maricq, J. Shi, J. J. Szente, L. Rimai, and E. W. Kaiser, *J. Phys. Chem.* **97**, 9686 (1993).
- ³T. J. Wallington, J. M. Andino, and S. M. Japar, *Chem. Phys. Lett.* **165**, 189 (1990).
- ⁴P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).
- ⁵T. J. Wallington, P. Dagaut, and M. J. Kurylo, *Chem. Rev.* **92**, 667 (1992).

O₃ + C₂HCl₃ → products

No new data have been published since our last evaluation.

Preferred Values

$$k < 5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The upper limit to the preferred value is taken from the data of Atkinson *et al.*,¹ with the upper limit being increased by a factor of ~ 2 to take into account additional uncertainties in the study of Atkinson *et al.*¹ This upper limit is consistent with the reported data for the reactions of O₃ with the chloroethenes,² which show that Cl atom substitution mark-

edly decreases the rate coefficients at room temperature, relative to that for ethene. The preferred value is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹R. Atkinson, S. M. Aschmann, D. R. Fitz, A. M. Winer, and J. N. Pitts, Jr., *Int. J. Chem. Kinet.* **14**, 13 (1982).
²R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

O₃ + C₂Cl₄ → products

No new data have been published since our last evaluation.

Preferred Values

$$k < 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The upper limit to the preferred value is derived from the very limited amount of data reported by Mathias *et al.*,¹ with the upper limit to the rate coefficient being increased by a factor of 50 over that reported. This upper limit to the rate coefficient for C₂Cl₄ is consistent with the kinetic data for the other chloroethenes,² which show that Cl atom substitu-

tion markedly decreases the reactivity of the chloroethenes towards O₃, compared to that for ethene. The preferred value is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹E. Mathias, E. Sanhueza, I. C. Hisatsune, and J. Heicklen, *Can. J. Chem.* **52**, 3852 (1974).
²R. Atkinson and W. P. L. Carter, *Chem. Rev.* **84**, 437 (1984).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

HCl + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
HCl + <i>hν</i> → H + Cl	432	277

Preferred Values

Absorption cross-sections for HCl photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
140	211	180	58.8
145	281	185	31.3
150	345	190	14.5
155	382	195	6.18
160	332	200	2.56
165	248	205	0.983
170	163	210	0.395
175	109	215	0.137
		220	0.048

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are those reported by Inn.¹ Photolysis is expected to occur with unit quantum efficiency. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

¹E. C. Y. Inn, *J. Atmos. Sci.* **32**, 2375 (1975).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

HOCl + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOCl + $h\nu \rightarrow$ HO + Cl (1)	239	500
$\rightarrow$ HCl + O(³ P) (2)	235	510

Preferred Values

Absorption cross-sections for HOCl photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	7.1	295	5.7
205	5.5	300	6.0
210	5.7	305	6.0
215	7.0	310	5.9
220	9.7	315	5.5
225	12.8	320	4.9
230	16.4	325	4.2
235	19.2	330	3.5
240	20.7	335	2.9
245	20.0	340	2.4
250	17.3	345	1.8
255	13.9	350	1.5
260	10.5	355	1.2
265	7.8	360	0.8
270	6.0	365	0.9
275	5.0	370	0.8
280	4.7	375	0.8
285	4.8	380	0.8
290	5.3		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported recently by Burkholder¹ (where values are tabulated at 2 nm intervals). They differ significantly from our previous recommendation (IUPAC, 1992²) which was based on the results of Permien *et al.*³ Earlier results are discussed in IUPAC, 1989.⁴ Discrepancies between studies arise in correcting for spectral interference from Cl₂O and Cl₂. The preferred quantum yield values are based on the results of Molina *et al.*,⁵ Butler and Phillips,⁶ and Vogt and Schindler.⁷

References

¹J. B. Burkholder, *J. Geophys. Res.* **98**, 2963 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³T. Permien, R. Vogt, and R. N. Schindler, in *Mechanisms of Gas Phase and Liquid Phase Chemical Transformations in Tropospheric Chemistry*, edited by R. A. Cox, Air Pollution Research Report No. 17, Environmental Research Program of the CEC, EUR 12035 EN, Brussels, Belgium.

⁴IUPAC, Supplement III, 1989 (see references in Introduction).

⁵M. J. Molina, T. Ishiwata, and L. T. Molina, *J. Phys. Chem.* **84**, 821 (1980).

⁶P. J. D. Butler and L. F. Phillips, *J. Phys. Chem.* **87**, 183 (1983).

⁷R. Vogt and R. N. Schindler, *J. Photochem. Photobiol. A: Chem.* **66**, 133 (1992).

Quantum Yield for HOCl Photolysis at 298 K

$\phi_1 = 1.0$ for $\lambda > 200$ nm.

OCIO + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
OCIO + $h\nu \rightarrow$ ClO + O(³ P) (1)	255	470
$\rightarrow$ Cl + O ₂ (2)	26	4700

Preferred Values

Absorption cross-sections of OCIO at the band peaks at 204 K, 296 K, and 378 K

λ/nm	$10^{20}\sigma/\text{cm}^2$		
	204 K	296 K	378 K
475.53	-	13	-
461.15	17	17	16
446.41	94	69	57
432.81	220	166	134
420.58	393	304	250
408.83	578	479	378
397.76	821	670	547
387.37	1046	844	698
377.44	1212	992	808
368.30	1365	1136	920
359.73	1454	1219	984
351.30	1531	1275	989
343.44	1507	1230	938
336.08	1441	1139	864
329.22	1243	974	746
322.78	1009	791	628
317.21	771	618	516
311.53	542	435	390
305.99	393	312	291
300.87	256	219	216
296.42	190	160	167
291.77	138	114	130
287.80	105	86	105
283.51	89	72	90
279.64	73	60	79
275.74	59	46	-
272.93	53	33	-

Quantum Yields for OCIO Photolysis at 298 K

$\phi_1 = 1.0$ throughout the wavelength range 270–480 nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections at the peak of the bands [a(0) to a(26)] at 204 K, 296 K, and 378 K are the values reported by Wahner *et al.*¹ The bands became appreciably sharper with decreasing temperature.¹ However,

the integrated band intensities remained constant for all bands between 204 K and 296 K, and therefore the solar photolysis rate is not expected to have a significant temperature dependence. The recommended quantum yield of unity for O-atom production is based on results reported by Colussi,² and results of earlier studies discussed in the review by Watson.³ Colussi,² in a laser flash photolysis study at 308 nm, determined the quantum yield for O atom production to be 1.02 ± 0.05 and the quantum yield for Cl atom production to be < 0.01 . Vaida and co-workers^{4,5} reported the detection of Cl atoms by resonance-enhanced multiphoton ionization (REMPI) in the photodecomposition of OCIO in the region 360–363 nm. They interpreted this as resulting from the photoisomerization of OCIO to ClOO followed by dissociation to Cl + O₂, but did not report quantum yields. Bishenden *et al.*,⁶ using REMPI detection of Cl atoms, report that the quantum yield for Cl atom formation near 360 nm is 0.15 ± 0.10 . In contrast, Lawrence *et al.*,⁷ using a technique involving charge transfer excitation of Cl-Xe collision pairs as a sensitive probe of Cl atoms, determined that the quantum yield for Cl atom production in the 359–368 nm region is $< 5 \times 10^{-4}$. In a molecular beam photofragment study over the wavelength range 350–475 nm, Davis and Lee⁸ observed the dominant products to be ClO + O and also observed Cl atom yields reaching a maximum of 3.9% near 404 nm, decreasing to $< 0.2\%$ in the wavelength range 350–370 nm, in qualitative agreement with the results of Lawrence *et al.*⁷

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Cl₂O + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
Cl ₂ O + $h\nu$ → Cl + ClO (1)	142	840
→ O + Cl ₂ (2)	168	710
→ O + 2 Cl (3)	410	292

Preferred Values**Absorption cross-sections for Cl₂O photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	71.0	330	8.40
210	23.8	340	3.58
220	8.6	350	1.54
230	28.1	360	0.73
240	103	370	0.40
250	191	380	0.36
260	195	390	0.51
270	151	400	0.79
280	126	420	1.26
290	103	440	1.11
300	71.0	460	0.63
310	40.3	480	0.32
320	19.5	500	0.22

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Knauth *et al.*¹ and are identical to our previous evaluation, IUPAC, 1992.² The preferred values are in excellent agreement with the values re-

ported by Molina and Molina,³ except for the 330–400 nm range where the values in Ref. 3 are higher, and they are in reasonable agreement with the values reported by Lin.⁴ Values for the 150–200 nm wavelength region have recently been reported by Nee.⁵

Photolysis proceeds predominantly by breaking of the Cl-O bond to yield Cl + ClO. However, in the most recent study of the products of Cl₂O photolysis, Sander and Friedl⁶ determined the quantum yield for formation of oxygen atoms from Cl₂O photolysis to be 0.25 ± 0.05 . In these experiments a broad-band photolysis source with a spectral distribution extending from the visible down to 180 nm was used, so that it was not possible to determine the wavelength dependence of the quantum yield.

References

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Cl₂O₂ + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
Cl ₂ O ₂ + $h\nu$ → ClO + ClO (1)	76	1580
→ Cl + ClOO (2)	91	1310

Preferred Values

Absorption cross-sections for Cl₂O₂ photolysis at 200–250 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
200	383.5	250	609.3	300	72.2	350	8.2
2	352.9	2	580.1	2	65.8	2	7.9
4	325.3	4	544.5	4	59.9	4	6.8
6	298.6	6	505.4	6	54.1	6	6.1
8	274.6	8	631.5	8	79.0	8	5.8
210	251.3	260	422.0	310	43.3	360	5.5
2	231.7	2	381.4	2	38.5	2	4.5
4	217.0	4	344.6	4	34.6	4	4.1
6	207.6	6	311.6	6	30.7	6	3.8
8	206.1	8	283.3	8	28.0	8	3.5
220	212.1	270	258.4	320	25.6	370	3.2
2	227.1	2	237.3	2	23.4	2	2.9
4	249.4	4	218.3	4	21.4	4	2.7
6	280.2	6	201.6	6	19.2	6	2.4
8	319.5	8	186.4	8	17.8	8	2.2
230	365.0	280	172.5	330	16.7	380	2.1
2	415.4	2	159.6	2	15.6	2	1.9
4	467.5	4	147.3	4	14.4	4	1.7
6	517.5	6	136.1	6	13.3	6	1.6
8	563.0	8	125.2	8	13.1	8	1.4
240	600.3	290	114.6	340	12.1	390	1.3
2	625.7	2	104.6	2	11.5	2	1.2
4	639.4	4	95.4	4	10.9	4	1.1
6	642.6	6	87.1	6	10.1	6	1.0
8	631.5	8	79.0	8	9.0	8	0.9

Quantum Yields

$\phi_2 = 1.0$ throughout this wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections given here are the values recommended in the NASA, 1994 evaluation.¹ For the wavelength range 200–360 nm they are the smoothed average of the results reported by Cox and

Hayman,² DeMore and Tschuikow-Roux,³ Permien *et al.*,⁴ and Burkholder *et al.*,⁵ for wavelengths greater than 360 nm the values were derived from a linear extrapolation of $\log \sigma(\lambda)$ vs λ using the expression: $\log(10^{20} \sigma/\text{cm}^2) = (7.589 - 0.01915 \lambda)$. These studies indicate that in the recombination reaction $\text{ClO} + \text{ClO} \rightarrow \text{products}$, the only stable species produced is ClOOC l . The structure of the recombination product has been established to be ClOOC l by the study of Birk *et al.*⁶ using submillimeter wave spectroscopy. Theoretical studies^{7–9} of thermochemical stabilities of Cl_2O_2 isomers are in agreement with these observations. The preferred quantum yield values are based on results of the study by Molina *et al.*¹⁰ in which the production of Cl atoms in the laser flash photolysis of ClOOC l at 308 nm was directly determined by time-resolved atomic resonance fluorescence. These results are in agreement with the interpretation of the steady-state photolysis experiments of Cox and Hayman.²

References

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Cl₂O₃ + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{Cl}_2\text{O}_3 + h\nu \rightarrow \text{ClO} + \text{OC lO}$ (1)	44	2720
$\rightarrow \text{Cl} + \text{ClO}_3$ (2)	201	595

Preferred Values

Absorption cross-sections for Cl_2O_3 photolysis at 200–260 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
220	968	280	1136
225	930	285	890
230	908	290	642
235	883	295	435
240	904	300	288
245	989	305	176
250	1154	310	107
255	1352	315	56
260	1512	320	36
265	1594		
270	1544		
275	1376		

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Burkholder *et al.*¹ They show no dependence on temperature over the range 200–260 K. The results of this more direct study¹ are preferred over those of Hayman and Cox,² which formed the basis for our previous recommendation.³ These two studies^{1,2} are in agreement on the shape of the spectrum, but the values reported by Hayman and Cox² are approximately 30–50% larger. The mechanism and quantum yield for photodissociation have not been determined.

References

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 $\text{ClNO} + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{ClNO} + h\nu \rightarrow \text{Cl} + \text{NO}$	160	750

Preferred Values

Absorption cross-sections for ClNO photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	4320	246	45.2	302	10.3	370	11.0
192	5340	248	37.7	304	10.5	375	9.95
194	6150	250	31.7	306	10.8	380	8.86
196	6480	252	27.4	308	11.1	385	7.82
198	6310	254	23.7	310	11.5	390	6.86
200	5860	256	21.3	312	11.9	395	5.97
202	5250	258	19.0	314	12.2	400	5.13
204	4540	260	17.5	316	12.5	405	4.40
206	3840	262	16.5	318	13.0	410	3.83
208	3210	264	15.3	320	13.4	415	3.38
210	2630	266	14.4	322	13.6	420	2.89
212	2180	268	13.6	324	14.0	425	2.45
214	1760	270	12.9	326	14.3	430	2.21
216	1400	272	12.3	328	14.6	435	2.20
218	1110	274	11.8	330	14.7	440	2.20
220	896	276	11.3	332	14.9	445	2.07
222	707	278	10.7	334	15.1	450	1.87
224	552	280	10.6	336	15.3	455	1.79
226	436	282	10.2	338	15.3	460	1.95
228	339	284	9.99	340	15.2	465	2.25
230	266	286	9.84	342	15.3	470	2.50
232	212	288	9.71	344	15.1	475	2.61
234	164	290	9.64	346	15.1	480	2.53
236	128	292	9.63	348	14.9	485	2.33
238	101	294	9.69	350	14.5	490	2.07
240	82.5	296	9.71	355	13.6	495	1.78
242	67.2	298	9.89	360	12.9	500	1.50
244	55.1	300	10.0	365	12.0		

Quantum Yields for ClNO Photolysis at 298 K

$\phi = 1.0$ over the entire wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K for the wavelength range 190–350 nm (unchanged from IUPAC, 1992¹) are the values reported by Tyndall *et al.*² and for the longer wavelengths are the values reported in the recent study of Roehl *et al.*³ Roehl *et al.*³ reported values over the wavelength range 350–650 nm and the temperature range 223–343 K. Earlier results are discussed in NASA, 1994.⁴ The preferred quantum yield values are taken from Calvert and Pitts.⁵

References

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ClONO + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
ClONO + $h\nu$ → Cl + NO ₂ (1)	98	1220
→ ClO + NO (2)	136	880

Preferred Values**Absorption cross-sections for ClONO photolysis at 231 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
235	215.0	320	80.3
240	176.0	325	75.4
245	137.0	330	58.7
250	106.0	335	57.7
255	65.0	340	43.7
260	64.6	345	35.7
265	69.3	350	26.9
270	90.3	355	22.9
275	110.0	360	16.1
280	132.0	365	11.3
285	144.0	370	9.0
290	144.0	375	6.9
295	142.0	380	4.1
300	129.0	385	3.3
305	114.0	390	2.2
310	105.0	395	1.5
315	98.1	400	0.6

Comments on Preferred Values

The preferred values of the absorption cross-sections at 231 K are the values reported by Molina and Molina.¹ Photolysis is expected to occur with unit quantum efficiency by breaking of the Cl-O bond to yield Cl + NO₂. The lifetime against photodissociation for ClONO in the atmosphere was calculated to 2 to 3 minutes.¹ The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

¹L. T. Molina and M. J. Molina, *Geophys. Res. Lett.* **4**, 83 (1977).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

ClONO₂ + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
ClONO ₂ + $h\nu$ → Cl + NO ₂ (1)	142	840
→ ClNO + O(³ P) (2)	288	415

Preferred Values**Absorption cross-sections for ClONO₂ photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	2690	290	17.3
200	468	300	14.9
210	320	310	12.1
220	339	320	8.87
230	226	330	5.84
240	133	340	3.54
250	90.6	350	2.04
260	61.3	360	1.15
270	35.3	370	0.69
280	22.0		

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported in the recent study of Ganske *et al.*¹ They are in good agreement with our previous recommendation,² which for 190–270 nm were the values reported by Illies and Takacs,³ and for 270–370 nm were the values reported by Nelson and Johnston.⁴ The latter authors⁴ showed that the higher values above 300 nm reported in Ref. 3 could be accounted for by a 6% Cl₂ impurity in the ClONO₂ sample. Nelson and Johnston⁴ determined that photolysis occurs with a quantum yield of unity (within experimental error) to produce Cl + NO₂ ($\phi_1=0.93\pm0.15$). They also reported a negligible production of oxygen atoms ($\phi_2<0.02$).

References

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ClONO₂ + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
ClONO ₂ + <i>hν</i> → ClO + NO ₂ (1)	112	1065
→ Cl + NO ₃ (2)	163	735
→ ClONO + O(³ P) (3)	282	425

Preferred Values**Absorption cross-sections for ClONO₂ photolysis at 296 K, 220 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	296 K	220 K		296 K	220 K
200	282	270	315	1.14	
205	284		320	0.831	0.578
210	314	315	325	0.613	
215	342		330	0.466	0.329
220	332	335	335	0.367	
225	278		340	0.302	0.230
230	208	200	345	0.258	
235	148		350	0.229	0.186
240	105	96.7	355	0.208	
245	76.4		360	0.200	0.169
250	56.0	49.7	365	0.180	
255	43.2		370	0.159	0.136
260	33.8	29.1	375	0.141	
265	26.5		380	0.121	0.104
270	20.5	17.3	385	0.137	
275	15.7		390	0.091	0.077
280	11.9	9.83	395	0.076	
285	8.80		400	0.064	0.052
290	6.41	5.15	405	0.054	
295	4.38		410	0.044	0.034
300	3.13	2.40	415	0.036	
305	2.24		420	0.032	0.023
310	1.60	1.16	425	0.023	
			430	0.019	0.013

Quantum Yields for ClONO₂ Photolysis

$\phi_2 = 0.90$ for $\lambda > 260$ nm.

$\phi_3 = 0.10$ for $\lambda > 260$ nm.

Comments on Preferred Values

The preferred values of the absorption cross-sections are taken from Burkholder *et al.*,¹ who measured values over the wavelength range 195–430 nm and the temperature range

220–296 K. They report,¹ every 2 nm, values of σ at 296 K and values of the parameters A_1 and A_2 needed to compute the temperature dependence by the equation:

$$\sigma(\lambda, T)/\sigma(\lambda, 296) = 1 + A_1(T - 296) + A_2(T - 296)^2.$$

In this data sheet, room temperature values at 5 nm intervals are given (odd wavelength values were calculated by linear interpolation) and, at 10 nm intervals, 220 K values calculated using the formula shown above and the parameters tabulated in the paper. For values of σ at every 2 nm and values of the temperature dependence parameters, the reader is referred to the original reference.¹ These values are in good agreement with those reported in IUPAC, 1992,² which were based on the results of Molina and Molina.³ The preferred quantum yield values are based on the direct results of Margitan⁴ at 266 nm and 355 nm. They are confirmed by the results of Knauth and Schindler⁵ based on final product analysis, and also by the results of Chang *et al.*⁶ and Burrows *et al.*,⁷ who report Cl + NO₃ as the photolysis products at 254 nm, with a quantum yield of unity. However, in contrast with these results, in a recent study using a molecular beam technique with pulsed laser photolysis, Minton *et al.*⁸ report comparable values of ϕ_1 and ϕ_2 at 193 nm and 248 nm.

References

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$\text{Cl}_2 + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$	242	495

Preferred Values

Absorption cross-sections for Cl_2 photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
260	0.20	370	8.4
270	0.82	380	5.0
280	2.6	390	2.9
290	6.2	400	1.8
300	11.9	410	1.3
310	18.5	420	0.96
320	23.7	430	0.73
330	25.5	440	0.54
340	23.5	450	0.38
350	18.8	460	0.26
360	13.2	470	0.16

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported in the recent study of Maric *et al.*¹ The results of the recent study of Ganske *et al.*² are in excellent agreement. Results of these two studies^{1,2} are in good agreement with the previous recommendation (IUPAC,

1992³) which was based on the study of Seery and Britton.⁴ Additional earlier studies are cited in IUPAC, 1992.³ Maric *et al.*¹ fitted the data for the wavelength region 250–550 nm with the following semiempirical expression:

$$10^{20} \sigma = \alpha^{0.5} \times 27.3 \exp\{-99.0 \alpha [\ln(329.5/\lambda)]^2\} \\ + \alpha^{0.5} \times 0.932 \exp\{-91.5 \alpha [\ln(406.5/\lambda)]^2\}$$

where $\alpha = \tanh(402.676/T)$.

This expression combines the semiempirical function originally proposed by Johnston *et al.*⁵ with the temperature dependence expressions proposed by Sulzer and Wieland.⁶

References

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CH₃Cl + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{Cl} + h\nu \rightarrow \text{CH}_3 + \text{Cl}$	349	343

Preferred Values**Absorption cross-sections for CH₃Cl photolysis at 295 K and 210 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
174	111	111	200	1.76	1.51
6	93.8	93.8	2	1.13	0.93
8	76.6	76.6	4	0.750	0.573
180	60.7	60.7	6	0.483	0.345
2	46.7	46.7	8	0.318	0.212
4	35.0	35.0	210	0.206	0.130
6	25.5	25.5	2	0.132	0.080
8	18.2	18.2	4	0.086	0.047
190	12.7	12.7	6	0.055	0.027
2	8.72	8.72			
4	5.88	5.88			
6	4.01	4.01			
8	2.66	2.43			

Comments on Preferred Values

The preferred values of the absorption cross-sections at

295 K and at 210 K are the values reported to Simon *et al.*¹ and are identical to our previous evaluation, IUPAC, 1992.² This publication¹ reports the results of the most comprehensive study of the temperature dependence. These values are in very good agreement with the room temperature values reported by Robbins,³ and are in reasonable agreement with the results of Hubrich *et al.*⁴ who also made low temperature measurements. In this wavelength region, photolysis occurs with unit quantum efficiency by breaking of the C-Cl bond to yield $\text{CH}_3 + \text{Cl}$. Photochemistry at shorter wavelengths is discussed by Shold and Rebbert.⁵

References

- ¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisenberg, *J. Atmos. Chem.* **7**, 107 (1988).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³D. E. Robbins, *Geophys. Res. Lett.* **3**, 213 (1976); erratum op. cit. **3**, 757 (1976).
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CHF₂Cl(HCFC-22) + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CHF}_2\text{Cl} + h\nu \rightarrow \text{CHF}_2 + \text{Cl}$	362	330

Preferred Values**Absorption cross-sections for CHF₂Cl photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
174	5.72	190	0.245
176	4.04	192	0.156
178	2.76	194	0.103
180	1.91	196	0.072
182	1.28	198	0.048
184	0.842	200	0.032
186	0.576	202	0.022
188	0.372	204	0.014

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Simon *et al.*¹ and are identical to our previous evaluation, IUPAC, 1992.² In the same study¹ the temperature dependence down to 210 K has been reported, with the values at the shorter wavelengths being temperature-independent while the values at longer wavelengths show a decrease as the temperature is lowered.¹ For values at low temperatures the reader is referred to the original reference. These results are in reasonable agreement with the results of earlier studies cited in NASA, 1990.³ Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $\text{CHF}_2 + \text{Cl}$.

References

¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 9, 1990 (see references in Introduction).

CF₂Cl₂(CFC-12) + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ Cl ₂ + <i>hν</i> → CF ₂ Cl + Cl (1)	346	346
→ CF ₂ + 2 Cl (2)	542	221

Preferred Values**Absorption cross-sections for CF₂Cl₂ photolysis at 295 K and 210 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
174	162	162	200	8.89	5.11
6	181	181	2	5.51	2.97
8	187	187	4	3.44	1.69
180	179	179	6	2.09	0.99
2	160	160	8	1.27	0.56
4	134	134	210	0.76	0.32
6	107	107	2	0.45	0.18
8	82.8	79.3	4	0.27	0.10
190	63.2	52.9	6	0.16	0.058
2	45.4	35.8	8	0.10	0.033
4	31.5	22.8	220	0.060	0.018
6	21.1	14.4	2	0.036	0.010
8	13.9	8.8	4	0.022	0.006
			6	0.013	0.003

Quantum yields for CF₂Cl₂ photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.59	0.41	210	0.85	0.15
180	0.62	0.38	220	0.96	0.04
190	0.67	0.33	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and at 210 K are the values reported by Simon *et al.*¹ This recent publication reports the results of the most comprehensive study of the temperature dependence.¹ The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1980,² where a detailed discussion of earlier work can be found. The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.³ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, J. Atmos. Chem. **7**, 107 (1988).

²CODATA, 1980 (see references in Introduction).

³R. E. Rebbert and P. J. Ausloos, J. Photochem. **4**, 419 (1975).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

CFCl₃(CFC-11) + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CFCl ₃ + <i>hν</i> → CFCl ₂ + Cl (1)	317	380
→ CFCl + 2 Cl (2)	507	236

Preferred Values

Absorption cross-sections for CFCl_3 photolysis at 295 K and 210 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
174	313	313	210	14.8	9.9
6	324	324	2	10.5	6.63
8	323	323	4	7.56	4.31
180	314	414	6	5.38	2.78
2	296	296	8	3.79	1.77
4	272	272	220	2.64	1.13
6	243	230	2	1.82	0.71
8	213	202	4	1.24	0.45
190	179	170	6	0.84	0.29
2	154	141	8	0.56	0.19
4	124	115	230	0.37	0.12
6	99.1	90.5	235	0.126	
8	78.0	71.8	240	0.046	
200	64.5	55.8	245	0.017	
2	50.0	42.0	250	0.0066	
4	37.4	30.0	255	0.0034	
6	28.0	21.6	260	0.0015	
8	19.7	14.9			

Quantum yields for CFCl_3 photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.57	0.43	210	0.84	0.16
180	0.66	0.34	220	0.94	0.06
190	0.66	0.34	230	1.0	
200	0.74	0.26	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections for 174–230 nm at 295 K and 210 K are the values reported by Simon *et al.*¹ This recent publication reports the results of the most comprehensive study of the temperature dependence.¹ The values are in good agreement with those recommended in our previous evaluation, CODATA, 1982,² where a detailed discussion of earlier work can be found. For $\lambda > 230$ nm, the absorption cross-section values are those reported by Hubrich and Stuhl.³ The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.⁴ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

- ¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, *J. Atmos. Chem.* **7**, 107 (1988).
- ²CODATA, Supplement I, 1982 (see references in Introduction).
- ³C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ⁴R. E. Rebbert and P. J. Ausloos, *J. Photochem.* **4**, 419 (1975).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

 $\text{CCl}_4 + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CCl}_4 + h\nu \rightarrow \text{CCl}_3 + \text{Cl}$ (1)	288	415
$\rightarrow \text{CCl}_2 + 2 \text{Cl}$ (2)	577	207

Preferred Values

Absorption cross-sections for CCl₄ photolysis at 295 K and 210 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
174	990	990	220	17.5	12.5
6	1010	1010	2	13.6	9.0
8	975	975	4	10.2	6.4
180	720	720	6	7.6	4.4
2	590	590	8	5.6	3.16
4	440	440	230	4.28	2.27
6	310	310	2	3.04	1.52
8	198	198	4	2.20	1.05
190	147	147	6	1.60	0.72
2	99.2	99.2	8	1.16	0.50
4	76.7	76.7	240	0.830	0.342
6	69.5	69.5	2	0.590	0.234
8	68.0	68.0	4	0.413	0.158
200	66.0	66.0	6	0.290	0.108
2	63.8	63.8	8	0.210	0.076
4	61.0	60.1	250	0.148	0.053
6	57.0	54.4	255	0.066	
8	52.5	48.3	260	0.025	
210	46.9	41.5	265	0.013	
2	41.0	34.8	270	0.006	
4	34.5	27.9	275	0.002	
6	27.8	21.7			
8	22.1	16.3			

Quantum yields for CCl₄ photolysis at 298 K

λ/nm	ϕ_1	ϕ_2	λ/nm	ϕ_1	ϕ_2
170	0.30	0.70	210	0.83	0.17
180	0.36	0.64	220	0.96	0.04
190	0.46	0.54	230	1.0	
200	0.63	0.37	240	1.0	

Comments on Preferred Values

The preferred values of the absorption cross-sections at 295 K and 210 K are the values reported by Simon *et al.*¹ This recent publication reports the results of the most comprehensive study of the temperature dependence.¹ The values at room temperature are in good agreement with those recommended in our previous evaluation, CODATA, 1982,² where a detailed discussion of earlier work can be found. For $\lambda > 250$ nm, the absorption cross-section values are those reported by Hubrich and Stuhl.³ The recommended quantum yield values are taken from Ref. 2, and are based on the results of Rebbert and Ausloos.⁴ The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

- ¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, *J. Atmos. Chem.* **7**, 107 (1988).
- ²CODATA, Supplement I, 1982 (see references in Introduction).
- ³C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ⁴R. E. Rebbert and P. J. Ausloos, *J. Photochem.* **6**, 265 (1976/77).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

CH₃CF₂Cl (HCFC-142b) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CF}_2\text{Cl} + h\nu \rightarrow \text{CH}_3\text{CF}_2 + \text{Cl}$	335 (est)	360

Preferred Values

Absorption cross-sections for CH₃CF₂Cl photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	0.94	210	0.017
2	0.66	2	0.010
4	0.46	4	0.007
6	0.31	6	0.004
8	0.21	8	0.003
200	0.14	220	0.002
2	0.09	2	0.0009
4	0.061	4	0.0005
6	0.039	6	0.0003
8	0.026	8	0.0002

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon¹ and Orlando *et al.*² The agreement between these

studies^{1,2} over the wavelength range of preferred values is good. The results of Hubrich and Stuhl³ are in reasonable agreement. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. They are in fair agreement at the shorter wavelengths, both studies reporting a significant decrease in absorption as the temperature is lowered. At the longer wavelengths they are in disagreement at low temperatures. For values at low temperatures the reader is referred to the original references.^{1,2} Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CH₃CF₂ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **12**, 269 (1991).
- ²J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5013 (1991).
- ³C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

CH₃CFCI₂(HCFC-141b) + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CFCI}_2 + h\nu \rightarrow \text{CH}_3\text{CFCI} + \text{Cl}$	335 (est)	360

Preferred Values**Absorption cross-sections for CH₃CFCI₂ photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	83.8	210	2.1
2	64.1	2	1.4
4	47.4	4	0.88
6	34.0	6	0.57
8	23.8	8	0.37
200	16.4	220	0.24
2	11.1	2	0.16
4	7.4	4	0.10
6	4.9	6	0.07
8	3.2	8	0.04

and the liquid phase (230–260 nm) at 298 K. Correction factors were used to convert these liquid-phase values into accurate gas-phase values at the long wavelengths. Results reported in this study¹ are in very good agreement with those reported by Gillotay and Simon.² The results of Talukdar *et al.*³ are lower at shorter wavelengths and higher at longer wavelengths. Gillotay and Simon² and Talukdar *et al.*³ report the temperature dependence down to 210 K. For values at low temperatures the reader is referred to the original references.^{2,3} Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CH₃CFCI + Cl.

References

- ¹A. Fahr, W. Braun, and M. J. Kurylo, *J. Geophys. Res.* **98**, 20467 (1993).
²D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **12**, 269 (1991).
³R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, *J. Phys. Chem.* **95**, 5815 (1991).

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Fahr *et al.*¹ In this study¹ measurements were made in the gas phase (190–260 nm)

CH₃CCl₃ + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CCl}_3 + h\nu \rightarrow \text{CH}_3\text{CCl}_2 + \text{Cl}$	335 (est)	360

Preferred Values

Absorption cross-sections for CH_3CCl_3 photolysis at 295 K and 210 K

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
182	315	315	210	24.0	19.8
4	280	280	2	16.8	13.2
6	250	250	4	12.0	8.8
8	220	220	6	8.6	6.1
190	192	192	8	6.0	4.2
2	163	163	220	4.1	2.9
4	140	140	2	2.9	1.2
6	118	118	4	2.0	1.2
8	99	99	6	1.5	0.76
200	81	81	8	1.0	0.51
2	66	64	230	0.70	0.33
4	52	49	2	0.49	0.18
6	40	36	4	0.33	0.11
8	31	26	6	0.23	0.064
			8	0.15	0.036
			240	0.10	0.024

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K and at 210 K are the values reported by Vanlaethem-

Meuree *et al.*¹ These values¹ are preferred over the substantially higher values reported by Hubrich and Stuhl,² in which study a correction was required for the presence of the UV-absorbing stabilizer 1,4-dioxane. In Ref. 1, absorption cross-section values are given for 295 K, 270 K, 250 K, 230 K, and 210 K. In a recent study Nayak *et al.*³ reported measurements in the gas phase (160–240 nm) and the liquid phase (235–260 nm) over the temperature range 220–330 K. A wavelength shift procedure was used to convert the liquid-phase values into effective gas-phase values at the long wavelengths. The reported room temperature values³ are in good agreement with those of Vanlaethem-Meuree *et al.*¹ in the range 210–240 nm, whereas in the 180–210 nm range they are 15% to 30% higher. Low temperature results are in relatively good agreement up to 230 nm. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $\text{CH}_3\text{CCl}_2 + \text{Cl}$.

References

- ¹N. Vanlaethem-Meuree, J. Wisemberg, and P. C. Simon, *Geophys. Res. Lett.* **6**, 451 (1979).
- ²C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ³A. K. Nayak, M. J. Kurylo, and A. Fahr, *J. Geophys. Res.* **100**, 11185 (1995).

 $\text{CF}_3\text{CHFCl}(\text{HCFC-124}) + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{CHFCl} + h\nu \rightarrow \text{CF}_3\text{CHF} + \text{Cl}$	335 (est)	360

Preferred Values

Absorption cross-sections for CF_3CHFCl photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	0.77	210	0.018
2	0.55	2	0.012
4	0.39	4	0.008
6	0.27	6	0.006
8	0.18	8	0.004
200	0.13	220	0.003
2	0.086	2	0.002
4	0.060	4	0.002
6	0.040	6	0.001
8	0.027	8	0.001

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the averages of the values reported by Orlando

*et al.*¹ and Gillotay and Simon,² which are in good agreement. Both studies investigated the temperature dependence down to about 210 K. The temperature dependences of Orlando *et al.*¹ are greater for shorter wavelengths (<200 nm) and less for the longer wavelengths than those reported by Gillotay and Simon.² The studies are in agreement on a significant decrease in absorption at the lowest temperature and the longer wavelengths, but over the same wavelength range and at the intermediate temperatures they are in poor agreement. For values at low temperatures the reader is referred to the original references.^{1,2} Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield $\text{CF}_3\text{CHF} + \text{Cl}$.

References

- ¹J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5013 (1991).
- ²D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **13**, 289 (1991).

CF₃CHCl₂(HCFC-123) + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ CHCl ₂ + <i>hν</i> → CF ₃ CHCl + Cl	335 (est)	360

Preferred Values**Absorption cross-sections for CF₃CHCl₂ photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	59.0	210	1.8
2	44.5	2	1.3
4	32.9	4	0.87
6	23.6	6	0.61
8	16.9	8	0.40
200	11.9	220	0.28
2	8.3	2	0.20
4	5.7	4	0.14
6	4.0	6	0.10
8	2.7	8	0.07

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K, which are unchanged from our previous evaluation,¹ are the mean of the values reported by Gillotay and Simon²

and Orlando *et al.*³ The agreement between these studies over the wavelength range of preferred values is very good. Results of the recent study by Nayak *et al.*⁴ are in good agreement with this recommendation, as are the results of Green and Wayne.⁵ The temperature dependence down to about 210 K has been reported by Gillotay and Simon,² Orlando *et al.*,³ and Nayak *et al.*⁴ For values at low temperatures the reader is referred to the original references. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF₃CHCl + Cl.

References

- ¹IUPAC, Supplement IV, 1992 (see references in Introduction).
- ²D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **12**, 269 (1991).
- ³J. J. Orlando, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5013 (1991).
- ⁴A. K. Nayak, T. J. Buckley, M. J. Kurylo, and A. Fahr, *J. Geophys. Res.* **101**, 9055 (1996).
- ⁵R. G. Green and R. P. Wayne, *J. Photochem.* **6**, 375 (1976/77).

CF₂ClCFCl₂(CFC-113) + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ ClCFCl ₂ + <i>hν</i> → CF ₂ ClCFCl + Cl (1)	346 (est)	346
→ CFCl ₂ CF ₂ + Cl (2)	346 (est)	346

Preferred Values**Absorption cross-sections for CF₂ClCFCl₂ photolysis at 295 K and 210 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$		λ/nm	$10^{20} \sigma/\text{cm}^2$	
	295 K	210 K		295 K	210 K
184	118	118	210	1.80	1.12
6	104	104	2	1.15	0.696
8	83.5	83.5	4	0.760	0.452
190	64.5	64.5	6	0.505	0.298
2	48.8	48.8	8	0.318	0.184
4	36.0	36.0	220	0.220	0.125
6	26.0	24.3	2	0.145	0.081
8	18.3	15.9	4	0.095	0.053
200	12.5	10.1	6	0.063	0.034
2	8.60	6.54	8	0.041	0.022
4	5.80	4.09	230	0.027	0.014
6	4.00	2.66			
8	2.65	1.68			

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon *et al.*¹ They are in very good agreement with the room temperature results of Chou *et al.*² and Hubrich and Stuhl,³ who also made low temperature measurements. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF₂ClCFCl + Cl or CFCl₂CF₂ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, *Ann. Geophysicae* **6**, 239 (1988).
- ²C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **82**, 1 (1978).
- ³C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

CF₂ClCF₂Cl(CFC-114) + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ ClCF ₂ Cl + <i>hν</i> → CF ₂ ClCF ₂ + Cl	346 (est)	346

Preferred Values**Absorption cross-sections for CF₂ClCF₂Cl photolysis at 295 K and 210 K**

10 ²⁰ σ/cm ²			10 ²⁰ σ/cm ²		
λ/nm	295 K	210 K	λ/nm	295 K	210 K
172	69	69	200	0.80	0.55
4	55	55	2	0.54	0.34
6	43	43	4	0.37	0.22
8	34	34	6	0.24	0.13
180	26	26	8	0.16	0.084
2	19.8	19.8	210	0.104	0.051
4	15.0	15.0	2	0.068	0.031
6	11.0	11.0	4	0.044	0.020
8	7.80	7.72	6	0.029	0.012
190	5.35	5.03	8	0.019	0.007
2	3.70	3.28	220	0.012	0.004
4	2.56	2.13			
6	1.75	1.39			
8	1.20	0.88			

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Simon *et al.*¹ They are in very good agreement with the room temperature results of Chou *et al.*² Hubrich and Stuhl³ reported higher values and a smaller temperature dependence. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF₂ClCF₂ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, *Ann. Geophysicae* **6**, 239 (1988).
- ²C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **82**, 1 (1978).
- ³C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

CF₃CF₂Cl(CFC-115) + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ CF ₂ Cl + <i>hν</i> → CF ₃ CF ₂ + Cl	346	346

Preferred Values**Absorption cross-sections for CF₃CF₂Cl photolysis at 295 K**

λ/nm	10 ²⁰ σ/cm ²	λ/nm	10 ²⁰ σ/cm ²
172	5.65	190	0.27
4	4.05	2	0.19
6	2.85	4	0.13
8	2.05	6	0.090
180	1.45	8	0.063
2	1.05	200	0.044
4	0.75	2	0.031
6	0.53	4	0.021
8	0.38		

Comments on Preferred Values

The preferred values of the absorption cross-sections are the values reported by Simon *et al.*¹ In this study measure-

ments were made down to 225 K, and the absorption cross-section values were found to be independent of temperature. They are in good agreement with the results of Hubrich and Stuhl,² who also made low temperature measurements. Earlier measurements of Chou *et al.*³ are 50% higher. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF₃CF₂ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

- ¹P. C. Simon, D. Gillotay, N. Vanlaethem-Meuree, and J. Wisemberg, *Ann. Geophysicae* **6**, 239 (1988).
- ²C. Hubrich and F. Stuhl, *J. Photochem.* **12**, 93 (1980).
- ³C. C. Chou, R. J. Milstein, W. S. Smith, H. Vera Ruiz, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **82**, 1 (1978).
- ⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

CF₃CF₂CHCl₂(HCFC-225ca) + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ CF ₂ CHCl ₂ + $h\nu$ → CF ₃ CF ₂ CHCl + Cl	335 (est)	360

Preferred Values**Absorption cross-sections for CF₃CF₂CHCl₂ photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
160	269	200	16
165	197	205	6.9
170	183	210	2.9
175	191	215	1.2
180	177	220	0.46
185	129	225	0.17
190	74	230	0.065
195	37	239	0.011

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun *et al.*¹ In the same study, absorption cross-section measurements in the liquid

phase were made over the wavelength range 205–270 nm.¹ Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–270 nm were fitted¹ with the expression:

$$\log_{10}\sigma = -17.966 + 4.542 \times 10^{-2}X - 2.036 \times 10^{-3}X^2 + 1.042 \times 10^{-5}X^3 \quad \text{where } X = (\lambda - 160 \text{ nm})$$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF₃CF₂CHCl + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. Geophys. Res. **96**, 13009 (1991).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

CF₂ClCF₂CHFCI(HCFC-225cb) + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ ClCF ₂ CHFCI + $h\nu$ → CF ₂ ClCF ₂ CHF + Cl (1)	335 (est)	360
→ CHFClCF ₂ CF ₂ + Cl (2)	335 (est)	360

Preferred Values**Absorption cross-sections for CF₂ClCF₂CHFCI photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
160	188	185	9.1
165	145	190	3.5
170	91	195	1.4
175	47	200	0.63
180	21	205	0.33
		210	0.25

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Braun *et al.*¹ In the same study, absorption cross-section measurements in the liquid phase were made over the wavelength range 205–250 nm.¹

Correction factors were used to convert these liquid-phase values into gas-phase values. The combined set of gas-phase values for the wavelength range 170–250 nm were fitted with the expression:

$$\log_{10}\sigma = -17.714 - 2.175 \times 10^{-2}X - 1.484 \times 10^{-3}X^2 + 1.147 \times 10^{-5}X^3 \quad \text{where } X = (\lambda - 160 \text{ nm})$$

Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Cl bond to yield CF₂ClCF₂CHF + Cl or CHFClCF₂CF₂ + Cl. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹W. Braun, A. Fahr, R. Klein, M. J. Kurylo, and R. E. Huie, J. Geophys. Res. **96**, 13009 (1991).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

HCOCI + $h\nu$ products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{HCOCI} + h\nu \rightarrow \text{HCO} + \text{Cl}$	340 (est)	350

Preferred Values**Absorption cross-sections of HCOCI at the band maxima
(298 K, 1013 mbar of N_2 , spectral resolution 0.7 nm)**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
236.1	3.8	280.2	2.4
241.5	4.9	282.7	2.3
247.3	5.6	285.3	1.64
251.4	5.4	286.8	1.04
253.7	6.0	288.0	0.86
256.1	5.6	289.4	0.97
258.2	5.8	292.2	0.81
260.2	6.0	294.9	0.46
263.5	5.1	296.7	0.32
265.7	5.3	298.1	0.22
267.9	5.2	299.5	0.25
269.1	3.9	302.3	0.172
270.2	3.5	305.2	0.080
271.4	4.0	308.1	0.027
273.8	4.1	309.3	0.021
276.3	3.4	311.1	0.020
277.7	2.4	314.1	0.013
278.9	2.1	316.7	0.008
		318.7	0.007

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, IUPAC, 1992.¹ The preferred values of the absorption cross-sections at 298 K are those reported by Libuda *et al.*² These are the values of the absorption cross-sections at the absorption maxima and were measured at a spectral resolution of 0.7 nm. The absorption bands for $\lambda > 265$ nm became distinctly sharper when the spectral resolution was improved to 0.4 nm. The spectrum of HCOCI is similar to that of HCHO but is shifted to shorter wavelengths by 45 nm. Although there have been no quantum yield studies of HCOCI photolysis, it is reasonable to assume by analogy with the photolysis of COCl_2 that the primary photolysis pathway proceeds by breaking of the C-Cl bond to yield $\text{HCO} + \text{Cl}$.

References¹IUPAC, Supplement IV, 1992 (see references in Introduction).²H. G. Libuda, F. Zabel, E. H. Fink, and K. H. Becker, *J. Phys. Chem.* **94**, 5860 (1990).**COFCl + $h\nu$ → products****Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{COFCl} + h\nu \rightarrow \text{COF} + \text{Cl}$ (1)	377	317
→ $\text{COCl} + \text{F}$ (2)	489	244
→ $\text{CO} + \text{F} + \text{Cl}$ (3)	517	231
→ $\text{CFCl} + \text{O}(^3\text{P})$ (4)	656	182

Preferred Values

Absorption cross-sections for COFCl photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
186.0	15.6	207.3	10.8
187.8	14.0	209.4	9.9
189.6	13.4	211.6	9.0
191.4	12.9	213.9	7.9
193.2	12.7	216.2	6.9
195.1	12.5	218.6	5.8
197.0	12.4	221.0	4.8
199.0	12.3	223.5	3.8
201.0	12.5	226.0	2.9
203.0	12.0	228.6	2.2
205.1	11.5	231.2	1.6

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Chou *et al.*¹ over the wavelength range 186 to 199 nm and those reported in the recent study of Nolle *et al.*² at longer wavelengths. The spectrum shows little structure; the values listed are averages over 500 cm^{-1} in-

tervals. Nolle *et al.*² reported values over the wavelength range 200–260 nm and the temperature range 298–223 K. Their room temperature values are in good agreement with those of Chou *et al.*¹ The effect of temperature on calculated photodissociation rates is negligible because no strong temperature dependence is observed in the atmospheric window region where photolysis occurs (190–230 nm). Hermann *et al.*³ photolyzed COFCl at 193 nm and analyzed the parent and products by FTIR spectroscopy. They could explain their results³ using only channels (1) and (3), and reported a total quantum yield of 1.0 independent of pressure from 10 to 900 mbar N_2 . The relative contribution of channels (1) and (3) was found to depend on pressure with an equal contribution of the two channels at 900 mbar N_2 .

References

- ¹G. C. Chou, G. Crescentini, H. Vera-Ruiz, W. S. Smith, and F. S. Rowland, Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.
- ²A. Nolle, H. Heydtmann, R. Meller, W. Schneider, and G. K. Moortgat, *Geophys. Res. Lett.* **20**, 707 (1993).
- ³M. Hermann, A. Nolle, and H. Heydtmann, *Chem. Phys. Lett.* **226**, 559 (1994).

 $\text{COCl}_2 + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{COCl}_2 + h\nu \rightarrow \text{COCl} + \text{Cl}$ (1)	324	369
$\rightarrow \text{CO} + 2 \text{Cl}$ (2)	352	340
$\rightarrow \text{CCl}_2 + \text{O}(^3\text{P})$ (3)	707	169

Preferred Values

Absorption cross-sections for COCl_2 photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
184.4	234	211.6	13.3
186.0	186	213.9	12.6
187.8	146	216.2	12.3
189.6	116	218.6	12.2
191.4	90.3	221.0	12.2
193.2	71.5	223.5	12.4
195.1	52.4	226.0	12.7
197.0	39.9	228.6	13.1
199.0	31.2	231.2	13.4
201.0	25.2	233.9	13.6
203.0	20.9	236.7	13.1
205.1	17.9	239.5	12.5
207.3	15.8	242.4	11.6
209.4	14.3		

Quantum Yield for COCl_2 Photolysis at 298 K

$\phi = 1.0$ for $\lambda > 184 \text{ nm}$.

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported in the recent study of Gillotay *et al.*¹ The spectrum is a continuum; the values listed are averaged over 500 cm^{-1} intervals. These results¹ are in good agreement with the earlier results of Chou *et al.*² Gillotay *et al.*¹ reported values over the wavelength range 170 to 310 nm and the temperature range 295–210 K. The temperature effect is only significant at longer wavelengths ($\lambda > 250 \text{ nm}$). The observations of Wijnen,³ Heicklen,⁴ and earlier investigators⁵ show that process (1) is the primary photolysis pathway.

References

- ¹D. Gillotay, P. C. Simon, and L. Dierickx, *Aeronomica Acta*, **A368** (1993), Institut d'Aeronomie Spatiale de Belgique, Brussels, Belgium; presented at Quadrennial Ozone Symposium, Charlottesville, Virginia, June, 1992.
- ²G. C. Chou, G. Crescentini, H. Vera-Ruiz, W. S. Smith, and F. S. Rowland, Results presented at the 173rd American Chemical Society National Meeting, New Orleans, March, 1977.
- ³W. H. Wijnen, *J. Am. Chem. Soc.* **83**, 3014 (1961).
- ⁴J. Heicklen, *J. Am. Chem. Soc.* **87**, 445 (1965).
- ⁵J. G. Calvert and J. N. Pitts, Jr., *Photochemistry* (Wiley, New York, 1966), p. 231.

CF₂ClCHO + *hν* → products**Primary photochemical transitions**

Reaction	$\Delta H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
CF ₂ ClCHO + <i>hν</i> → CF ₂ Cl + HCO (1)		
→ CF ₂ CICO + H (2)		
→ CHF ₂ Cl + CO (3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
240–370	Rattigan and Cox, 1993 ¹	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

- (a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 245–298 K. The UV spectrum of di-

fluorochloroacetaldehyde shows a broad band, centered at 300 nm and extending out to 365 nm. Values of σ were given at 5 nm intervals at 245 K and 298 K.

Preferred Values

Absorption cross-sections at 298 and 245 K

Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	
	298 K	245 K
240	0.384	0.417
245	0.703	0.751
250	1.184	1.276
255	1.910	2.021
260	2.875	3.082
265	4.181	4.451
270	5.802	6.154
275	7.623	8.108
280	9.651	10.29
285	11.61	12.32
290	13.48	14.37
295	14.74	15.59
300	15.67	16.70
305	15.49	16.08
310	15.18	15.99
315	13.22	13.80
320	11.63	12.13
325	9.367	10.03
330	6.553	6.583
335	4.800	4.840
340	2.784	2.944
345	1.516	1.393
350	0.730	0.599
355	0.113	0.070
360	0.034	0.024
365	0.011	0.007
370	0.000	0.000

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan and Cox.¹ There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

¹O. Rattigan and R. A. Cox, Final Report to SPA-AFEAS, Washington, DC (1993).

 $\text{CFCl}_2\text{CHO} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CFCl}_2\text{CHO} + h\nu \rightarrow \text{CFCl}_2 + \text{HCO}$ (1)		
$\rightarrow \text{CFCl}_2\text{CO} + \text{H}$ (2)		
$\rightarrow \text{CHFCl}_2 + \text{CO}$ (3)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–340	Rattigan and Cox, 1993 ¹	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

- (a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 253–296 K. The UV spectrum of dichlorofluoroacetaldehyde shows a broad band, centered at 295 nm and extending out to 365 nm. Values of σ were given at 5 nm intervals at 296 K and 253 K.

Preferred Values

Absorption cross-sections at 296 and 253 K

Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	
	296 K	253 K
240	0.795	0.546
245	1.069	0.934
250	1.587	1.541
255	2.377	2.405
260	3.470	3.569
265	4.853	5.022
270	6.514	6.753
275	8.343	8.662
280	10.10	10.48
285	11.79	12.22
290	12.98	13.38
295	13.76	14.16
300	13.60	13.87
305	12.91	12.91
310	11.52	11.52
315	9.783	9.427
320	7.969	7.733
325	5.599	5.159
330	3.904	3.654
335	2.449	2.108
340	1.229	1.048
345	0.623	0.446
350	0.244	0.164
355	0.041	0.025
360	0.016	0.012
365	0.007	0.004
370	0.000	0.000

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan and Cox.¹ There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

- ¹O. Rattigan and R. A. Cox, Final Report to SPA-AFEAS, Washington, DC (1993).

 $\text{CCl}_3\text{CHO} + h\nu \rightarrow \text{products}$

Primary photochemical transitions

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CCl}_3\text{CHO} + h\nu \rightarrow \text{CCl}_3 + \text{HCO}$ (1)		
$\rightarrow \text{CCl}_3\text{CO} + \text{H}$ (2)		
$\rightarrow \text{CHCl}_3 + \text{CO}$ (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
200–340	Rattigan <i>et al.</i> , 1993 ¹	(a)

Quantum yield data

There are no reported quantum yield data.

Comments

- (a) Absolute absorption cross-sections were measured using a dual-beam diode array spectrometer over the temperature range 240–300 K. The UV spectrum of trichloroacetaldehyde shows a broad band, centered at 290 nm and extending out to 360 nm. Values of σ were given at 5 nm intervals at 296 K and 243 K. A second absorption band appears at <230 nm.

Preferred Values

Absorption cross-sections at 296 and 243 K

Wavelength/nm	$10^{20} \sigma/\text{cm}^2$	
	296 K	243 K
200	115.1	110.7
205	86.14	81.89
210	48.19	43.20
215	23.88	20.32
220	10.92	9.179
225	4.759	3.527
230	2.034	1.264
235	0.944	0.430
240	0.774	0.418
245	1.135	0.882
250	1.827	1.633
255	2.799	2.659
260	3.977	3.910
265	5.360	5.388
270	6.722	6.878
275	8.012	8.368
280	9.318	9.625
285	10.08	10.35
290	10.32	10.62
295	9.886	10.06
300	9.019	9.245
305	7.671	7.602
310	6.074	5.942
315	4.572	4.446
320	3.063	2.790
325	1.901	1.741
330	1.121	0.951
335	0.498	0.322
340	0.194	0.114
345	0.086	0.043
350	0.020	0.004
355	0.002	0.000
360	0.000	0.000

Quantum Yields

No recommendation.

Comments on Preferred Values

The preferred values for the cross-sections are based on the data reported by Rattigan *et al.*¹ There are no data on the quantum yields but, by analogy with acetaldehyde which shows a similar absorption spectrum, photodissociation is expected to be predominantly by channel (1).

References

- ¹O. V. Rattigan, O. Wild, R. L. Jones, and R. A. Cox, *J. Photochem. Photobiol. A: Chem.* **73**, 1 (1993).

CF₃COCl + *hν* → products**Primary photochemical transitions**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ COCl + <i>hν</i> → CF ₃ + COCl (1)		
→ CF ₃ CO + Cl (2)		

Absorption cross-section data

Wavelength range/nm	References	Comments
200–330	Meller, Boglu, and Moortgat, 1993 ¹	(a)

Quantum yield data

Measurement	Wavelength/ nm	Reference	Comments
$\phi(1) + \phi(2) = 0.955 \pm 0.06$	254	Meller, Boglu, and Moortgat, 1993 ¹	(b)

Comments

- (a) Absolute absorption cross-sections were measured using a diode array spectrometer over the temperature range 223–298 K. The UV spectrum of trifluoroacetyl chloride shows two overlapping bands, the first having a maximum at 255 nm ($\sigma = 6.78 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$), and the second at $\lambda < 200 \text{ nm}$. There is significant absorption at wavelengths $\lambda > 300 \text{ nm}$, where the cross-sections become increasingly temperature dependent. Values of σ were given at 5 nm intervals at 298 K and 240 K as well as temperature coefficients in the long wavelength tail at $\lambda > 270 \text{ nm}$.
- (b) Average of 10 measurements of the overall loss of CF₃COCl during photolysis in air ($\phi = 0.95 \pm 0.05$) and 7 measurements in N₂ ($\phi = 0.96 \pm 0.06$) at 298 K, relative to the loss of COCl₂ for which $\phi = 1$. No pressure dependence was observed in the total pressure range 50–400 Torr.

Preferred Values**Absorption cross-sections at 298 K and 223 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$		$10^3 \times B/\text{K}^{-1}$
	298 K	223 K	
205	13.51	11.02	2.72
210	3.58	2.71	3.72
215	1.72	1.50	1.76
220	1.85	1.81	0.28
225	2.51	2.50	0.07
230	3.38	3.35	0.10
235	4.32	4.27	0.15
240	5.23	5.16	0.18
245	6.03	5.96	0.15
250	6.56	6.45	0.23
255	6.71	6.55	0.32
260	6.49	6.27	0.45
265	5.90	5.62	0.65
270	5.03	4.72	0.82
275	4.02	3.70	1.11
280	3.00	2.69	1.45
285	2.07	1.77	2.11
290	1.33	1.09	2.60
295	0.778	0.598	3.51
300	0.406	0.300	4.03
305	0.190	0.127	5.33
310	0.074	0.040	8.37
315	0.025	0.009	13.36
320	0.008	0.002	19.69
325	0.003		

^aTemperature dependence: $\log_e\{\sigma(T)/\sigma(293)\} = B(T-293)$.

Quantum Yields

$\phi(1) + \phi(2) = 1.0$ over the wavelength range 200–315 nm.

Comments on Preferred Values

The data of Meller *et al.*¹ are in generally excellent agreement with the earlier results of Rattigan *et al.*² and Jemi-Alade *et al.*,³ except in the region of minimum absorption near 220 nm. The preferred values for the cross-sections are those reported by Meller *et al.*¹ They differ significantly from the previously recommended values of Rattigan *et al.*² only in the range 215–235 nm. The temperature-dependence of the cross-section is also from Meller *et al.*¹ The quantum yield is based on the measurements of Meller *et al.*¹

References

- ¹R. Meller, D. Boglu, and G. K. Moortgat, "Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere," STEP-HALOCSIDE/AFEAS Workshop, Dublin, Eire, March 23–25, 1993, pp. 130–138.
- ²O. V. Rattigan, O. Wild, R. L. Jones, and R. A. Cox, *J. Photochem. Photobiol. A: Chem.* **73**, 1 (1993).
- ³A. A. Jemi-Alade, P. D. Lightfoot, and R. Lesclaux, *Chem. Phys. Lett.* **179**, 119 (1991).

4.8. Bromine Species

$$\Delta H^\circ = -35 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(2.5 \pm 0.4) \times 10^{-11}$	298	Monks <i>et al.</i> , 1993 ¹	(a)
<i>Reviews and Evaluations</i> 2.5×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Discharge flow system with MS detection. The pseudo-first-order decays of the HOBr concentration in the presence of excess concentrations of O(³P) atoms were monitored.
- (b) Based on the results of Monks *et al.*¹

Comments on Preferred Values

The preferred value is based on the room temperature results of Monks *et al.*¹ This is the only experimental study of this reaction. Note that the rate coefficient for this reaction is a factor of 200 greater than the rate coefficient for the corresponding reaction of O(³P) atoms with HOCl (this evaluation).

Preferred Values

$$k = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

References

¹ P. S. Monks, F. L. Nesbitt, M. Scanlon, and L. J. Stief, *J. Phys. Chem.* **97**, 11699 (1993).

² NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = -262 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $1.9 \times 10^{-11} \exp[(230 \pm 76)/T]$ 4.1×10^{-11}	233–328 298	Thorn <i>et al.</i> 1995 ¹	(a)
<i>Reviews and Evaluations</i> 3×10^{-11} $1.7 \times 10^{-11} \exp(260/T)$	298 230–330	IUPAC, 1992 ² NASA, 1994 ³	(b) (c)

Comments

- (a) Dual laser flash photolysis/long path absorption/resonance fluorescence technique.
- (b) Based on the results of Clyne *et al.*⁴
- (c) Based on the results of Thorn *et al.*¹ (then unpublished).

Preferred Values

$$k = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.9 \times 10^{-11} \exp(230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{--}330 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the results reported by Thorn *et al.*¹ using a dual laser flash photolysis/long path absorption/resonance fluorescence technique in which the decay of O(³P) in the presence of excess BrO was monitored. Clyne *et al.*⁴ reported an approximately 40% lower room temperature value.

References

¹R. P. Thorn, J. M. Crunkhite, J. M. Nicovich, and P. H. Wine, *J. Chem. Phys.* **102**, 4131 (1995).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, *Int. J. Chem. Kinet.* **8**, 425 (1976).

$$\Delta H^\circ = -163 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.4 \times 10^{-11} \exp(-590/T) \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 260\text{--}390 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

This recommendation is based on results obtained over the 260–390 K temperature range by Toohey *et al.*,¹ using a discharge flow system with LMR detection to monitor the decays of HO₂ radicals in excess Br. The value determined

by Laverdet *et al.*² is in good agreement with this recommendation. Laverdet *et al.*² have reinterpreted previous indirect measurements conducted in the same laboratory, by Poulet *et al.*,³ to give a range of values higher than had been reported³ and in agreement with the present recommendation. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

¹D. W. Toohey, Wm. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **91**, 1215 (1987).

²G. Laverdet, G. Le Bras, A. Mellouki, and G. Poulet, *Chem. Phys. Lett.* **172**, 430 (1990).

³G. Poulet, G. Laverdet, and G. Le Bras, *J. Chem. Phys.* **80**, 1922 (1984).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = 2.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 14 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values ($k = k_1 + k_2$)

$$k = < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The upper limit to the preferred value is based on the data of Toohey *et al.*,¹ who also obtained the same upper limit at 378 K using a discharge flow–resonance fluorescence/LMR

technique. This preferred value is identical to that in our previous evaluation, IUPAC, 1992.²

References

¹D. W. Toohey, Wm. H. Brune, and J. G. Anderson, *J. Phys. Chem.* **91**, 1215 (1987).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -130 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.7 \times 10^{-11} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 195–392 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
 $\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The recommended Arrhenius expression is based on a fit to the results of Toohey *et al.*,¹ Clyne and Watson,² Leu and DeMore,³ Michael *et al.*,⁴ Michael and Payne,⁵ and Nicovich

*et al.*⁶ The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁷

References

- ¹D. W. Toohey, W. H. Brune, and J. G. Anderson, *Int. J. Chem. Kinet.* **20**, 131 (1988).
- ²M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **71**, 336 (1975).
- ³M. T. Leu and W. B. DeMore, *Chem. Phys. Lett.* **48**, 317 (1977).
- ⁴J. V. Michael, J. H. Lee, W. A. Payne, and L. J. Stief, *J. Chem. Phys.* **68**, 4093 (1978).
- ⁵J. V. Michael and W. A. Payne, *Int. J. Chem. Kinet.* **11**, 799 (1979).
- ⁶J. M. Nicovich, K. D. Kreutter, and P. H. Wine, *Int. J. Chem. Kinet.* **22**, 399 (1990).
- ⁷IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -82 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 4.2 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The recommended values of Ref. 1 are consistent with theoretical predictions. The falloff curves are represented with $F_c = 0.55$ at 298 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.4$ over the range 200–300 K.

Comments on Preferred Values

See comments on k_0 . There is only a single determination of k_∞ , but the measured falloff curve appears well behaved

with rate coefficients close to those of the reactions $\text{I} + \text{NO} + \text{M}$ and $\text{I} + \text{NO}_2 + \text{M}$ (see this evaluation). These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

- ¹K. D. Kreutter, J. M. Nicovich, and P. H. Wine, *J. Phys. Chem.* **95**, 4020 (1991).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 19 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.6 \times 10^{-11} \exp(-1300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over
 the temperature range 200–450 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred value at 298 K is the mean of the values reported by Toohey¹ and Clyne and Watson.² The latter study² required correction for the effect of the reverse reaction on the decay of OClO, which was not taken into account

in the earlier study of Clyne and Coxon³ and which is therefore disregarded. The temperature dependence of Toohey¹ is accepted. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

¹D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. Thesis, Harvard University, Cambridge, MA (1988).

²M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **73**, 1169 (1977).

³M. A. A. Clyne and J. A. Coxon, *Proc. R. Soc. London, Ser. A* **298**, 424 (1967).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -77.1 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-11} \exp[-(435 \pm 30)/T]$ $(4.8 \pm 0.2) \times 10^{-12}$	233–404 298	Stevens and Anderson, 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
$2.1 \times 10^{-11} \exp(-520/T)$	220–298	IUPAC, 1992 ²	(b)
$2.1 \times 10^{-11} \exp(-470/T)$	220–400	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow system. The pseudo-first-order decays of Br atoms in excess Cl_2O were measured, with detection by resonance fluorescence.
- (b) Based on the results of Sander and Friedl.⁴
- (c) Based on the results of Stevens and Anderson¹ and Sander and Friedl.⁴

Preferred Values

$k = 4.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.1 \times 10^{-11} \exp(-470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the
 temperature range 220–400 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred value is based on the results reported by Stevens and Anderson¹ and Sander and Friedl.⁴ These results obtained using totally different techniques^{1,4} are in good agreement. The significantly lower value (by a factor of 4) reported earlier by Basco and Dogra⁵ has been rejected. In that same study, Basco and Dogra⁵ reported a value of $k(\text{Cl} + \text{Cl}_2\text{O})$ more than two orders of magnitude less than that recommended in this evaluation, suggesting the possibility of a systematic error in their method of determination of ClO radical concentrations.

References

¹P. S. Stevens and J. G. Anderson, *J. Phys. Chem.* **96**, 1708 (1992).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³NASA Evaluation No. 11, 1994 (see references in Introduction).

⁴S. P. Sander and R. R. Friedl, *J. Phys. Chem.* **93**, 4764 (1989).

⁵N. Basco and S. K. Dogra, *Proc. R. Soc. London, Ser. A* **323**, 401 (1971).

$\Delta H^\circ = -127.4 \text{ kJ} \cdot \text{mol}^{-1}$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on results of the discharge flow-mass spectrometric study of Friedl.¹ The preferred value is identical to that in our previous evaluation, IUPAC, 1992.²

References

¹R. R. Friedl, unpublished data (1991).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

Br + HCHO → HBr + HCO

$$\Delta H^\circ = 2.2 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.7 \times 10^{-11} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 223\text{--}480 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 250 \text{ K.}$$

Comments on Preferred Values

The preferred rate expression is obtained from a least-squares analysis of the absolute rate coefficient data of Nava *et al.*¹ and Poulet *et al.*,² which are in reasonably good agreement. The Arrhenius expression is identical to our previous evaluation, IUPAC, 1992.³

References

¹D. F. Nava, J. V. Michael, and L. J. Stief, *J. Phys. Chem.* **85**, 1896 (1981).

²G. Poulet, G. Laverdet, and G. Le Bras, *J. Phys. Chem.* **85**, 1892 (1981).

³IUPAC, Supplement IV, 1992 (see references in Introduction).

Br + CH₃CHO → HBr + CH₃CO

$$\Delta H^\circ = -6.7 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.3 \times 10^{-11} \exp(-360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficients of Nicovich *et al.*¹ and Islam *et al.*² and the relative rate coefficient of Niki *et al.*³ The temperature dependence is that measured by Nicovich *et al.*,¹ with the A factor being adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is

consistent with the recent relative rate studies of Barnes *et al.*⁴ and Wallington *et al.*⁵ [which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH₃CHO]. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁶

References

¹J. M. Nicovich, C. J. Shackelford, and P. H. Wine, *J. Photochem. Photobiol., A: Chemistry*, **51**, 141 (1990).

²T. S. A. Islam, R. M. Marshall, and S. W. Benson, *Int. J. Chem. Kinet.* **16**, 1161 (1984).

³H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, *Int. J. Chem. Kinet.* **17**, 525 (1985).

⁴I. Barnes, V. Bastian, K. H. Becker, R. Overath, and Z. Tong, *Int. J. Chem. Kinet.* **21**, 499 (1989).

⁵T. J. Wallington, L. M. Skewes, W. O. Siegl, and S. M. Japar, *Int. J. Chem. Kinet.* **21**, 1069 (1989).

⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -132.9 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.97 \pm 0.46) \times 10^{-11}$	170	Sims <i>et al.</i> , 1995 ¹	(a)
$(1.16 \pm 0.04) \times 10^{-11}$	295		
<i>Reviews and Evaluations</i>			
1.1×10^{-11}	249–416	IUPAC, 1992 ²	(b)
1.1×10^{-11}	249–416	NASA, 1994 ³	(b)

Comments

- (a) Pulsed laser photolysis system with LIF detection of HO radicals, using an isentropic expansion of gas through a Laval nozzle to provide a collimated flow of cold gas at a uniform temperature, density, and velocity. Experiments were carried out over the temperature range 23–295 K, with the measured rate coefficient decreasing with increasing temperature from $(1.07 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 23 K to $(1.16 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K. Combined with the rate coefficients of Ravishankara *et al.*,⁴ the temperature-dependent expression $k = (1.26 \pm 0.24) \times 10^{-11} (T/298)^{-(0.86 \pm 0.10)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived.
- (b) Based on the absolute rate coefficients of Ravishankara *et al.*,^{4,5} Jourdain *et al.*,⁶ and Cannon *et al.*⁷

trast, the absolute rate coefficients measured by Ravishankara *et al.*⁴ over the temperature range 249–416 K were independent of temperature within the experimental uncertainties.

The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Ravishankara *et al.*,^{4,5} Jourdain *et al.*,⁶ Cannon *et al.*,⁷ and Sims *et al.*¹ The temperature dependence is obtained from the rate coefficients of Sims *et al.*¹ over the temperature range 23–295 K. The preferred rate expression predicts rate coefficients at 249 K and 416 K of $1.27 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $8.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, with that at 249 K being in excellent agreement with the rate coefficient measured by Ravishankara *et al.*⁴ [$(1.31 \pm 0.08) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] and that at 416 K being 30% lower than that measured by Ravishankara *et al.*⁴ The uncertainties on the values of n in $k = A (T/298)^{-n}$ encompass a temperature-independent rate coefficient.

Preferred Values

$$k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.1 \times 10^{-11} (T/298)^{-0.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta n = \begin{matrix} +0.8 \\ -0.2 \end{matrix}$$

Comments on Preferred Values

The recent absolute rate study of Sims *et al.*¹ yields rate coefficients which exhibit a significant negative temperature dependence over the temperature range 23–295 K. In con-

References

1. R. Sims, I. W. M. Smith, D. C. Clary, P. Bocherel, and B. R. Rowe, *J. Chem. Phys.* **102**, 1748 (1995).
2. IUPAC, Supplement IV, 1992 (see references in Introduction).
3. NASA Evaluation No. 11, 1994 (see references in Introduction).
4. A. R. Ravishankara, P. H. Wine, and J. R. Wells, *J. Chem. Phys.* **83**, 447 (1985).
5. A. R. Ravishankara, P. H. Wine, and A. O. Langford, *Chem. Phys. Lett.* **63**, 479 (1979).
6. J. L. Jourdain, G. Le Bras, and J. Combourieu, *Chem. Phys. Lett.* **78**, 483 (1981).
7. B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, *Chem. Phys. Lett.* **105**, 380 (1984).

$$\Delta H^\circ = -8 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 4.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.2 \times 10^{-11} \exp(400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–360 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The rate constant is reasonably well determined at room temperature, and the recommended value is the mean of those reported in Refs. 1–4. Boodaghians *et al.*² found a near zero temperature dependence over the range 262–303 K. In

contrast, the data of Toohey³ display a significant negative temperature dependence in the range 260–360 K. The latter result is preferred, and the recommendation for E/R is based on this study.³ Loewenstein and Anderson¹ determined that the products are exclusively $\text{Br} + \text{HOBr}$. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

- ¹L. M. Loewenstein and J. G. Anderson, *J. Phys. Chem.* **88**, 6277 (1984).
- ²R. B. Boodaghians, I. W. Hall, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **83**, 529 (1987).
- ³D. W. Toohey, private communication (1988).
- ⁴G. Poulet, G. Laverdet, and G. Le Bras, *Chem. Phys. Lett.* **94**, 129 (1983).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -74.0 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.86 \times 10^{-12} \exp[-(1230 \pm 150)/T]$	248–390	Chichinin <i>et al.</i> , 1994 ¹	(a)
$(3.03 \pm 0.45) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$3.84 \times 10^{-18} T^2 \exp[-(692 \pm 46)/T]$	298–360	Hsu and DeMore, 1994 ²	(b)
3.16×10^{-14}	298		
<i>Reviews and Evaluations</i>			
$1.9 \times 10^{-12} \exp(-1240/T)$	240–300	IUPAC, 1992 ³	(c)
$3.62 \times 10^{-18} T^2 \exp(-711/T)$	233–400	Atkinson, 1994 ⁴	(d)
$4.0 \times 10^{-12} \exp(-1470/T)$	233–400	NASA, 1994 ⁵	(e)

Comments

- (a) Discharge flow system with EPR detection of HO radicals.
- (b) Relative rate method. HO radicals were generated from the UV photolysis of O_3 in the presence of water vapor, in $\text{O}_3\text{-H}_2\text{O-CH}_3\text{Br-CH}_3\text{CHF}_2\text{-O}_2\text{-N}_2$ mixtures. The concentrations of CH_3Br and CH_3CHF_2 were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{Br})/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (1.94 \pm 0.28) \exp[-(232 \pm 46)/T]$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 1.98 \times 10^{-18} T^2 \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Derived from the absolute rate coefficients of Mellouki *et al.*⁶ and Zhang *et al.*⁷
- (d) Derived from the absolute rate coefficients of Mellouki *et al.*⁶ and Zhang *et al.*⁷ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (e) Based on the rate coefficients of Mellouki *et al.*,⁶ Zhang *et al.*,⁷ Chichinin *et al.*,¹ and Hsu and DeMore.²

Preferred Values

$k = 2.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.7 \times 10^{-12} \exp(-1215/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 150 \text{ K}$.

Comments on Preferred Values

The recent absolute rate coefficient measurements of Mellouki *et al.*,⁶ Zhang *et al.*,⁷ and Chichinin *et al.*,¹ which are in excellent agreement, are significantly lower than those previously determined by Howard and Evenson⁸ and Davis *et al.*⁹ The relative rate coefficients of Hsu and DeMore² are also in excellent agreement with the absolute rate coefficients of Mellouki *et al.*,⁶ Zhang *et al.*,⁷ and Chichinin *et al.*¹ A unit-weighted least-squares analysis of the rate coefficients of Mellouki *et al.*,⁶ Zhang *et al.*,⁷ and Chichinin *et al.*,¹ using the three parameter expression $k = CT^2 \exp(-D/T)$, leads to $k = 3.44 \times 10^{-18} T^2 \exp(-687/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over

the temperature range 233–400 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K and is derived from three parameter expression with $A=C e^2 T^2$ and $B=D+2T$.

References

- ¹A. Chichinin, S. Téton, G. Le Bras, and G. Poulet, *J. Atmos. Chem.* **18**, 239 (1994).
²K.-J. Hsu and W. B. DeMore, *Geophys. Res. Lett.* **21**, 805 (1994).

- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
⁴R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
⁶A. Mellouki, R. K. Talukdar, A.-M. Schmoltner, T. Gierczak, M. J. Mills, S. Solomon, and A. R. Ravishankara, *Geophys. Res. Lett.* **19**, 2059 (1992).
⁷Z. Zhang, R. D. Saini, M. J. Kurylo, and R. E. Huie, *Geophys. Res. Lett.* **19**, 2413 (1992).
⁸C. J. Howard, and K. M. Evenson, *J. Chem. Phys.* **64**, 197 (1976).
⁹D. D. Davis, G. Machado, B. C. Conaway, Y. Oh, and R. T. Watson, *J. Chem. Phys.* **65**, 1268 (1976).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.91 \times 10^{-12} \exp[-(840 \pm 100)/T]$ $(1.13 \pm 0.11) \times 10^{-13}$	243–380 298	Mellouki <i>et al.</i> , 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.9 \times 10^{-12} \exp(-840/T)$	243–380	NASA, 1994 ²	(b)

Comments

- (a) Laser photolysis system with LIF detection of HO radicals.
 (b) Based on the absolute rate coefficients of Mellouki *et al.*¹

Preferred Values

$k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.5 \times 10^{-12} \exp(-775/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Mellouki *et al.*¹ have been fitted to the three parameter equation $k=CT^2 \times \exp(-D/T)$, resulting in $k=2.86 \times 10^{-18} T^2 \exp(-246/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 243–380 K. The preferred Arrhenius expression, $k=A \exp(-B/T)$, is centered at 265 K and is derived from the three parameter equation with $A=C e^2 T^2$ and $B=D+2T$.

References

- ¹A. Mellouki, R. K. Talukdar, A.-M. Schmoltner, T. Gierczak, M. J. Mills, S. Solomon, and A. R. Ravishankara, *Geophys. Res. Lett.* **19**, 2059 (1992).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$9.3 \times 10^{-13} \exp[-(1326 \pm 33)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(1.10 \pm 0.09) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$3.18 \times 10^{-20} T^{2.58} \exp[-(622 \pm 31)/T]$	283–368	Hsu and DeMore, 1995 ²	(b)
9.60×10^{-15}	298		
<i>Reviews and Evaluations</i>			
$7.7 \times 10^{-13} \exp(-1310/T)$	240–300	IUPAC, 1992 ³	(c)
$1.48 \times 10^{-18} T^2 \exp(-779/T)$	233–432	Atkinson, 1994 ⁴	(d)
$1.1 \times 10^{-12} \exp(-1400/T)$	233–460	NASA, 1994 ⁵	(e)

Comments

- (a) Discharge flow system with EPR detection of HO radicals.
- (b) Relative rate method. HO radicals were generated by the UV photolysis of O₃ in the presence of water vapor in O₃-H₂O-CHF₂Br-CH₄-O₂-N₂ mixtures. The concentrations of CHF₂Br and CH₄ were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CHF}_2\text{Br})/k(\text{HO} + \text{CH}_4) = (0.33 \pm 0.03) \times \exp[(460 \pm 31)/T]$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{CH}_4) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation).
- (c) Based on the absolute rate coefficients of Talukdar *et al.*⁶
- (d) Based on the absolute rate coefficients of Talukdar *et al.*,⁶ using the three parameter equation $k = CT^2 \exp(-D/T)$.
- (e) Derived from the absolute rate coefficients of Talukdar *et al.*⁶ and Orkin and Khamaganov¹ and the relative rate coefficients of Hsu and DeMore.²

Preferred Values

$k = 9.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.1 \times 10^{-13} \exp(-1315/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta(E/R) = \pm 150 \text{ K}$.

Comments on Preferred Values

The absolute and relative rate coefficients of Talukdar *et al.*,⁶ Orkin and Khamaganov,¹ and Hsu and DeMore² are in excellent agreement, but are significantly lower than the absolute rate coefficients of Brown *et al.*⁷ The absolute rate coefficients of Talukdar *et al.*⁶ and Orkin and Khamaganov¹ have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.56 \times 10^{-18} T^2 \exp(-786/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 233–460 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is obtained from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$.

References

- ¹V. L. Orkin and V. G. Khamaganov, *J. Atmos. Chem.* **16**, 169 (1993).
- ²K.-J. Hsu and W. B. DeMore, *J. Phys. Chem.* **99**, 1235 (1995).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
- ⁵NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁶R. Talukdar, A. Mellouki, T. Gierczak, J. B. Burkholder, S. A. McKeen, and A. R. Ravishankara, *Science* **252**, 693 (1991).
- ⁷A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, *Nature* **347**, 541 (1990).

HO + CF₃Br(Halon 1301) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$<4 \times 10^{-16}$	298	Orkin and Khamaganov, 1993 ¹	(a)
$<4 \times 10^{-16}$	460		
<i>Reviews and Evaluations</i>			
$<1 \times 10^{-16}$	298	IUPAC, 1992 ²	(b)
$<1 \times 10^{-16}$	298	Atkinson, 1994 ³	(b)
$<1.2 \times 10^{-16}$	298	NASA, 1994 ⁴	(b)

Comments

- (a) Discharge flow system with EPR detection of HO radicals.
- (b) Based on the data of Burkholder *et al.*⁵

$\times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ determined by Burkholder *et al.*⁵ at 294 and 373 K, and is identical to our previous evaluation, IUPAC, 1992.²

Preferred Values

$k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient at 298 K is based on the upper limits to the rate coefficients of <1

References

- ¹V. L. Orkin and V. G. Khamaganov, *J. Atmos. Chem.* **16**, 169 (1993).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
⁵J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).

HO + CF₂ClBr(Halon 1211) → products

No new data have been published since our last evaluation.

Preferred Values

$k < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Holt,² and is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).
²M. A. A. Clyne and P. M. Holt, *J. Chem. Soc. Faraday Trans. 2*, **75**, 569 (1979).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

HO + CF₂Br₂(Halon 1202) → products

No new data have been published since our last evaluation.

Preferred Values

$k < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Burkholder *et al.*¹ The preferred upper limit to the rate coefficient at 298 K is confirmed by the values of $k \leq 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured at 384 and 424 K,¹ and is identical to our previous evaluation, IUPAC, 1992.²

Comments on Preferred Values

The preferred upper limit is based on the sole study of

References

²IUPAC, Supplement IV, 1992 (see references in Introduction).

¹J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$8.5 \times 10^{-13} \exp[-(1113 \pm 35)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(2.05 \pm 0.16) \times 10^{-14}$	298		
$1.39 \times 10^{-12} \exp[-(1350 \pm 195)/T]$	280–353	Nelson, Zahniser, and Kolb, 1993 ²	(b)
$(1.45 \pm 0.13) \times 10^{-14}$	294		
<i>Reviews and Evaluations</i>			
$1.44 \times 10^{-12} \exp(-1337/T)$	280–460	Atkinson, 1994 ³	(c)

Comments

$$\Delta(E/R) = \pm 300 \text{ K.}$$

- (a) Discharge flow system with EPR detection of HO radicals.
 (b) Discharge flow system with LIF detection of HO radicals.
 (c) Based on the absolute rate coefficients of Orkin and Khamaganov¹ and Nelson *et al.*²

Comments on Preferred Values

The rate coefficients of Nelson *et al.*² are $\sim 15\%$ – 25% lower than those of Orkin and Khamaganov¹ over the temperature range common to both studies (298–353 K). A least-squares analysis of the rate coefficients of Orkin and Khamaganov¹ and Nelson *et al.*² yields the preferred Arrhenius expression.

Preferred Values

$k = 1.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.4 \times 10^{-12} \exp(-1335/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 280–460 K.

References

- ¹V. L. Orkin and V. G. Khamaganov, *J. Atmos. Chem.* **16**, 169 (1993).
²D. D. Nelson, Jr., M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **20**, 197 (1993).
³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$7.2 \times 10^{-13} \exp[-(1111 \pm 32)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(1.75 \pm 0.17) \times 10^{-14}$	298		
<i>Reviews and Evaluations</i>			
$1.1 \times 10^{-12} \exp(-1250/T)$	270–430	IUPAC, 1992 ²	(b)
$8.09 \times 10^{-13} \exp(-1157/T)$	279–460	Atkinson, 1994 ³	(c)

Comments

- (c) Based on the absolute rate coefficients of Brown *et al.*⁴ and Orkin and Khamaganov.¹

Preferred Values

$k = 1.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

- (a) Discharge flow system with EPR detection of HO radicals.
 (b) Based on the absolute rate coefficients of Brown *et al.*⁴

$k = 8.1 \times 10^{-13} \exp(-1155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 279–460 K.

analysis of the rate coefficients of Brown *et al.*⁴ and Orkin and Khamaganov¹ yields the preferred values.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The absolute rate coefficients of Brown *et al.*⁴ and Orkin and Khamaganov¹ are in good agreement. A least-squares

References

¹V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

⁴A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell, and R. P. Wayne, Nature **347**, 541 (1990).

HO + CF₃CHClBr (Halon 2311) → H₂O + CF₃CClBr

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.28 \times 10^{-12} \exp[-(995 \pm 38)/T]$	298–460	Orkin and Khamaganov, 1993 ¹	(a)
$(4.50 \pm 0.40) \times 10^{-14}$	298		
<i>Reviews and Evaluations</i>			
5.8×10^{-14}	298	IUPAC, 1992 ²	(b)
$1.2 \times 10^{-12} \exp(-970/T)$	298–460	Atkinson, 1994 ³	(c)

Comments

- (a) Discharge flow system with EPR detection of HO radicals.
- (b) Based on the absolute rate coefficient of Brown *et al.*⁴
- (c) Based on the absolute rate coefficients of Orkin and Khamaganov.¹

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficient of Brown *et al.*⁴ at 303 K is ~25% higher than that calculated from the Arrhenius expression of Orkin and Khamaganov.¹ A least-squares analysis of the rate coefficients of Orkin and Khamaganov¹ leads to the preferred Arrhenius expression.

Preferred Values

$k = 4.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.2 \times 10^{-12} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 298–460 K.

Reliability

$\Delta \log k = \pm 0.20$ at 298 K.

References

¹V. L. Orkin and V. G. Khamaganov, J. Atmos. Chem. **16**, 169 (1993).

²IUPAC, Supplement IV, 1992 (see references in Introduction).

³R. Atkinson, J. Phys. Chem. Ref. Data, **Monograph 2**, 1 (1994).

⁴A. C. Brown, C. E. Canosa-Mas, A. D. Parr, and R. P. Wayne, Atmos. Environ. **24A**, 2499 (1990).

HO + CF₂BrCF₂Br (Halon 2402) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$<4\times 10^{-16}$	298	Orkin and Khamaganov, 1993 ¹	(a)
$<4\times 10^{-16}$	460		
<i>Reviews and Evaluations</i>			
$<1.3\times 10^{-16}$	298	IUPAC, 1992 ²	(b)
$<1.5\times 10^{-16}$	298	Atkinson, 1994 ³	(b)
$<1.5\times 10^{-16}$	298	NASA, 1994 ⁴	(b)

Comments

- (a) Discharge flow system with EPR detection of HO radicals.
- (b) Based on the upper limits to the rate coefficients measured by Burkholder *et al.*⁵

ation, IUPAC, 1992.² The upper limit to the rate coefficient at 374 K of $<1.4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ⁵ confirms the upper limit observed at 298 K.

Preferred Values

$$k < 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the study of Burkholder *et al.*⁵ and is identical to our previous evalu-

References

- ¹V. L. Orkin and V. G. Khamaganov, *J. Atmos. Chem.* **16**, 169 (1993).
²IUPAC, Supplement IV, 1992 (see references in Introduction).
³R. Atkinson, *J. Phys. Chem. Ref. Data*, **Monograph 2**, 1 (1994).
⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
⁵J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).

$$\Delta H^\circ = -27 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.6 \pm 0.5) \times 10^{-11}$	298	Mellouki <i>et al.</i> , 1989 ¹	(a)
<i>Reviews and Evaluations</i>			
1.6×10^{-11}	298	NASA, 1994 ²	(b)

Comments

- (a) Discharge flow system. The decays of Br atoms in excess concentrations of the NO₃ radical were monitored by EPR. Computer simulations of the decays were carried out with a mechanism consisting of five reactions.
- (b) Based on the results of Mellouki *et al.*¹

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the room temperature results of Mellouki *et al.*¹ This study,¹ using the discharge flow-EPR technique, is the only experimental study of this reaction.

References

- ¹A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, *J. Phys. Chem.* **93**, 8017 (1989).
²NASA Evaluation No. 11, 1994 (see references in Introduction).

Preferred Values

$$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$\Delta H^\circ = -57 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(0.3-3.0) \times 10^{-12}$	298	Mellouki <i>et al.</i> , 1989 ¹	(a)
<i>Reviews and Evaluations</i>			
1.0×10^{-12}	298	NASA, 1994 ²	(b)

Comments

- (a) Discharge flow system. The decays of Br atoms and BrO radicals were monitored by EPR. Computer simulations of the results were carried out with a mechanism consisting of five reactions.
- (b) Based on the results of Mellouki *et al.*¹

Preferred Values

$$k = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the room temperature results of Mellouki *et al.*¹ This study,¹ using the discharge flow-EPR technique, is the only experimental study of this reaction. The preferred value is the geometric mean of the upper and lower limits,¹ which are encompassed within the stated uncertainty factor. The Br-O₂ bond is very weak and the bond energy has been estimated by Blake *et al.*³ to be 4 kJ mol⁻¹. Thus the product BrOO will quickly fall apart to yield Br + O₂.

References

- ¹ A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, *J. Phys. Chem.* **93**, 8017 (1989).
² NASA Evaluation No. 11, 1994 (see references in Introduction).
³ J. A. Blake, R. J. Browne, and G. Burns, *J. Chem. Phys.* **53**, 3320 (1970).

$$\Delta H^\circ = -60.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 1 \times 10^{-16}$	298	Mellouki <i>et al.</i> , 1989 ¹	(a)
$(1.3 \pm 1.1) \times 10^{-16}$	298	Canosa-Mas <i>et al.</i> , 1989 ²	(b)
<i>Reviews and Evaluations</i>			
$< 1 \times 10^{-16}$	298	NASA, 1994 ³	(c)

Comments

- (a) Discharge flow-EPR technique. Value derived from fitting the measured data to a complex mechanism.
- (b) Discharge flow-multipath absorption technique. Value derived from fitting the measured data to a complex mechanism.
- (c) Based on the results of Mellouki *et al.*¹

Preferred Values

$$k = < 1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is the upper limit reported by Mellouki *et al.*¹ in a study using the discharge flow-EPR technique. Canosa-Mas *et al.*² reported a value derived from fitting their data to a complex mechanism which, within the stated uncertainty limits, is consistent with the upper limit reported by Mellouki *et al.*¹

References

- ¹ A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, *J. Phys. Chem.* **93**, 8017 (1989).
² C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, *J. Chem. Soc. Faraday Trans. 2*, **85**, 709 (1989).
³ NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ(1) = -190 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -33 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.3 \pm 0.5) \times 10^{-11}$	298	Poulet <i>et al.</i> , 1992 ¹	(a)
$(3.4 \pm 1.0) \times 10^{-11}$	298	Bridier, Veyret, and Lesclaux, 1993 ²	(b)
<i>Reviews and Evaluations</i>			
$6.2 \times 10^{-12} \exp(500/T)$	200–300	IUPAC, 1992 ³	(c)
$6.2 \times 10^{-12} \exp(500/T)$	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge flow system in which the pseudo-first-order decays of BrO in excess HO₂ were monitored by mass spectrometry.
- (b) Flash photolysis/UV absorption technique.
- (c) Based on the room temperature results of Poulet *et al.*¹ and an estimated temperature dependence.
- (d) Based on the room temperature results of Poulet *et al.*¹ and Bridier *et al.*² and an estimated temperature dependence.

Preferred Values

$$k = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 6.2 \times 10^{-12} \exp(500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The preferred value at 298 K is based on the recent study of Poulet *et al.*¹ in which BrO radical decays in excess HO₂

were monitored by DF/MS. This room temperature rate coefficient value is confirmed by the recent results of Bridier *et al.*² using a completely different technique. These new results are preferred over those reported in the earlier study of Cox and Sheppard⁵ by molecular modulation-UV absorption in which a much lower value (by a factor of 6) was reported. The temperature dependence is our estimate, based on analogy with the ClO + HO₂ reaction. In the study of Poulet *et al.*,¹ the only product observed was HOBr. From a study of the reverse reaction at above room temperature, Mellouki *et al.*⁶ have determined by extrapolation that the yield of HBr + O₃ is negligible (<0.01%) down to 200 K.

References

- ¹ G. Poulet, M. Pirre, F. Maguin, R. Ramaroson, and G. Le Bras, *Geophys. Res. Lett.* **19**, 2305 (1992).
- ² I. Bridier, B. Veyret, and R. Lesclaux, *Chem. Phys. Lett.* **201**, 563 (1993).
- ³ IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴ NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵ R. A. Cox and D. W. Sheppard, *J. Chem. Soc. Faraday Trans. 2*, **78**, 1383 (1982).
- ⁶ A. Mellouki, R. K. Talukdar, and C. J. Howard, *J. Geophys. Res.* **99**, 22949 (1994).

$$\Delta H^\circ = -156 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$< 5 \times 10^{-17}$	298	Mauldin, Wahner, and Ravishankara, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$< 5 \times 10^{-15}$	298	IUPAC, 1992 ²	(b)
$< 1 \times 10^{-12} \exp(-3000/T)$	200–300	NASA, 1994 ³	(c)

Comments

- (a) Flash photolysis-long path UV absorption technique. The upper limit was derived from an analysis of the [BrO] temporal profiles.
- (b) Based on the results of Sander and Watson.⁴
- (c) Based on the room temperature upper limit of Mauldin *et al.*¹ and an estimated *A*-factor.

Preferred Values

$$k = < 5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred upper limit is based on the results reported by Mauldin *et al.*¹ As a result of improved sensitivity for detection of BrO, this upper limit is a factor of 100 less than that reported by Sander and Watson,⁴ who carried out similar experiments. The 298 K value should also be a reasonably good upper limit for stratospheric temperatures.

References

- ¹R. L. Mauldin III, A. Wahner, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 7585 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴S. P. Sander and R. T. Watson, *J. Phys. Chem.* **85**, 4000 (1981).

$$\Delta H^\circ = -70 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.7 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 224\text{--}425 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies^{1–3} and the high pressure UV absorption study,⁴ which all used pseudo-first-order conditions, are in excellent agreement at 298 K and are considered to be more reliable than the earlier low pressure UV absorption study of Clyne and Cruse.⁵ The results of the two temperature dependence studies^{3,4} are in good agreement. The preferred Arrhenius expression is derived from a least-squares fit to all the data in

Refs. 1–4. By combining the data reported in the high pressure UV absorption study⁴ with those from the mass spectrometric studies,^{1–3} it can be shown that this reaction does not exhibit any observable pressure dependence between 1 mbar and 1 bar total pressure. The temperature dependences of the rate coefficient for the analogous ClO and HO₂ reactions are also negative and similar in magnitude. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁶

References

- ¹M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **71**, 336 (1975).
- ²G. W. Ray and R. T. Watson, *J. Phys. Chem.* **85**, 2955 (1981).
- ³M. T. Leu, *Chem. Phys. Lett.* **61**, 275 (1979).
- ⁴R. T. Watson, S. P. Sander, and Y. L. Yung, *J. Phys. Chem.* **83**, 2936 (1979).
- ⁵M. A. A. Clyne and H. W. Cruse, *Trans. Faraday Soc.* **66**, 2227 (1970).
- ⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -111 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$5.4 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2]$	248–346	Thorn, Daykin, and Wine, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$4.7 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2]$	200–300	IUPAC, 1992 ²	(b)
$5.2 \times 10^{-31} (T/300)^{-3.2} [\text{air}]$	200–300	NASA, 1994 ³	(c)
$1.7 \times 10^{-30} [\text{N}_2]$	200	Rayez and Destriau, 1993 ⁴	(d)
$5.2 \times 10^{-31} [\text{N}_2]$	300		

Comments

- (a) Photolysis of $\text{Br}_2\text{-NO}_2\text{-N}_2$ (or CF_4) mixtures at 351 nm. BrO was generated by the reaction $\text{O}(^3\text{P}) + \text{Br}_2 \rightarrow \text{BrO} + \text{Br}$ and monitored by absorption at 338.3 nm in a multipass system (up to 552 cm). Bath gas pressures were varied over the range 16–800 Torr. Data are based on an analysis with $F_c = \exp(-T/327)$. If a $F_c = 0.6$ is used, a rate coefficient of $k_0 = 5.2 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is obtained.
- (b) Average of the data of Refs. 1 (preliminary version), 5, and 6 using $F_c = \exp(-T/327)$ for the falloff extrapolation.
- (c) Recommended value was based on the values from Ref. 1, which are in excellent agreement with those of Ref. 5.
- (d) Theoretical calculation⁷ of k_0 using $\Delta H_0^\circ = 135 \text{ kJ mol}^{-1}$ and $\beta_c = 0.37$ and 0.28 at 200 K and 300 K,

respectively. If $\Delta H_0^\circ = 151 \text{ kJ mol}^{-1}$ is employed, β_c values of 0.16 and 0.12 are obtained at 200 K and 300 K, respectively.

Preferred Values

$$k_0 = 4.7 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}300 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta n = \pm 1.$$

Comments on Preferred Values

The preferred values, which are based on data from Refs. 1, 5, and 6, are identical to our previous evaluation, IUPAC, 1992.²

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-11} (T/300)^{-1.2}$	248–346	Thorn, Daykin, and Wine, 1993 ¹	(a)
<i>Reviews and Evaluations</i>			
$1.7 \times 10^{-11} (T/298)^{-0.6}$	200–300	IUPAC, 1992 ²	(b)
$6.9 \times 10^{-12} (T/300)^{-2.9}$	200–300	NASA, 1994 ³	(c)
4.0×10^{-12}	200	Rayez and Destriau, 1993 ⁴	(d)
5.0×10^{-12}	300		

Comments

- (a) See comment (a) for k_0 . If instead of $F_c = \exp(-T/327)$, a fixed value of $F_c = 0.6$ is employed in fitting the falloff curves, a rate coefficient of $k_\infty = 6.9 \times 10^{-12} (T/300)^{-2.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is obtained.

- (b) See comment (b) for k_0 . A temperature-independent value would be also compatible with the available data.
- (c) See comment (c) for k_0 .
- (d) Theoretical calculations⁸ using $\Delta H_0^\circ = 135 \text{ kJ mol}^{-1}$. If $\Delta H_0^\circ = 151 \text{ kJ mol}^{-1}$ is employed, $k_\infty = 5.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are obtained at 200 K and 300 K, respectively.

Preferred Values

$k_{\infty} = 1.7 \times 10^{-11} (T/300)^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.1$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹R. P. Thorn, E. P. Daykin, and P. H. Wine, *Int. J. Chem. Kinet.* **25**, 521 (1993).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁴M. T. Rayez and M. Destriau, *Chem. Phys. Lett.* **206**, 278 (1993).
- ⁵S. P. Sander, G. W. Ray, and R. T. Watson, *J. Phys. Chem.* **85**, 199 (1981).
- ⁶F. Danis, F. Caralp, J. Masanet, and R. Lesclaux, *Chem. Phys. Lett.* **167**, 450 (1990).
- ⁷J. Troe, *J. Chem. Phys.* **66**, 4758 (1977); *J. Phys. Chem.* **83**, 114 (1979).
- ⁸J. Troe, *Z. Phys. Chem. NF* **161**, 209 (1989).

$$\Delta H^{\circ}(1) = -19 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^{\circ}(2) = -17 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^{\circ}(3) = -212 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k_1 = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 6.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_3 = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1 = 1.6 \times 10^{-12} \exp(430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

$k_2 = 2.9 \times 10^{-12} \exp(220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

$k_3 = 5.8 \times 10^{-13} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.1$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \Delta(E_3/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

In recent years there has been a substantial improvement in the data-base for this rate coefficient. Friedl and Sander,¹ using discharge flow-mass spectrometry techniques, measured the overall rate constant over the temperature range 220–400 K and also over this temperature range determined directly the branching ratios for the reaction channels producing BrCl and OCIO. In a separate study the same authors, using flash photolysis-ultraviolet absorption techniques,² determined the overall rate constant over the temperature range 220–400 K and pressure range 50–750 Torr and also determined at 220 K and 298 K the branching ratio for OCIO production. The results by these two independent techniques^{1,2} are in excellent agreement, with the overall rate constant showing a negative temperature dependence. Too-

hey and Anderson,³ using discharge flow-resonance fluorescence/LMR techniques, reported room temperature values of the overall rate constant and the branching ratio for OCIO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state. Poulet *et al.*,⁴ using discharge flow-mass spectrometry techniques, reported room temperature values of the overall rate constant and branching ratios for OCIO and BrCl production.

All the above-mentioned results^{1–4} are in reasonably good agreement. Hills *et al.*,⁵ using a discharge flow-mass spectrometry technique, obtained an overall rate constant which was independent of temperature over the range 241–308 K and substantially lower than the room temperature average of the above mentioned studies; they also reported no BrCl production. Room temperature overall rate constant values reported also include that from the discharge flow-mass spectrometry study of Clyne and Watson⁶ and the very low value derived in the flash photolysis study of Basco and Dogra⁷ using a different interpretation of the reaction mechanism. The recommended Arrhenius expressions for the individual reaction channels are taken from the study of Friedl and Sander.¹ That study¹ and the recent study of Turnipseed *et al.*⁸ contain the most comprehensive sets of rate coefficient and branching ratio data. The overall rate coefficients reported in these two studies are in good agreement (within 20%) at room temperature and are in excellent agreement at stratospheric temperatures. Both of these studies, as well as that of Sander and Friedl,² show that OCIO production by channel (1) becomes dominant at very low temperature. Both studies show an $\sim 8\%$ yield of BrCl by channel (3). The recommended expressions are consistent with the body of

data from all studies except those of Refs. 5 and 7. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁹

References

- ¹R. R. Friedl and S. P. Sander, *J. Phys. Chem.* **93**, 4756 (1989).
²S. P. Sander and R. R. Friedl, *J. Phys. Chem.* **93**, 4764 (1989).
³D. W. Toohey and J. G. Anderson, *J. Phys. Chem.* **92**, 1705 (1988).

- ⁴G. Poulet, I. T. Lancar, G. Laverdet, and G. Le Bras, *J. Phys. Chem.* **94**, 278 (1990).
⁵A. J. Hills, R. J. Cicerone, J. G. Calvert, and J. W. Birks, *J. Phys. Chem.* **92**, 1853 (1988).
⁶M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **73**, 1169 (1977).
⁷Basco and S. K. Dogra, *Proc. Roy. Soc. London A*, **323**, 417 (1971).
⁸A. A. Turnipseed, J. W. Birks, and J. G. Calvert, *J. Phys. Chem.* **95**, 4356 (1991).
⁹IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ(1) = -26 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -219 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.75 \pm 0.57) \times 10^{-12}$	298	Mauldin, Wahner, and Ravishankara, 1993 ¹	(a)
$k_2 = (4.45 \pm 0.82) \times 10^{-13}$	298		
$(3.1 \pm 0.4) \times 10^{-12}$	298	Bridier, Veyret, and Lesclaux, 1993 ²	(b)
<i>Branching Ratios</i>			
$k_1/k = 0.84 \pm 0.01$	298	Mauldin, Wahner, and Ravishankara, 1993 ¹	(a)
$k_1/k = 0.68 \pm 0.05$	220		
<i>Reviews and Evaluations</i>			
$1.1 \times 10^{-12} \exp(250/T)$	223–400	IUPAC, 1992 ³	(c)
$k_1 = 2.1 \times 10^{-12}$	298		
$k_2 = 4.1 \times 10^{-13}$	298		
$k_1 = 4.0 \times 10^{-12} \exp(-190/T)$	200–300	NASA, 1994 ⁴	(d)
$k_2 = 4.2 \times 10^{-14} \exp(660/T)$	200–300		

Comments

- (a) Flash photolysis/long path absorption technique. Measurements were made at 298 and 220 K over a pressure range of 75–600 Torr He, N₂, and SF₆. The overall rate coefficient was found to be independent of pressure at 298 K, but at 220 K to increase from $2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 100 Torr to $3.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 400 Torr. The branching ratio was found to be independent of pressure at 298 K and 220 K. An additional, transient absorption feature was observed at 220 K and was tentatively attributed to Br₂O₂.
- (b) Flash photolysis/UV absorption technique.
- (c) Recommended Arrhenius expression for overall rate coefficient was based on the temperature dependent data of Sander and Watson⁵ and Turnipseed *et al.*⁶ and the room temperature data of Clyne and Watson⁷ and Lancar *et al.*⁸ The value of the branching ratio at room temperature was based on the data of Refs. 5, 6, 8–10.

- (d) Recommended expressions for k_1 and k_2 were those proposed by Mauldin *et al.*¹ for atmospheric modeling.

Preferred Values

$$k_1 = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 3.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_1 = 4.0 \times 10^{-12} \exp(-190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}400 \text{ K.}$$

$$k_2 = 4.2 \times 10^{-14} \exp(660/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 220\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k_1 = \Delta \log k_2 = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E_1/R) = \pm 150 \text{ K.}$$

$$\Delta(E_2/R) = \pm 300 \text{ K.}$$

Comments on Preferred Values

The total rate coefficient for disappearance of BrO ($k = k_1 + k_2$) has been studied by a variety of techniques, including discharge flow-mass spectrometry (Clyne and Watson,⁷

Turnipseed *et al.*,⁶ and Lancar *et al.*⁸) and flash photolysis-ultraviolet absorption (Sander and Watson,⁵ Bridier *et al.*,² and Mauldin *et al.*¹).

The partitioning of the total rate coefficient into its two components, k_1 and k_2 , has been measured at room temperature by Sander and Watson,⁵ Turnipseed *et al.*,⁶ and Lancar *et al.*,⁸ by Jaffe and Mainquist¹⁰ from 258 to 333 K, by Cox *et al.*⁹ from 278 to 348 K, and by Mauldin *et al.*¹ from 220 to 298 K. All are in agreement that $k_1/k=0.85\pm0.03$ at 298 K. Mauldin *et al.*¹ reported the overall rate coefficient to be independent of pressure at 298 K but to increase with increasing pressure at 220 K. The recommended expressions for k_1 and k_2 are those proposed by Mauldin *et al.*¹ for atmospheric modeling. They are derived from an analysis of published data at pressures less than 100 Torr from the studies of Clyne and Watson,⁷ Sander and Watson,⁵ Turnipseed *et al.*,⁶ and Mauldin *et al.*¹ They are consistent with an overall rate coefficient value of $(2.5\pm0.9)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹, independent of temperature. They are based on values of $k_1/k=0.85$ at 298 K (all studies) and 0.68 at 220

K (Mauldin *et al.*¹ and Cox *et al.*,⁹ extrapolated value). In the study of Mauldin *et al.*,¹ an additional, short-lived, absorption feature was observed at 220 K and was tentatively attributed to the dimer Br₂O₂.

References

- ¹R. L. Mauldin, A. Wahner, and A. R. Ravishankara, *J. Phys. Chem.* **97**, 7585 (1993).
- ²I. Bridier, B. Veyret, and R. Lesclaux, *Chem. Phys. Lett.* **201**, 563 (1993).
- ³IUPAC, Supplement IV, 1992 (see references in Introduction).
- ⁴NASA Evaluation No. 11, 1994 (see references in Introduction).
- ⁵S. P. Sander and R. T. Watson, *J. Phys. Chem.* **85**, 4000 (1981).
- ⁶A. A. Turnipseed, J. W. Birks, and J. G. Calvert, *J. Phys. Chem.* **94**, 7477 (1990).
- ⁷M. A. A. Clyne and R. T. Watson, *J. Chem. Soc. Faraday Trans. 1*, **71**, 336 (1975).
- ⁸I. T. Lancar, G. Laverdet, G. Le Bras, and G. Poulet, *Int. J. Chem. Kinet.* **23**, 37 (1991).
- ⁹R. A. Cox, D. W. Sheppard, and M. P. Stevens, *J. Photochem.* **19**, 189 (1982).
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Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\leq 3.26 \times 10^{-11}$	298	Nielsen <i>et al.</i> , 1991 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Nielsen <i>et al.</i> , 1991 ¹	(c)
<i>Reviews and Evaluations</i>			
$k_{\text{obs}} = 3.0 \times 10^{-11}$	298	Lightfoot <i>et al.</i> , 1992 ²	(d)

Comments

- (a) k is defined by $-d[\text{CH}_2\text{BrO}_2]/dt = 2k[\text{CH}_2\text{BrO}_2]^2$ and has been derived from the measured overall second-order decay of CH₂BrO₂ radicals (k_{obs}).
- (b) Pulse radiolysis study of CH₃Br-O₂-SF₆ mixtures with CH₂BrO₂ radicals being monitored by UV absorption [$\sigma_{250} = (7.20 \pm 0.83) \times 10^{-18}$ cm² molecule⁻¹]. The derived value of $k_{\text{obs}} = (3.26 \pm 0.31) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K, which was independent of wavelength over the range 250–310 nm and of pressure over the range 114–760 Torr of SF₆, is an upper limit to k because of the possibility of secondary reactions giving rise to an enhanced decay of CH₂BrO₂ radicals (see Comments on Preferred Values).
- (c) CH₂BrO₂ radicals were generated from the steady-state photolysis of Cl₂ in the presence of CH₃Br-air mix-

tures. Two major carbon-containing products, CO and HCOBr, were observed by FTIR spectroscopic analysis.

- (d) Based on the data of Nielsen *et al.*¹

Preferred Values

$$k \leq 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2/k \leq 1.0 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

Following Lightfoot *et al.*,² we have recommended an upper limit to the overall rate coefficient at 298 K based on the results of Nielsen *et al.*¹ We note, however, that the absorption spectrum of the CH₂BrO₂ radical is surprisingly different from that of other published spectra of RO₂ radicals and this raises some uncertainty in the assignment.

The product study of Nielsen *et al.*¹ indicated the forma-

tion of HCOBr, which is assumed to arise from the reaction $\text{CH}_2\text{BrO} + \text{O}_2 \rightarrow \text{HCOBr} + \text{HO}_2$. HCOBr was unstable and slowly decomposed to CO, the second major observed product. The absence of any $\text{CH}_2\text{BrOOBrCH}_2$ product indicates that reaction (1) is insignificant. The lack of detailed quantitative information on the branching ratio, k_2/k , and on the rate coefficient of the $\text{CH}_2\text{BrO}_2 + \text{HO}_2$ reaction precludes any correction of the loss of CH_2BrO_2 radicals by this route. Consequently, the experimental value to k_{obs} can only be taken as an upper limit value to k in the meantime.

It is interesting to note that the rate coefficient for the

self-reaction of the CH_2BrO_2 radical is significantly greater than those observed for analogous reactions of any other alkyl peroxy radicals.

References

- ¹O. J. Nielsen, J. Munk, G. Locke, and T. J. Wallington, *J. Phys. Chem.* **95**, 8714 (1991).
- ²P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, and F. Zabel, *Atmos. Environ.* **26A**, 1805 (1992).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
3.9×10^{-12}	298	Crowley and Moortgat, 1992 ¹	(a,b)
<i>Branching Ratios</i>			
$k_2/k=0.58$	298	Yarwood, Peng, and Niki, 1992 ²	(c)

Comments

- (a) k is defined by $-\text{d}[\text{BrCH}_2\text{CH}_2\text{O}_2]/\text{dt} = 2k[\text{BrCH}_2\text{CH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{BrCH}_2\text{CH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Molecular modulation study of the photolysis of Br_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at total pressures up to 600 Torr. $\text{BrCH}_2\text{CH}_2\text{O}_2$ radicals were monitored by absorption at 240 nm. The observed second-order decay of $\text{BrCH}_2\text{CH}_2\text{O}_2$ corresponded to $k_{\text{obs}} = (6.2 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, from which the above value of k was derived by taking $k_2/k=0.58$.
- (c) Steady-state photolysis of Br_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at 700 Torr total pressure, with FTIR spectroscopic determination of products. The major products observed were BrCH_2CHO , $\text{BrCH}_2\text{CH}_2\text{OH}$, and $\text{BrCH}_2\text{CH}_2\text{OOH}$. The branching ratio, $k_2/k_1=1.35 \pm 0.07$, was determined from the yields of BrCH_2CHO and $\text{BrCH}_2\text{CH}_2\text{OH}$ relative to the loss of C_2H_4 .

Preferred Values

$k = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 0.58$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value is derived from the measured value of k_{obs} determined by Crowley and Moortgat¹ and correcting for secondary removal of $\text{BrCH}_2\text{CH}_2\text{O}_2$ radicals by use of the branching ratio $k_2/k=0.58$ derived from the data of Yarwood *et al.*²

Confirmation of both k and k_2/k is needed, but the above value of k is consistent with the data for other halogenated alkyl peroxy radicals, which show enhanced self-reaction rate coefficients relative to the unsubstituted alkyl peroxy radicals.

References

- ¹J. N. Crowley and G. K. Moortgat, *J. Chem. Soc. Faraday Trans.* **88**, 2437 (1992).
- ²G. Yarwood, N. Peng, and H. Niki, *Int. J. Chem. Kinet.* **24**, 369 (1992).

BrO + CH₃SCH₃ → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(2.65 \pm 0.65) \times 10^{-13}$	298	Barnes <i>et al.</i> , 1989 ¹	(a)
$(2.7 \pm 0.5) \times 10^{-13}$	298	Barnes <i>et al.</i> , 1991 ²	(a)
<i>Reviews and Evaluations</i>			
2.7×10^{-13}	298	NASA, 1994 ³	(b)

Comments

- (a) Fast flow discharge system used. BrO radicals were produced by the reaction $\text{Br}_2 + \text{O} \rightarrow \text{BrO} + \text{Br}$, and were monitored by mass spectrometry.
- (b) Based on the rate coefficient of Barnes *et al.*²

Preferred Values

$k < 2.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

The two available measurements of the rate coefficient come from the same laboratory using basically the same technique.^{1,2} In the earlier study of this reaction¹ and of the corresponding reaction of ClO with CH₃SCH₃, difficulties were encountered due to wall reactions. In this respect the later study² is much improved.

There is good agreement between the two results but measurements on the IO and ClO radical reactions with

CH₃SCH₃ in the same study² gave values for the rate coefficients for these radicals reacting with CH₃SCH₃ some 30 times smaller than the reaction of BrO. In view of this unexpected difference and the difficulties associated with the measurements, it is suggested that the value of k obtained by Barnes *et al.*² be taken as an upper limit to k until further studies are made.

The reaction is usually assumed to produce CH₃S(O)CH₃ + Br but, although the sulfoxide has been detected¹ as expected, no yields have been measured.

References

- ¹I. Barnes, K. H. Becker, D. Martin, P. Carlier, G. Mouvier, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Biogenic Sulfur in the Environment*, edited by E. S. Saltzman and W. J. Cooper, ACS Symposium Series, No. 393, p. 464 (1989).
- ²I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.* **23**, 579 (1991).
- ³NASA Evaluation No. 11, 1994 (see references in Introduction).

HOBr + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOBr + $h\nu \rightarrow \text{HO} + \text{Br}$ (1)	201	595
→ HBr + O(³ P) (2)	263	455
→ BrO + H (3)	393	304

Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–400	Orlando and Burkholder, 1995 ¹	(a)

Comments

The absorption spectrum of HOBr was recorded using a diode-array spectrometer with a resolution of 0.4 nm. The spectrum consists of two bands, the stronger band peaking

near 280 nm and a weaker band peaking near 350 nm. HOBr was prepared by the reaction of Br₂O with H₂O. The spectrum of Br₂O was also reported.

Preferred Values

Absorption cross-sections for photolysis of HOBr

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
240	0.43	320	3.9
245	1.9	325	4.2
250	4.5	330	4.9
255	8.2	335	5.3
260	12.9	340	5.7
265	18.5	345	6.0
270	24.0	350	6.0
275	28.5	355	5.9
280	30.8	360	5.7
285	30.4	365	5.2
290	27.3	370	4.5
295	22.3	375	3.8
300	16.4	380	3.0
305	11.0	385	2.2
310	7.0	390	1.7
315	4.8	395	1.1
		400	0.18

Comments on Preferred Values

The preferred cross-section values are from the recent study of Orlando and Burkholder.¹ This is the first reported study of the gas-phase UV/visible absorption spectrum. Previously, in the absence of experimental data for HOBr in the gas phase, it was suggested² that modelers use the recommended HOCl cross-section data redshifted by 30 nm. Using the new spectral data Orlando and Burkholder¹ calculated atmospheric photolysis rates to be significantly slower than those estimated previously. The new data yield a lifetime with respect to photolysis to be about 1 hour at ground level and about 0.5 hour in the lower stratosphere. By analogy with HOCl photolysis is expected to occur with unit quantum efficiency by breaking of the O-Br bond to yield HO + Br.

References

- ¹J. J. Orlando and J. B. Burkholder, J. Phys. Chem. **99**, 1143 (1993).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

BrO + $h\nu$ → products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrO + $h\nu$ → Br + O(³ P) (1)	232	515
→ Br + O(¹ D) (2)	422	283

Preferred Values

Absorption cross-sections for BrO photolysis at 303 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
300–305	200	340–345	515
305–310	259	345–350	399
310–315	454	350–355	228
315–320	391	355–360	172
320–325	600	360–365	161
325–330	753	365–370	92
330–335	628	370–375	51
335–340	589		

and absorption cross-section values at 0.4 nm resolution are reported by Wahner *et al.*¹ The strongest absorption feature is the (7,0) band at 338.5 nm; the cross-section for 0.18 nm resolution was determined to be $(1.71 \pm 0.14) \times 10^{-17} \text{ cm}^2$ at 298 K and $(2.21 \pm 0.16) \times 10^{-17} \text{ cm}^2$ at 223 K.¹

The preferred values given here are the averaged values over 5 nm intervals reported by Cox *et al.*;² in that paper the authors used these data to calculate a lifetime against solar photodissociation of 30 seconds for a solar zenith angle of 30 degrees. Earlier studies are discussed in previous evaluations.^{3,4}

References

- ¹A. Wahner, A. R. Ravishankara, S. P. Sander, and R. R. Friedl, Chem. Phys. Lett. **152**, 507 (1988).
²R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. **19**, 189 (1982).
³CODATA, 1980 (see references in Introduction).
⁴CODATA, Supplement II, 1984 (see references in Introduction).

Comments on Preferred Values

The BrO radical has a banded absorption spectrum in the 290–380 nm range. The absorption cross-section values at the band peaks are dependent on temperature and spectral resolution. The band locations, vibrational level assignments,

BrONO₂ + *hν* → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
BrONO ₂ + <i>hν</i> → BrO + NO ₂ (1)	111	1080
→ Br + NO ₃ (2)	129	930
→ BrONO + O(³ P) (3)	306	390
→ BrONO + O(¹ D) (4)	496	240

Preferred Values**Absorption cross-sections for BrONO₂ photolysis**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
186	1500	280	29
190	1300	285	27
195	1000	290	24
200	720	295	22
205	430	300	19
210	320	305	18
215	270	310	15
220	240	315	14
225	210	320	12
230	190	325	11
235	170	330	10
240	130	335	9.5
245	100	340	8.7
250	78	345	8.5
255	61	350	7.7
260	48	360	6.2
265	39	370	4.9
270	34	380	4.0
275	31	390	2.8

Quantum Yields

No recommendation is given for the relative importance of the possible pathways since there are no data which provide a basis for a recommendation.

Comments on Preferred Values

This data sheet is reproduced from our previous evaluation, CODATA, 1982.¹ The recommended values are taken from Spencer and Rowland.² They are unchanged from those given in CODATA, 1980,³ where a detailed discussion can be found.

References

- ¹CODATA, Supplement I, 1982 (see references in Introduction).
²J. E. Spencer and F. S. Rowland, J. Phys. Chem. **82**, 7 (1978).
³CODATA, 1980 (see references in Introduction).

CH₃Br + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{Br} + h\nu \rightarrow \text{CH}_3 + \text{Br}$	295	405

Preferred Values**Absorption cross-sections for CH₃Br photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	44	230	15
2	53	2	12
4	62	4	9.9
6	69	6	7.6
8	76	8	5.9
200	79	240	4.5
2	80	2	3.3
4	79	4	2.5
6	77	6	1.8
8	73	8	1.3
210	67	250	0.96
2	61	2	0.69
4	56	4	0.49
6	49	6	0.34
8	44	8	0.23
220	38	260	0.16
2	32		
4	28		
6	23		
8	19		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the values reported by Gillotay and Simon.¹ Molina *et al.*² reported values at 5 nm intervals, and Robbins³ reported values at 2 nm intervals. The agreement among these three studies^{1–3} over the wavelength range of our preferred values is very good. The temperature dependence down to 210 K has been reported in Ref. 1. At shorter wavelengths the cross-section is independent of temperature,¹ while at $\lambda > 210$ nm there is a decrease in absorption as the temperature is lowered.¹ For values at low temperatures the reader is referred to the original reference.¹ Photolysis has been shown by Talukdar *et al.*⁴ to occur with unit quantum efficiency by breaking of the C-Br bond to yield CH₃ + Br.

References

- ¹D. Gillotay and P. C. Simon, *Annales Geophysicae*, **6**, 211 (1988).
- ²L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).
- ³D. E. Robbins, *Geophys. Res. Lett.* **3**, 213 (1976).
- ⁴R. K. Talukdar, G. L. Vaghjani, and A. R. Ravishankara, *J. Chem. Phys.* **96**, 8194 (1992).

CF₃Br (Halon-1301) + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₃ Br + $h\nu$ → CH ₃ + Br	286	420

Preferred Values**Absorption cross-sections for CF₃Br photolysis at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	6.4	230	3.1
2	7.5	2	2.4
4	8.5	4	1.9
6	9.5	6	1.4
8	10.4	8	1.1
200	11.2	240	0.81
2	11.8	2	0.59
4	12.2	4	0.43
6	12.4	6	0.31
8	12.4	8	0.22
210	12.0	250	0.16
2	11.4	2	0.11
4	10.7	4	0.076
6	9.8	6	0.053
8	8.8	8	0.037
220	7.7	260	0.026
2	6.7	2	0.018
4	5.7	4	0.012
6	4.7	6	0.009
8	3.8	8	0.006

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon¹ and Burkholder *et al.*² Molina *et al.*³ reported values

at 5 nm intervals. The agreement among these three studies¹⁻³ over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. At $\lambda > 220$ nm both studies reported a decrease in absorption as the temperature is lowered.^{1,2} Near the absorption peak (about 205 nm) Burkholder *et al.*² reported the cross-section to be independent of temperature, while Gillotay and Simon¹ found the absorption to increase with decreasing temperature, with a 20% increase at the lowest temperature studied. For values at low temperatures the reader is referred to the original references.^{1,2} Photolysis has been shown by Talukdar *et al.*⁴ to occur with unit quantum efficiency by breaking of the C-Br bond to yield CF₃ + Br. CF₃Br has no apparent tropospheric chemical loss mechanism² and is estimated to have a tropospheric lifetime against direct solar photoexcitation of greater than 1000 years.³

References

- ¹D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **8**, 41 (1989).
- ²J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).
- ³L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).
- ⁴R. K. Talukdar, G. L. Vaghjani, and A. R. Ravishankara, *J. Chem. Phys.* **96**, 8194 (1992).

CF₂ClBr (Halon-1211) + $h\nu$ → products**Primary photochemical processes**

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ ClBr + $h\nu$ → CF ₂ Cl + Br	271	440

Preferred Values

Absorption cross-sections for CF₂ClBr photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	47	240	18
2	15	2	15
4	70	4	12
6	83	6	10
8	96	8	8
200	112	250	6.5
2	118	2	5.1
4	121	4	4.0
6	122	6	3.2
8	121	8	2.4
210	117	260	1.9
2	112	2	1.4
4	106	4	1.1
6	98	6	0.84
8	90	8	0.63
220	81	270	0.48
2	72	2	0.36
4	64	4	0.27
6	56	6	0.20
8	49	8	0.15
230	42	280	0.11
2	36	2	0.079
4	31	4	0.058
6	26	6	0.043
8	22	8	0.031

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon¹ and Burkholder *et al.*² Molina *et al.*³ reported values

at 5 nm intervals, and Giolondo *et al.*⁴ reported values at 10 nm intervals. The agreement among these four studies¹⁻⁴ over the wavelength range of our preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. At $\lambda > 230$ nm both studies reported a decrease in absorption as the temperature is lowered.^{1,2} Near the absorption peak (about 205 nm) Burkholder *et al.*² reported the cross-section to be independent of temperature, while Gillotay and Simon¹ found the absorption to increase with decreasing temperature reaching nearly a 20% increase at the lowest temperature. For values at low temperatures the reader is referred to the original references.^{1,2} Over the wavelength range of the preferred values photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield CF₂Cl + Br. Baum and Huber,⁵ in a photofragment translational spectroscopy study of the photodissociation of CF₂ClBr at 193 nm, found the dominant primary photodissociation process to occur by breaking of the C-Br bond and a second, minor process to occur by breaking of the stronger C-Cl bond. CF₂ClBr has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 15 to 20 years.^{2,3}

References

- ¹D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **8**, 41 (1989).
- ²J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjiani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).
- ³L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).
- ⁴D. M. Giolondo, G. B. Fazekas, W. D. Taylor, and G. A. Takacs, *J. Photochem.* **14**, 335 (1980).
- ⁵G. Baum and J. R. Huber, *Chem. Phys. Lett.* **213**, 427 (1993).

CF₂Br₂(Halon-1202) + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CF ₂ Br ₂ + $h\nu \rightarrow$ CF ₂ Br + Br	280 (est)	430

Preferred Values

Absorption cross-sections for CF₂Br₂ photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	114	250	59
2	109	2	47
4	100	4	37
6	91	6	29
8	82	8	23
200	75	260	18
2	72	2	13
4	74	4	10
6	81	6	7.6
8	93	8	5.7
210	110	270	4.2
2	136	2	3.1
4	155	4	2.2
6	180	6	1.6
8	203	8	1.2
220	224	280	0.89
2	242	2	0.65
4	251	4	0.48
6	253	6	0.34
8	250	8	0.24
230	241	290	0.18
2	227	2	0.13
4	209	4	0.096
6	189	6	0.068
8	168	8	0.050
240	147	300	0.036
2	125	2	0.026
4	106	4	0.019
6	88	6	0.014
8	73	8	0.010

Quantum Yields

$\phi = 1.0$ throughout this wavelength range.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay and Simon¹ and Burkholder *et al.*² Molina *et al.*³ reported values at 5 nm intervals. The agreement among these three studies^{1–3} over the wavelength range of our preferred values is very good. The temperature dependence down to 210 K has been reported in Refs. 1 and 2, with fair agreement between the studies.^{1,2} At $\lambda > 250$ nm both studies reported a decrease in absorption as the temperature is lowered.^{1,2} Near the absorption peak (about 230 nm) both studies report an 11% increase in absorption at the lowest temperature.^{1,2} For values at low temperatures the reader is referred to the original references.^{1,2} It has been shown by Molina and Molina⁴ and confirmed by Talukdar *et al.*⁵ that CF₂Br₂ photodissociates with unit quantum efficiency over the 200–300 nm region by breaking of the C-Br bond to yield CF₂Br + Br. Because its absorption extends into the 290–310 nm wavelength range, CF₂Br₂ has a short tropospheric lifetime against direct solar photoexcitation of about 3 years.²

References

- ¹D. Gillotay and P. C. Simon, *J. Atmos. Chem.* **8**, 41 (1989).
- ²J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).
- ³L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).
- ⁴L. T. Molina and M. J. Molina, *J. Phys. Chem.* **87**, 1306 (1983).
- ⁵R. K. Talukdar, G. L. Vaghjani, and A. R. Ravishankara, *J. Chem. Phys.* **96**, 8194 (1992).

CHBr₃ + $h\nu \rightarrow$ products

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CHBr ₃ + $h\nu \rightarrow$ CHBr ₂ + Br	276	433

Preferred Values

Absorption cross-sections for CHBr_3 photolysis at 296 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	399	270	31
2	360	2	25
4	351	4	20
6	366	6	16
8	393	8	12
200	416	280	9.9
2	433	2	7.8
4	440	4	6.1
6	445	6	4.81
8	451	8	3.75
210	468	290	2.88
2	493	2	2.22
4	524	4	1.70
6	553	6	1.28
8	574	8	0.951
220	582	300	0.719
2	578	2	0.530
4	558	4	0.394
6	527	6	0.298
8	487	8	0.226
230	441	310	0.171
2	397	2	0.127
4	362	4	0.095
6	324	6	0.071
8	295	8	0.053
240	273	320	0.039
2	253	2	0.029
4	234	4	0.021
6	214	6	0.016
8	194	8	0.009
250	174	330	0.009
2	158	2	0.007
4	136	4	0.005
6	116	6	0.004
8	99	8	0.003
260	83	340	0.002
2	69		
4	57		
6	47		
8	38		

Comments on Preferred Values

There have been two studies of the absorption cross-sections of CHBr_3 . Gillotay *et al.*¹ reported values over the wavelength range 170–310 nm and the temperature range 295–240 K; Moortgat *et al.*² reported values from 245–360 nm and the temperature range 296–256 K. In the region where the measurements overlap, the agreement is very good. The preferred values at room temperature are those reported by Gillotay *et al.*¹ over the wavelength range 190–284 nm and those reported by Moortgat *et al.*² at longer wavelengths. For values at lower temperatures, the following expression, $\ln \sigma(\lambda, T) = (0.06183 - 0.000241 \lambda) (273 - T) - (2.376 + 0.14757 \lambda)$, was derived by Moortgat *et al.*² from a fit to the combined data of their study² and that of Gillotay *et al.*¹ It is valid for the wavelength range 290–340 nm and the temperature range 300–210 K. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield $\text{CHBr}_2 + \text{Br}$.

References

- ¹D. Gillotay, A. Jenouvrier, B. Coquart, M. F. Merrienne, and P.C. Simon, *Planet. Space Sci.* **37**, 1127 (1989).
- ²G. K. Moortgat, R. Meller, and W. Schneider, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker, NATO ASI Series, Volume 17 (Springer-Verlag, Berlin, 1993).

 $\text{CF}_2\text{BrCF}_2\text{Br}(\text{Halon-2402}) + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_2\text{BrCF}_2\text{Br} + h\nu \rightarrow \text{CF}_2\text{BrCF}_2 + \text{Br}$	280 (est)	430

Preferred Values

Absorption cross-sections for $\text{CF}_2\text{BrCF}_2\text{Br}$ photolysis at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
190	109	240	13
2	114	2	11
4	119	4	8.4
6	122	6	6.7
8	124	8	5.2
200	124	250	4.1
2	124	2	3.1
4	120	4	2.3
6	117	6	1.8
8	112	8	1.3
210	106	260	0.95
2	100	2	0.71
4	92	4	0.53
6	85	6	0.39
8	77	8	0.28
220	69	270	0.21
2	61	2	0.16
4	54	4	0.11
6	47	6	0.082
8	40	8	0.060
230	35	280	0.044
2	29		
4	24		
6	20		
8	16		

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are the mean of the values reported by Gillotay *et al.*¹ and Burkholder *et al.*² Molina *et al.*³ have also reported values at 5 nm intervals. The agreement among these three studies over the wavelength range of preferred values is excellent. The temperature dependence down to 210 K has been reported in Refs. 1 and 2. The results differ qualitatively. For values at low temperatures the reader is referred to the original references.^{1,2} Photolysis is expected to occur with unit quantum efficiency by breaking of the C-Br bond to yield $\text{CF}_2\text{BrCF}_2 + \text{Br}$, and $\text{CF}_2\text{BrCF}_2\text{Br}$ has been estimated to have a tropospheric lifetime against direct solar photoexcitation of 34 years.²

References

- ¹D. Gillotay, P. C. Simon, and L. Dierickx, *Aeronomica Acta* **335**, 1 (1988).
- ²J. B. Burkholder, R. R. Wilson, T. Gierczak, R. Talukdar, S. A. McKeen, J. J. Orlando, G. L. Vaghjani, and A. R. Ravishankara, *J. Geophys. Res.* **96**, 5025 (1991).
- ³L. T. Molina, M. J. Molina, and F. S. Rowland, *J. Phys. Chem.* **86**, 2672 (1982).

4.9. Iodine Species

$$\Delta H^\circ = -98 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 250 \text{ K}$.

Comments on Preferred Values

The recommended rate coefficient is based on the data of Ray and Watson¹ and is consistent with the trend observed in the rate coefficients for the $\text{O} + \text{X}_2$ reaction, which increase steadily: $< 1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{X} = \text{F}$,² $4.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{X} = \text{Cl}$ ³ and 1.4×10^{-11}

$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{X} = \text{Br}$ ⁴ at 298 K. The molecular beam study of Parrish and Herschbach⁵ suggests a zero activation energy, consistent with the near gas-kinetic value of k at 298 K. The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁶

References

¹G. W. Ray and R. T. Watson, *J. Phys. Chem.* **85**, 2955 (1981).

²R. H. Krech, G. J. Diebold, and D. L. McFadden, *J. Am. Chem. Soc.* **99**, 4605 (1977).

³R. T. Watson, *J. Phys. Chem. Ref. Data* **6**, 871 (1977).

⁴IUPAC, Supplement III, 1989 (see references in Introduction).

⁵D. D. Parrish and D. R. Herschbach, *J. Am. Chem. Soc.* **95**, 6133 (1973).

⁶IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -249 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

This estimate is probably accurate to within a factor of 3, and is based upon the assumption that the reactivity of IO is similar to that of ClO and BrO (this is true in the case of XO

+ NO where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$). The recommended rate constants for ClO and BrO at $\sim 298 \text{ K}$ are $3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (see present evaluations). The temperature dependence of the rate constant is expected to be small. The preferred value is identical to that in our previous evaluation, IUPAC, 1992.¹

References

¹IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -94.9 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.5 \times 10^{-11} \exp(-1090/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the two experimental studies reported by Jenkin *et al.*,¹ which are the only reported measurements for this reaction. The rate coefficients k at 298 K agree quite well although both studies exhibited significant experimental error. The Arrhenius expression suggested by Jenkin *et al.*¹ is accepted for the temperature dependence. These preferred values are identical to those in our previous evaluation, IUPAC, 1992.²

References

²IUPAC, Supplement IV, 1992 (see references in Introduction).¹M. E. Jenkin, R. A. Cox, A. Mellouki, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **94**, 2927 (1990).

$$\Delta H^\circ = -142 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.0 \times 10^{-11} \exp(-890/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–350 K.

mean value at 298 K from the three studies of Buben *et al.*,¹ Jenkin and Cox,² and Sander.³ The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred Arrhenius expression uses the activation energy from Buben *et al.*¹ with an *A* factor adjusted to give the

References

¹S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, *Khim. Fiz.* **9**, 116 (1990).²M. E. Jenkin and R. A. Cox, *J. Phys. Chem.* **89**, 192 (1985).³S. P. Sander, *J. Phys. Chem.* **90**, 2194 (1986).⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -75.7 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 1.8 \times 10^{-32} (T/300)^{-1.0} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 300 K.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are based on the rate coefficients for *M*=Ar determined by van den Bergh *et al.*¹ and Basco and Hunt,² which agree remarkably well. The collision efficien-

cies for He, Ar, and N₂ follow the usual trends. The transition to the high pressure limit is of no importance for pressures below 1 bar ($k_\infty = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K, $F_c = 0.75$ at 298 K, see Ref. 3). The preferred values are identical to those in our previous evaluation, IUPAC, 1992.⁴

References

¹H. van den Bergh, N. Benoit-Guyot, and J. Troe, *Int. J. Chem. Kinet.* **9**, 223 (1977).²N. Basco and J. E. Hunt, *Int. J. Chem. Kinet.* **10**, 733 (1978).³CODATA, Supplement I, 1982 (see references in Introduction).⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -79.8 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_0 = 3.0 \times 10^{-31} (T/300)^{-1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are from Refs. 1–3. The data of Ref. 4 for M=He are also consistent with the data of Refs. 1–3. Falloff extrapolations are made with a fitted¹ $F_c = 0.63$ near 300 K.

High-pressure rate coefficients

No new data have been published since our last evaluation.

Preferred Values

$k_\infty = 6.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–400 K.

Comments on Preferred Values

See comments on k_0 . The preferred values for k_0 and k_∞ are identical to those in our previous evaluation, IUPAC, 1992.⁵

References

¹H. van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

²H. van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. **9**, 223 (1977).

³S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Kin. i Kataliz **31**, 973 (1990).

⁴A. Mellouki, G. Laverdet, J. L. Jourdain, and G. Poulet, Int. J. Chem. Kinet. **21**, 1161 (1989).

⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

$\Delta H^\circ = -40 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(4.5 \pm 1.9) \times 10^{-10}$	298	Chambers, Heard, and Wayne, 1992 ¹	(a)

Comments

- (a) Discharge flow system with resonance fluorescence detection of I atoms. NO_3 radicals were measured by visible absorption spectroscopy. The $\text{O} + \text{I}_2$ reaction was used to generate I atoms and NO_3 radicals were produced by the reaction $\text{F} + \text{HNO}_3$. Pseudo-first-order conditions were used with NO_3 in excess. Correction of k^1 of up to 33% was applied to compensate for diffusion effects; the overall error takes into account the uncertainties in $[\text{NO}_3]$ (26%) and k^1 (15% at the 95% confidence limits).

Comments on Preferred Values

This is a new data sheet. The only reported measurement of this rate constant was made using the discharge flow technique at room temperature.¹ Some difficulties were encountered due to wall reactions, and the pseudo first-order plots exhibited pronounced curvature at contact times longer than 3 ms. Lancar *et al.*² state that they failed to observe a reaction between I atoms and NO_3 radicals. In view of these uncertainties, no recommendation for the rate coefficient is made at this time.

References

¹R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).

²I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

Preferred Values

No recommendation.

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i> $(1.5 \pm 0.5) \times 10^{-12}$	292–423	Chambers, Heard, and Wayne, 1992 ¹	(a)

Comments

- (a) Discharge flow system with simultaneous fluorescence detection of I_2 and visible absorption spectroscopic measurement of NO_3 radicals. NO_3 radicals were produced by the $\text{F} + \text{HNO}_3$ reaction. Pseudo-first-order conditions were used with NO_3 radical concentrations in excess over I_2 . Experiments were performed to substantiate that I_2 loss was due to reaction with NO_3 radicals. Correction of k^{I} of up to 2% was applied to compensate for diffusion effects; the overall error takes into account the uncertainties in $[\text{NO}_3]$ (26%).

Reliability

$$\Delta \log k = \pm 0.3.$$

Comments on Preferred Values

This is a new data sheet. The only reported measurement of this rate constant¹ was made using the discharge flow technique and is the basis of the recommended value. Thermochemical data give a substantial endothermicity for XONO_2 formation in the reactions of the other halogens with the NO_3 radical, and the rapid rate of the $\text{I}_2 + \text{NO}_3$ reaction implies an upper limit of $\sim 29 \text{ kJ mol}^{-1}$ for ΔH° (IONO_2). Other possible channels giving $\text{I} + \text{IO} + \text{NO}_2$, $\text{I} + \text{O}_2 + \text{INO}$ or $\text{IO} + \text{INO}_2$ are all apparently endothermic.

Preferred Values

$k = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–450 K.

References

- ¹R. M. Chambers, A. C. Heard, and R. P. Wayne, *J. Phys. Chem.* **96**, 3321 (1992).

$$\Delta H^\circ = -200.9 \text{ kJ} \cdot \text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

preferred value is identical to our previous evaluation, IUPAC, 1992.⁴

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value is based on the results of Mac Leod *et al.*¹ and Lancar *et al.*,² which are more than a factor of two higher than the earlier results of Takacs and Glass.³ The

References

- ¹H. Mac Leod, C. Balestra, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Int. J. Chem. Kinet.* **22**, 1167 (1990).
²I. T. Lancar, A. Mellouki, and G. Poulet, *Chem. Phys. Lett.* **177**, 554 (1991).
³G. A. Takacs and G. P. Glass, *J. Phys. Chem.* **77**, 1948 (1973).
⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

No new data have been published since our last evaluation.

Preferred Values

$k = 1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The two reported values of Loewenstein and Anderson¹ and Jenkin *et al.*² agree well, considering the quoted error limits. The preferred value is the mean of these two studies,^{1,2} and is identical to our previous evaluation, IUPAC, 1992.³

References

- ¹L. M. Loewenstein and J. G. Anderson, *J. Phys. Chem.* **89**, 5371 (1985).
²M. E. Jenkin, K. C. Clemmshaw, and R. A. Cox, *J. Chem. Soc. Faraday Trans. 2*, **80**, 1633 (1984).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = -65.2 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$k = 7.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.1 \times 10^{-12} \exp(-1120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–430 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
 $\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred rate coefficients are based on the sole study of Brown *et al.*,¹ and are identical to our previous evaluation, IUPAC, 1992.² The uncertainty limits in the preferred values take into account the significant error limits (± 30 –50% except at 298 K) cited by Brown *et al.*¹

References

- ¹A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, *Atmos. Environ.* **24A**, 361 (1990).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.2) \times 10^{-13}$	295	Garraway and Donovan, 1979 ¹	(a)
$(3.1 \pm 0.5) \times 10^{-14}$	300	Brown <i>et al.</i> , 1990 ²	(b)

Comments

- (a) Flash photolysis system with resonance absorption detection of HO radicals.
 (b) Discharge flow system with resonance fluorescence detection of HO radicals. The stated purity level of the CF_3I used was $>97\%$.

with impurities and/or heterogeneous wall reactions³ in the study of Brown *et al.*² (which yields a significantly lower rate coefficient than obtained by Garraway and Donovan¹), the rate coefficient obtained by Brown *et al.*² is taken as an upper limit value.

References

- ¹J. Garraway and R. J. Donovan, *J. Chem. Soc., Chem. Comm.* 1108 (1979).
²A. C. Brown, C. E. Canosa-Mas, and R. P. Wayne, *Atmos. Environ.* **24A**, 361 (1990).
³R. P. Wayne, C. E. Canosa-Mas, A. C. Heard, and A. D. Parr, *Atmos. Environ.* **26A**, 2371 (1992).

Preferred Values

$k < 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

In view of the potential for secondary reactions, reactions

$$\Delta H^\circ = -128.6 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

No recommendation.

Comments on Preferred Values

Although the rate coefficients measured in the single study¹ of this reaction from the decay of NO_3 using MS and I atom production using EPR spectrometry were in agreement, there is a serious potential for secondary chemistry occurring in the system leading to an overestimation of the rate coefficient for the elementary process. The authors state that the reaction of $\text{I} + \text{NO}_3 \rightarrow \text{IO} + \text{NO}_2$ does not occur,¹

while Chambers *et al.*² observed that this $\text{I} + \text{NO}_3$ reaction is extremely rapid, with a rate coefficient of $k(\text{I} + \text{NO}_3) = 4.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, and that I atoms are regenerated from subsequent reactions of IO. While this uncertainty exists, no recommendation can be made.

References

- ¹I. T. Lencar, A. Mellouki, and G. Poulet, *Chem. Phys. Lett.* **177**, 554 (1991).
- ²R. M. Chambers, A. C. Heard, and R. P. Wayne, *J. Phys. Chem.* **96**, 3321 (1992).

$$\Delta H^\circ = -212 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(1.03 \pm 0.13) \times 10^{-10}$	298	Maguin <i>et al.</i> , 1992 ¹	(a)
<i>Reviews and Evaluations</i>			
6.4×10^{-11}	298	IUPAC, 1992 ²	(b)

Comments

- (a) Discharge flow system with MS detection of HO_2 and IO radicals and HOI. IO radicals were produced by the reaction of $\text{O}(^3\text{P})$ atoms with I_2 and HO_2 radicals by the reaction $\text{Cl} + \text{CH}_3\text{OH} + \text{O}_2$. Pseudo-first-order decays of IO radicals were measured in the presence of excess HO_2 . The k value is the average of 28 experiments. HOI was shown to be a major product. The uniqueness of channel (1) could not be established, although no evidence was found for ozone formation by the alternative channel of $\text{IO} + \text{HO}_2 \rightarrow \text{HI} + \text{O}_3$.
- (b) Based on the measurements of Jenkin *et al.*³

Preferred Values

$$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3.$$

Comments on Preferred Values

The new study by Maguin *et al.*¹ provides a more direct determination of this rate coefficient than the earlier measurement³ using the molecular modulation technique, which required computer simulations to derive the rate coefficient from the observed concentration-time profiles of IO and HO_2 radicals. The preferred value is therefore based on the more recent study,¹ which also provides strong evidence that HOI is the major product. On the basis of current thermochemical data for the IO radical, the channel forming $\text{HI} + \text{O}_3$ is endothermic by 47.6 kJ mol^{-1} . The value of k at 298 K is consistent with the emerging reactivity pattern for the halogen oxide radicals with the HO_2 radical. The temperature dependence is expected to be small.

References

- ¹F. Maguin, G. Laverdet, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **96**, 1775 (1992).
- ²IUPAC, Supplement IV, 1992 (see references in Introduction).
- ³M. E. Jenkin, R. A. Cox, and G. D. Hayman, *Chem. Phys. Lett.* **177**, 272 (1991).

$$\Delta H^\circ(1) = -152 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -0.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2+k_3+k_4 [\text{M}]$)

No new data have been published since our last evaluation.

Preferred Values

$$k=5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k=1.7 \times 10^{-12} \exp(1020/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{--}373 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

The most recent data of Barnes *et al.*¹ confirm that the pressure independence of the rate of this reaction, observed

by Sander,² extends to low pressures as indicated by the less reliable results of Martin *et al.*³ No new data relating to the branching ratios have been reported and therefore no recommendation can be made. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

¹I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.* **23**, 579 (1991).

²S. P. Sander, *J. Phys. Chem.* **90**, 2194 (1986).

³D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Int. J. Chem. Kinet.* **19**, 503 (1987).

⁴IUPAC, Supplement III, 1989 (see references in Introduction).

$$\Delta H^\circ = -57 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k=2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k=7.3 \times 10^{-12} \exp(330/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 150 \text{ K.}$$

Comments on Preferred Values

The studies of Buben *et al.*¹ and Daykin and Wine² give values of k at 298 K midway between those reported in earlier studies.^{3,4} The preferred value at 298 K is the mean of

the values reported in Refs. 1–4. The temperature dependence measurements of Daykin and Wine² appear to be of excellent quality and provide the basis for the recommendation, which uses the preferred 298 K value with the E/R from Daykin and Wine.² The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

¹S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, in press (1995).

²E. P. Daykin and P. H. Wine, *J. Phys. Chem.* **94**, 4528 (1990).

³G. Inoue, M. Suzuki, and N. Washida, *J. Chem. Phys.* **79**, 4730 (1983).

⁴G. W. Ray and R. T. Watson, *J. Phys. Chem.* **85**, 2955 (1981).

⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.6 \pm 1.0) \times 10^{-31} \text{ [He]}$	298	Maguin <i>et al.</i> , 1992 ¹	(a)
$(7.9 \pm 2.2) \times 10^{-31} \text{ [N}_2\text{]}$	298		
<i>Reviews and Evaluations</i>			
$7.7 \times 10^{-31} (T/300)^{-5} \text{ [N}_2\text{]}$	250–350	IUPAC, 1992 ²	(b)
$7.7 \times 10^{-31} \text{ [N}_2\text{]}$	300	Rayez and Destriau, 1993 ³	(c)
$5.9 \times 10^{-31} (T/300)^{-3.5} \text{ [N}_2\text{]}$	200–300	NASA, 1994 ⁴	(d)

Comments

- (a) Discharge-flow study with detection of IO and IONO₂ by mass spectrometry. IO radicals were generated by the reaction $\text{O} + \text{I}_2 \rightarrow \text{IO} + \text{I}$. The pressure range was 1.2–2.1 Torr of He. Using a relative third-body efficiency of N₂ and He for the analogous reaction $\text{BrO} + \text{NO}_2 + \text{M}$ [ratio $k_0(\text{N}_2)/k_0(\text{He})=2.2$] from Ref. 5, the value reported above was derived.
- (b) Based on Ref. 6, with falloff extrapolations being made with $F_c=0.4$.
- (c) Theoretical evaluation⁷ of k_0 using $\Delta H_0^\circ=121 \text{ kJ mol}^{-1}$ and $\beta_c=0.73$. If $\Delta H_0^\circ=147 \text{ kJ mol}^{-1}$ is employed, a value of $\beta_c=0.17$ is obtained.
- (d) Based on the data from Ref. 6.

Preferred Values

$k_0=7.7 \times 10^{-31} (T/300)^{-5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 2$.

Comments on Preferred Values

The value of Maguin *et al.*,¹ derived with the given ratio of efficiencies for N₂ and He, agrees very well with the previous preferred values,² which remain unchanged.

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Reviews and Evaluations</i>			
1.6×10^{-11}	250–350	IUPAC, 1992 ²	(a)
6.0×10^{-12}	300		(b)
$9.0 \times 10^{-12} (T/300)^{-1.5}$	200–300		(c)

Comments

- (a) The preferred values were based on the data of Refs. 6 and 8. Falloff extrapolations were made with $F_c=0.4$ at 300 K.
- (b) Theoretical calculations⁹ using a $\Delta H_0^\circ=121 \text{ kJ mol}^{-1}$. If $\Delta H_0^\circ=147 \text{ kJ mol}^{-1}$ is employed, a rate coefficient of $k_\infty=8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ results.
- (c) See comment (d) for k_0 .

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250–350 K.

Comments on Preferred Values

The preferred value for k_∞ is unchanged from our previous evaluation, IUPAC, 1992.²

Preferred Values

$k_\infty=1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–350 K.

References

- ¹F. Maguin, G. Laverdet, G. Le Bras, and G. Poulet, *J. Phys. Chem.* **96**, 1775 (1992).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

³M. T. Rayez and M. Destriau, *Chem. Phys. Lett.* **206**, 278 (1993).

⁴NASA Evaluation No. 11, 1994 (see references in Introduction).

⁵S. P. Sander, G. W. Ray, and R. T. Watson, *J. Phys. Chem.* **85**, 199 (1981).

⁶E. P. Daykin and P. H. Wine, *J. Phys. Chem.* **94**, 4528 (1990).

⁷J. Troe, *J. Chem. Phys.* **66**, 4758 (1977); *J. Phys. Chem.* **83**, 114 (1979).

⁸M. E. Jenkin and R. A. Cox, *J. Phys. Chem.* **89**, 192 (1985).

⁹J. Troe, *Z. Phys. Chem. NF* **161**, 209 (1989).

IO + CH₃SCH₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 1.5) \times 10^{-11}$	296	Barnes <i>et al.</i> , 1987 ¹	(a)
$(1.5 \pm 0.5) \times 10^{-11}$	298	Martin <i>et al.</i> , 1987 ²	(b)
$\leq 3.5 \times 10^{-14}$	298	Daykin and Wine, 1990 ³	(c)
$(1.5 \pm 0.2) \times 10^{-14}$	298	Maguin <i>et al.</i> , 1991 ⁴	(d)
$(8.8 \pm 2.1) \times 10^{-15}$	298	Barnes <i>et al.</i> , 1991 ⁵	(d)
<i>Reviews and Evaluations</i>			
1.2×10^{-14}	298	IUPAC, 1992 ⁶	(e)
1.2×10^{-14}	298	NASA, 1994 ⁷	(e)

Comments

- Photolysis of NO₂-I₂-CH₃SCH₃-N₂ mixtures. Photolytic production of O(³P) atoms from NO₂ gives IO via O(³P) + I₂ → IO + I reaction. Concentrations of NO, NO₂, CH₃SCH₃, and CH₃SOCH₃ were followed as a function of time by FTIR. A computer fit of product yields to reaction mechanism gave k .
- Fast flow discharge system. IO radicals were produced by the reaction O(³P) + I₂ → IO + I. He carrier gas at approximately 1 Torr. CH₃SCH₃ consumption was monitored by mass spectrometry under second-order conditions.
- Pulsed laser photolysis of NO₂-I₂-CH₃SCH₃-N₂-O₂ mixtures at 351 nm. [IO] was monitored by long-path length absorption at 471 nm. Slow flow conditions used.
- Fast-flow discharge study. IO radicals were produced by the reaction O(³P) + I₂ → IO + I. Total pressure was "a few Torr" of He. [IO] was monitored by mass spectrometry.
- Derived from the rate coefficients of Maguin *et al.*⁴ and Barnes *et al.*,⁵ which are consistent with the upper limit to the rate coefficient measured by Daykin and Wine.³

Preferred Values

$$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

In the earlier studies of this reaction by Barnes *et al.*¹ and Martin *et al.*,² erroneously high values were obtained which are now believed to have been due to features of the secondary chemistry and heterogeneous processes occurring under the conditions used.

The two most recent studies,^{4,5} both using the same technique, give much lower values but differ from each other by nearly a factor of two. Support for these lower values comes from the study by Daykin and Wine³ where an upper limit to k was obtained.

The preferred value of k is the mean of the values found by Maguin *et al.*⁴ and Barnes *et al.*,⁵ but in view of the differences between the results from these studies substantial error limits are assigned. The preferred value is identical to our previous evaluation, IUPAC, 1992.⁶

The reaction products are usually assumed to be CH₃S(O)CH₃ + I. CH₃S(O)CH₃ has been detected in a number of studies,^{1,2,4,5} and a semi-quantitative measurement of the yield by Barnes *et al.*⁵ gives 84 ± 40%.

References

- I. Barnes, K. H. Becker, P. Carlier, and G. Mouvier, *Int. J. Chem. Kinet.* **19**, 489 (1987).
- D. Martin, J. L. Jourdain, G. Laverdet, and G. Le Bras, *Int. J. Chem. Kinet.* **19**, 503 (1987).
- E. P. Daykin and P. H. Wine, *J. Geophys. Res.* **95**, 18547 (1990).
- F. Maguin, A. Mellouki, G. Laverdet, G. Poulet, and G. Le Bras, *Int. J. Chem. Kinet.* **23**, 237 (1991).
- I. Barnes, V. Bastian, K. H. Becker, and R. D. Overath, *Int. J. Chem. Kinet.* **23**, 579 (1991).
- IUPAC, Supplement IV, 1992 (see references in Introduction).
- NASA Evaluation No. 11, 1994 (see references in Introduction).

$$\Delta H^\circ = 0.3 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 8.4 \times 10^{-11} \exp(-2620/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 300\text{--}450 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.4 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 600 \text{ K.}$$

Comments on Preferred Values

The results from the study of Van den Bergh and Troe¹ are preferred over those from Basco and Hunt² because of a much wider range of conditions studied. The preferred values are identical to our previous evaluation, IUPAC, 1992.³

References

- ¹H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
²N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).
³IUPAC, Supplement IV, 1992 (see references in Introduction).

$$\Delta H^\circ = 8.4 \text{ kJ}\cdot\text{mol}^{-1}$$

No new data have been published since our last evaluation.

Preferred Values

$$k = 4.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.9 \times 10^{-11} \exp(-2600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 298\text{--}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 1000 \text{ K.}$$

Comments on Preferred Values

The preferred values are based on the measured rate constant at 350 K from Van den Bergh and Troe¹ and an assumed value for E/R equal to that for the reaction $\text{INO} + \text{INO} \rightarrow \text{I}_2 + 2\text{NO}$. In the analogous reactions for other halogens this behavior appears to apply (see Ref. 1). The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Comments
<i>Absolute Rate Coefficients</i>			
$\sim 9 \times 10^{-11}$	295	Sehested, Ellermann, and Nielsen, 1994 ¹	(a)

Comments

- (a) Pulse radiolysis UV absorption spectrometric study of $\text{CH}_3\text{I-O}_2\text{-SF}_6$ mixtures at a total pressure of 1000 mbar. CH_2IO_2 radicals were monitored by UV absorption with $\sigma_{370} = (2.1 \pm 0.5) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The interpretation of the kinetic data is complicated by

the presence of CH_3O_2 radicals, which leads to mixed-order kinetics. The above approximate value of k was derived on the basis of several assumptions.

Preferred Values

No recommendation.

Comments on Preferred Values

The approximate and exceptionally large rate coefficient obtained by Sehested *et al.*¹ should be regarded with caution owing to the inherent complications in their experimental system. Until more work is carried out in this reaction, we make no recommendation.

References

- ¹J. Sehested, T. Ellermann, and O. J. Nielsen, *Int. J. Chem. Kinet.* **26**, 259 (1994).

HOI + $h\nu$ → products

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOI + $h\nu$ → HO + I (1)	236	507
→ HI + O(³ P) (2)	366	327
→ IO + H (3)	415	288
→ HI + O(¹ D) (4)	555	216

Preferred Values**Absorption cross-sections of HOI at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
300–305	0.02	385–390	11.8
305–310	3.29	390–395	14.0
310–315	5.80	395–400	16.7
315–320	9.10	400–405	20.0
320–325	12.9	405–410	22.8
325–330	17.0	410–415	23.3
330–335	20.6	415–420	21.9
335–340	21.4	420–425	19.2
340–345	19.5	425–430	16.2
345–350	16.7	430–435	13.5
350–355	14.3	435–440	11.0
355–360	12.4	440–445	9.10
360–365	11.0	445–450	7.50
365–370	10.2	450–455	5.80
370–375	9.90	455–460	4.11
375–380	9.90	460–465	2.47
380–385	10.4	465–470	1.10
		470–475	0.28

Quantum Yields

No recommendation. Reaction (1) is the most likely pathway for photolysis in the lower atmosphere.

Comments on Preferred Values

The recommended values for the cross-sections are those given by Jenkin,¹ which are the only available data for the gas phase. Confirmation of these data are required. The preferred values are identical to our previous evaluation, IUPAC, 1992.²

References

- ¹M. E. Jenkin, Ph.D Thesis, University of East Anglia (1991).
²IUPAC, Supplement IV, 1992 (see references in Introduction).

IO + $h\nu$ → products

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
IO + $h\nu$ → I + O(³ P) (1)	249	480
→ I + O(¹ D) (2)	439	270

Preferred Values

Absorption cross-sections

λ/nm	$10^{18} \sigma/\text{cm}^2$	λ/nm	$10^{18} \sigma/\text{cm}^2$
415–420	8.4	445–450	14.1
420–425	9.3	450–455	4.0
425–430	16.4	455–460	10.0
430–435	2.9	460–465	4.2
435–440	10.2	465–470	2.8
440–445	3.1		

Temperature dependence of the IO absorption cross-section at 427.2 nm

Temp./K	$10^{17} \sigma/\text{cm}^2$
250	5.3 ± 0.5
273	4.3 ± 0.4
298	3.1 ± 0.3
317	2.3 ± 0.2
341	2.3 ± 0.2
373	2.1 ± 0.2

Comments on Preferred Values

Sander,¹ Stickel *et al.*,² and Cox and Coker³ all report the same value of $\sigma = 3.1 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ for the 4-0 band at a resolution of 0.27 nm or less. The preferred absorption cross-sections at 298 K are based on this value.

The preferred values, which are averaged over 5 nm intervals, are based on the data reported by Cox and Coker.³

Stickel *et al.*² pointed out an error in Table II of Ref. 3 where the listed σ values averaged over 5 nm are a factor of 10 higher than the true values based on the data plotted in Figure 1 of that work. The atmospheric photolysis rate calculated from the tabulated data for a solar zenith angle of 40° (i.e., 0.3 s^{-1}) is consequently a factor of 10 too high. Stickel *et al.*² do not present averaged cross-section data, so it is not possible to utilize their measurements over the whole spectral range.

Sander¹ reported cross-sections at the head of the 4-0 band measured at six temperatures in the range 250–373 K. A strong temperature dependence is apparent at temperatures $< 317 \text{ K}$, with σ increasing with decreasing temperature.

No recommendation is given for the quantum yield. Durie and Ramsay⁴ report extensive predissociation in the A-X progression of IO; therefore the quantum yield for process (1) is probably unity throughout the wavelength region of the preferred σ values.

The preferred values are identical to our previous evaluation, IUPAC, 1992.⁵

References

- ¹S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).
- ²R. E. Stickel, A. J. Hynes, J. D. Bradshaw, W. L. Chameides, and D. D. Davis, J. Phys. Chem. **92**, 1862 (1988).
- ³R. A. Cox and G. B. Coker, J. Phys. Chem. **87**, 4478 (1983).
- ⁴R. A. Durie and D. A. Ramsay, Can. J. Phys. **36**, 35 (1958).
- ⁵IUPAC, Supplement IV, 1992 (see references in Introduction).

INO + $h\nu \rightarrow$ products

No new data have been published since our last evaluation.

Primary photochemical transitions

Reactions	$\Delta H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
INO + $h\nu \rightarrow$ I + NO	76	1570

Preferred Values

Absorption cross-sections of INO at 298 K

λ/nm	$10^{17} \sigma/\text{cm}^2$	λ/nm	$10^{17} \sigma/\text{cm}^2$
230	1.4	380	0.065
235	5.3	390	0.078
238	7.0	400	0.92
245	6.5	410	1.10
251	5.9	420	0.10
260	2.4	430	0.094
270	1.0	440	0.080
300	0.09	450	0.060
360	0.045	460	0.040
370	0.059		

Comments on Preferred Values

The absorption cross-section values are the averages from the data of Refs. 1–3. The deviations between the results of these studies are only small. No quantum yield data are available. Presumably the photolysis quantum yield is unity over the whole wavelength range. The preferred values are identical to our previous evaluation, IUPAC, 1992.⁴

References

¹H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

²N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).

³E. Forte, H. Hippler, and H. Van den Bergh, Int. J. Chem. Kinet. **13**, 1227 (1981).

⁴IUPAC, Supplement IV, 1992 (see references in Introduction).

 $\text{INO}_2 + h\nu \rightarrow \text{products}$

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{INO}_2 + h\nu \rightarrow \text{I} + \text{NO}_2$	80	1500

Absorption cross-section data

No absorption spectrum has been detected to date, although the spectrum has been searched for in the NO_2 -catalyzed recombination of iodine atoms.¹ It is presumed that $\sigma(\text{INO}_2) < \sigma(\text{NO}_2)$ over the wavelength range 250–600 nm.

References

¹H. Van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

 $\text{IONO}_2 + h\nu \rightarrow \text{products}$

No new data have been published since our last evaluation.

Primary photochemical processes

Reactions	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{IONO}_2 + h\nu \rightarrow \text{IO} + \text{NO}_2$ (1)		
$\rightarrow \text{I} + \text{NO}_3$ (2)		
$\rightarrow \text{IONO} + \text{O}(^3\text{P})$ (3)		
$\rightarrow \text{IONO} + \text{O}(^1\text{D})$ (4)		

Note: There are no thermodynamic data for IONO_2 .

Absorption cross-section data

No experimental data are available.

Quantum yield data

No experimental data are available.

Preferred Values

Neither qualitative absorption spectra or absolute cross sections have been measured for IONO_2 . It is suggested that in the absence of experimental data the absorption cross-

section data for BrONO_2 be used (this will probably lead to an underestimate of the IONO_2 photolysis rate J as the IONO_2 spectrum is expected to be red-shifted relative to the BrONO_2 spectrum by ~ 50 nm).

 $\text{CH}_3\text{I} + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reactions	$\Delta H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}(^2\text{P}_{3/2})$	239	500
$\rightarrow \text{CH}_3 + \text{I}^*(^2\text{P}_{1/2})$	330	362

Absorption cross-section data

Wavelength range/nm	Reference	Comments
205–335	Jenkin <i>et al.</i> , 1993 ¹	(a)
160–335	Fahr, Nayak, and Kurylo, 1995 ²	(b)

Comments

- (a) The absorption spectrum of CH_3I was recorded using a diode array spectrometer with a resolution of approximately 1 nm using a purified sample. The absolute cross-section at the maximum of absorption at 257.9 nm was $\sigma = 1.22 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (b) Absorption spectrum was measured over the temperature range 223–333 K. In addition to the gas-phase measurements over the wavelength range 160–335 nm, liquid-phase measurements over the range 330–400 nm were also reported. The liquid-phase values were converted into accurate gas-phase values at long wavelengths. The spectral resolution was approximately 0.1 nm. Cross-section values were reported at 0.5 nm intervals.

Preferred Values

Absorption cross-sections for CH_3I photolysis at 295 K, 253 K, and 223 K

λ / nm	$10^{20} \sigma / \text{cm}^2$			λ / nm	$10^{20} \sigma / \text{cm}^2$		
	295 K	253 K	223 K		295 K	253 K	223 K
220	6.87	6.06	6.39	290	8.71	7.01	5.83
225	9.09	8.46	8.56	295	4.15	3.18	2.69
230	12.7	11.5	11.9	300	2.09	1.57	1.34
235	20.8	19.8	19.9	305	1.11	0.84	0.75
240	39.1	37.4	37.7	310	0.62	0.49	0.44
245	69.4	67.9	69.0	315	0.37	0.29	0.27
250	105.7	104.9	108.4	320	0.24	0.20	0.16
255	133.9	134.9	140.1	325	0.13	0.11	–
260	138.8	140.9	148.5	330	0.067	0.055	–
265	119.8	120.2	123.9	335	0.039	0.032	–
270	87.2	86.1	87.2	340	0.020	0.020	–
275	56.1	52.9	52.2	345	0.010	0.010	–
280	32.8	31.0	26.9	350	0.005	0.005	–
285	16.7	14.4	12.9	355	0.005	0.003	–
				360	0.003	0.001	–

Comments on Preferred Values

The preferred values of the absorption cross-sections are those reported by Fahr *et al.*² These authors² reported measurements in the gas phase (160–335 nm) and the liquid phase (330–400 nm) over the temperature range 223–333 K. For the range of preferred values given here (220–360 nm), values were reported at 0.5 nm intervals.² A wavelength-shift procedure was used to convert the liquid-phase values into accurate gas-phase values at the long wavelengths.² Near the band maximum at 258.5 nm the cross-sections increased slightly (less than 15%) with a decrease in temperature.² For wavelengths greater than 275 nm the cross-sections decreased with a decrease in temperature.² The room temperature values reported in Ref. 2 are in good agreement (5–10%) with those reported by Jenkin *et al.*¹ for the wavelength regions $\lambda < 245$ nm and $\lambda > 280$ nm, but are 10–15% higher in the region of strongest absorption (250–270 nm). Other earlier room temperature results^{3,4} appear to be in reasonably good agreement with the preferred values. No other studies of the temperature dependence of the UV absorption cross-section have been reported.

Photolysis is expected to occur with unit quantum yield by breaking of the C-I bond to yield $\text{CH}_3 + \text{I}$. Photodissociation is known to produce both ground state iodine atoms and iodine atoms in the $\text{I}^*(^2\text{P}_{1/2})$ excited state lying 91 kJ mol^{-1} above the ground state. Flash photolysis of CH_3I was the source of the first $\text{I}^*(^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2})$ laser at $1.315 \mu\text{m}$.⁵ The quantum yield for production of $\text{I}^*(^2\text{P}_{1/2})$ atoms has been shown to be strongly dependent on the photodissociation wavelength; for example, Baughcum and Leone⁴ report that the value of $\phi(\text{I}^*)$ decreases from 0.81 at 248 nm to 0.05 at 308 nm.

References

- ¹M. E. Jenkin, T. P. Murrells, S. J. Shalliker, and G. D. Hayman, *J. Chem. Soc. Faraday Trans.* **89**, 433 (1993).
- ²A. Fahr, A. K. Nayak, and M. J. Kurylo, *Chem. Phys.* **197**, 195 (1995).
- ³D. Porrett and C. F. Goodeve, *Trans. Faraday Soc.* **33**, 690 (1937).
- ⁴S. L. Baughcum and S. R. Leone, *J. Chem. Phys.* **72**, 6531 (1980).
- ⁵J. V. V. Kasper and G. C. Pimentel, *Appl. Phys. Lett.* **5**, 231 (1964).

 $\text{CF}_3\text{I} + h\nu \rightarrow \text{products}$

Primary photochemical processes

Reaction	$\Delta H^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CF}_3\text{I} + h\nu \rightarrow \text{CF}_3 + \text{I}$	228	525

Preferred Values

Absorption cross sections for CF_3I photolysis at 298 K^a

λ/nm	$10^{20} \sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
240	13.7	0.58
245	21.9	0.28
250	33.4	-0.04
255	46.9	-0.36
260	59.5	-0.61
265	66.9	-0.70
270	66.5	-0.57
275	59.0	-0.17
280	47.0	0.52
285	34.8	1.5
290	23.6	2.7
295	14.8	3.8
300	8.9	4.9
305	5.2	6.0
310	2.9	6.8
315	1.6	7.3
320	0.93	7.5
325	0.50	7.7
330	0.27	7.9
335	0.15	8.2
340	0.08	8.5
345	0.04	8.3

^aTemperature dependence given by the expression: $\log_e \sigma = \log_e \sigma(298) + B(T-298)$ where T is temperature (K).

Absorption cross-section values have been reported by Solomon *et al.*¹ over the wavelength range 216–370 nm at 298 K and over the range 216–344 nm for $T = 200$ –298 K; and by Fahr *et al.*² over the wavelength range 160–240 nm for temperatures 240, 295, and 355 K and over the range 240–350 nm for $T = 218$ –333 K. The preferred values at 298 K are the average of the values reported by Solomon *et al.*¹ and by Fahr *et al.*² Results of these studies are in very good agreement at room temperature and agree to better than 15% at all temperatures. The temperature coefficient B values are those tabulated in Solomon *et al.*¹ At the longer wavelengths the cross-section values decrease significantly at lower temperatures; at 320 nm the value decreases by nearly 50% at 200 K. Photolysis is expected to occur with unit quantum efficiency by breaking of the C-I bond to yield $\text{CF}_3 + \text{I}$.

References

- ¹S. Solomon, J. B. Burkholder, A. R. Ravishankara, and R. R. Garcia, *J. Geophys. Res.* **99**, 20929 (1994).
- ²A. Fahr, A. K. Nayak, and R. E. Huie, *Chem. Phys.* **199**, 275 (1995).

5. HETEROGENEOUS REACTIONS

5.1. Introduction

Heterogeneous reactions taking place on surfaces of atmospheric particulates are now recognized to be important in the polar stratosphere of the southern as well as the northern hemisphere. Furthermore, heterogeneous processes occurring on sulfate/sulfuric acid aerosols in the stratosphere, under both background as well as volcanically enhanced conditions, are believed to be involved in the perturbed ozone chemistry observed in these situations. In addition, it is becoming increasingly clear that significant heterogeneous processes also take place in the free troposphere on atmospheric particulates related to emissions from air traffic. The assessment of the importance of heterogeneous chemical reactions taking place on surfaces of particulates present in the troposphere is an area of ongoing studies.

Heterogeneous reactions taking place at the gas-solid or gas-liquid interface are complex in contrast to the gas-phase rate processes presented in this compilation which involve elementary reactions. The primary experimental observable in a heterogeneous system is the rate of uptake of a trace gas species and in some cases the rate of formation of one or several product species. The uptake kinetics are often described in terms of the uptake coefficient, γ , a dimensionless parameter describing the probability that a gas phase species is removed irreversibly from the gas phase owing to the presence of an active surface in relation to the total number of gas-surface collisions with that surface. The uptake coefficient is defined in terms of the following equations depending upon whether the rate law for adsorption of the gas species is known or not:

$$\gamma = \frac{4R_{\text{up}}}{\langle c \rangle n_g}$$

$$\gamma = \frac{k_{\text{up}}}{\omega} \quad \text{where} \quad \omega = \frac{\langle c \rangle}{4V}$$

R_{up} and k_{up} are the experimentally determined uptake rate and rate coefficient, respectively, $\langle c \rangle$ is the average molecular speed of the gas, n_g is the concentration of the molecular species in the gas phase, ω is the gas-surface collision frequency in s^{-1} and V is the volume of the reaction vessel.

The observable rate of uptake of a species by a surface is a complex process and depends on several elementary processes such as gas-phase diffusion towards the surface of interest, the mass accommodation rate, the desorption rate from the surface back to the gas phase, the chemical transformation at the interface, the diffusion into the bulk of the condensed phase and possible chemical reactions within the bulk phase. The accommodation coefficient (α) describing the rate of mass accommodation relates to an elementary process and is not normally accessible to direct measurement or observation. The uptake coefficient γ refers to a series of processes and has therefore to be corrected for the various contributions in order to obtain information on α . A number of experiments are performed under conditions such that

some or all of the contributions to γ vanish except those from α . In this case the uptake coefficient can be interpreted as a mass accommodation coefficient.

This evaluation concentrates on the presentation of kinetic data for the uptake of atmospheric trace gas species onto a condensed phase, i.e., uptake and accommodation coefficients. We have not included data from the older literature on heterogeneous reaction kinetics when it was clear that the results are at variance with most of the more recent conclusions. Conspicuously absent from our evaluations are Henry's law solubilities governing the uptake of trace gases into the fluid condensed phase and isotherms controlling the adsorption of gases onto solids. It is intended to include these data in a future evaluation. The standard reaction enthalpy and entropy changes have only been listed in selected cases where the condensed phase has been sufficiently well characterized.

The uptake coefficient or reaction probability γ listed in the Tables is presented in a variety of forms depending upon the experimental technique used:

- γ_{ss} describes an experimentally determined uptake coefficient obtained from measurements at steady state even though the physical state of the system may change fairly rapidly with time, for instance due to surface saturation. Several uptake experiments of flowing gases on solid surfaces are conducted at very low trace gas concentrations in order to avoid surface saturation. In this case the measured uptake coefficient will approximate to the mass accommodation coefficient.

- γ_0 corresponds to an experimentally determined initial uptake coefficient that was changing rapidly with time. This value may have been obtained either through extrapolation of time-dependent γ values or it corresponds to an uptake coefficient resulting from a pulsed experiment. In cases without additional complications, γ_0 may approach the mass accommodation coefficient.

- γ corresponds to an uptake coefficient that was processed or corrected through major algebraic manipulations such as corrections for gas-phase diffusion, liquid-phase saturation in relation to limiting Henry's law solubilities, and condensed-phase diffusion. This value often corresponds to the mass accommodation coefficient.

- γ_{obs} , γ_{max} correspond to the observed value of the uptake coefficient under defined experimental conditions and to its maximum value, respectively.

- γ_X corresponds to the uptake coefficient of species X in cases where more than one gas phase species has been exposed to the surface of interest.

For mixtures of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{HNO}_3\text{-H}_2\text{O}$, and ternary mixtures containing HCl the composition is given in weight percent (% H_2SO_4 , % HNO_3 , %HCl), the concentrations are given in mol dm^{-3} ; rh means relative humidity in percent based on the partial pressure of H_2O , $p(\text{H}_2\text{O})$, even when solid substrates other than pure water ice are used and is calculated from:

$$\text{rh}(\%) = 100 p(\text{H}_2\text{O})/p_{\text{ice}}(T/K),$$

where $p_{\text{ice}}(T/K)$ corresponds to the vapor pressure of ice at temperature $T(K)$. In some cases experimental results are listed without explicit knowledge of the nature and composition of the substrate. NAT, NAD, NAM, and SAT mean nitric acid trihydrate ($\text{HNO}_3 \cdot 3\text{H}_2\text{O}$), nitric acid dihydrate ($\text{HNO}_3 \cdot 2\text{H}_2\text{O}$), nitric acid monohydrate ($\text{HNO}_3 \cdot \text{H}_2\text{O}$), and sulfuric acid tetrahydrate ($\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$), respectively. Additional hydrates are listed by name rather than by their acronyms. The abbreviations used in the experimental descriptions are defined in the Guide to the Data Sheets for the Thermal Reactions.

The effect of surface porosities on the uptake kinetics of trace gases on "porous" surfaces such as ice and NaCl is not yet well defined. The term porosity implies that the sample in question is presented with significant interstitial void such as a powder or a rough condensed film rather than having pores

on the molecular scale. One school of thought prepares substrates that are as smooth as possible to demonstrate the lack of a dependence of the measured kinetic results upon the substrate thickness. Another approach applies correction factors to the measured uptake coefficients ranging from a factor of four to sixteen, making the "true" uptake coefficient smaller than the measured one. It seems that the dependence of the uptake coefficient on the substrate porosity is observed for some gases (N_2O_5 , ClONO_2) and not for others (H_2O , HNO_3).

Excluded from the present work are papers dealing with solubility-limited uptake experiments and their time-dependent uptake coefficients. These references will be compiled and evaluated in a future edition, which will also include Henry's law constants of importance to atmospheric chemistry.

5.2. Heterogeneous Reactions—Data Sheets

5.2.1. Uptake Kinetics with Chemical Reaction

(including uptake studies)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
<i>Sulfate/H₂SO₄ (liquid) Substrates</i>					
γ_{ss}	$(4.9 \pm 0.7) \times 10^{-2}$	NH ₄ HSO ₄ aerosol, 45–75% rh	293	Mozurkewich and Calvert, 1988 ¹	(a)
	$(8.5 \pm 1.9) \times 10^{-2}$	NH ₄ HSO ₄ aerosol, 55–75% rh	274		
	$(1.0 \pm 0.1) \times 10^{-1}$	H ₂ SO ₄ aerosol, 1–10% rh	293	Hanson and Ravishankara, 1991 ²	(b)
γ_{ss}	$(1.39 \pm 0.09) \times 10^{-1}$	H ₂ SO ₄ aerosol, 1–10% rh	274		
	$(1.2 \pm 0.3) \times 10^{-1}$	40% H ₂ SO ₄	225.5		
	$(1.4 \pm 0.3) \times 10^{-1}$	60% H ₂ SO ₄	225.5		
	$(1.0 \pm 0.2) \times 10^{-1}$	70% H ₂ SO ₄	225.5		
	$(1.0 \pm 0.2) \times 10^{-1}$	75% H ₂ SO ₄	225.5	Van Doren <i>et al.</i> , 1991 ³	(c)
γ	$(5.8 \pm 0.6) \times 10^{-2}$	73% H ₂ SO ₄ droplets	283		
γ_{ss}	$(5.5 \pm 1.0) \times 10^{-2}$	74%–96% H ₂ SO ₄	220±5	Golden <i>et al.</i> , 1992 ⁴ ; Williams <i>et al.</i> , 1994 ⁵ ; Manion <i>et al.</i> , 1994 ⁶	(d)
γ_{ss}	$(6 \pm 4) \times 10^{-2}$	78.7%–83.6% H ₂ SO ₄	293	Fried <i>et al.</i> , 1994 ⁷	(e)
	$(1.03 \pm 0.06) \times 10^{-1}$	64.0%–81.4% H ₂ SO ₄	273		
	$(1.20 \pm 0.16) \times 10^{-1}$	56.6%–76.2% H ₂ SO ₄	260		
	$(1.48 \pm 0.11) \times 10^{-1}$	63.2%–76.0% H ₂ SO ₄	247		
	$(0.86 \pm 0.09) \times 10^{-1}$	60.7%–62.1% H ₂ SO ₄	247		
	$(1.46 \pm 0.36) \times 10^{-1}$	68.6%–70.9% H ₂ SO ₄	230–234		
	$(1.02 \pm 0.11) \times 10^{-1}$	64.5%–68.6% H ₂ SO ₄	231–234		
	$(0.77 \pm 0.19) \times 10^{-1}$	54.0%–63.7% H ₂ SO ₄	225–231		
<i>Sulfate/H₂SO₄ (solid) Substrates</i>					
γ_{ss}	$5.0 \times 10^{-3} < \gamma < 8.0 \times 10^{-3}$	57.5% H ₂ SO ₄	195–205	Hanson and Ravishankara, 1993 ⁸	(f)
	$2.4 \times 10^{-3} < \gamma < 5.0 \times 10^{-3}$	60% H ₂ SO ₄	192–205		
<i>HNO₃–H₂O Substrates</i>					
γ_{max}	$(1.3 \pm 0.3) \times 10^{-2}$	bulk NAT	188	Quinlan <i>et al.</i> , 1990 ⁹	(g)
γ_{ss}	$(6 \pm 3) \times 10^{-4}$	NAT film	200	Hanson and Ravishankara, 1991 ¹⁰	(h)
γ_{ss}	6×10^{-4}	NAT	191	Hanson and Ravishankara, 1992 ¹¹	(i)
γ_{11}	$(3 \pm 1) \times 10^{-4}$	NAT	191	Hanson and Ravishankara, 1993 ¹²	(j)
γ_0	$\leq 1 \times 10^{-4}$	NAT film	160–205	Kenner, Ryan, and Plumb, 1994 ¹³	(k)
<i>H₂O (solid) Substrates</i>					
γ_{ss}	$\geq 1.0 \times 10^{-3}$ ($\pm 50\%$)	ice film	185	Tolbert, Rossi, and Golden, 1988 ¹⁴	(l)
γ_{ss}	$(2.8 \pm 1.1) \times 10^{-2}$	ice film	195	Leu, 1988 ¹⁵	(m)
γ_{max}	$(3.4 \pm 0.8) \times 10^{-2}$	bulk ice	188	Quinlan <i>et al.</i> , 1990 ⁹	(n)
	$(2.3 \pm 0.8) \times 10^{-2}$	ice film	188		

(including uptake studies)—Continued

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(2.4 \pm 0.8) \times 10^{-2}$	ice film	200	Hanson and Ravishankara, 1991 ¹⁰	(h)
γ_{ss}	1.3×10^{-2}	ice film	191	Hanson and Ravishankara, 1992 ¹¹ , 1993 ¹²	(i,j)
γ_0	$\geq 1.0 \times 10^{-2}$	ice film	160–205	Kenner, Ryan, and Plumb, 1994 ¹³	(k)
<i>H₂O (liquid) Substrates</i>					
γ	$(4.0 \pm 0.5) \times 10^{-2}$	H ₂ O droplets	282	Van Doren <i>et al.</i> , 1990 ¹⁶	(o)
	$(6.1 \pm 0.4) \times 10^{-2}$	H ₂ O droplets	271		
γ	$5.0 \times 10^{-3} \leq \gamma \leq 1.0 \times 10^{-2}$	liquid jet	293.1	Kirchner <i>et al.</i> , 1990 ¹⁷	(p)
γ	$(3.0 \pm 0.2) \times 10^{-2}$	H ₂ O droplets	262	George <i>et al.</i> , 1994 ¹⁸	(q)
	$(1.3 \pm 0.8) \times 10^{-2}$	H ₂ O droplets	277		
<i>Other Substrates</i>					
γ	3.0×10^{-3}	charcoal	300	Brouwer, Rossi, and Golden, 1986 ¹⁹	(r)
	5.0×10^{-3}	charcoal + H ₂ O	300		

Comments

- (a) Uptake experiment in high-pressure (0.8 atm) flow tube using slow-flow conditions and fine size-selected aerosol. Three size classes in the range between 40–100 nm diameter were used in the uptake experiments. The maximum number density of 2.5×10^5 particles cm^{-3} was observed at 40 nm diameter. The value for the uptake coefficient was weakly dependent (increasing) on aerosol size in the range indicated and within experimental error. The significant value of γ_{ss} below the deliquescence point ($\text{rh} \leq 40\%$) is explained by evaporation of NH_3 and generation of a water-containing H_2SO_4 layer. By increasing the NH_4^+ content by 25%, γ_{ss} decreases at low and high rh . No significant uptake of N_2O_5 on $(\text{NH}_4)_2\text{SO}_4$ aerosol was observed at $\text{rh} = 25\%$ at 293 K owing to the absence of a liquid layer on the aerosol surface. At 60% rh , γ_{ss} was measured as $(4.3 \pm 0.5) \times 10^{-2}$. The uptake of N_2O_5 on H_2SO_4 - H_2O was independent on rh in the range 1–10%. The negative temperature dependence of γ_{ss} observed throughout this work is interpreted in terms of increasing reevaporation of N_2O_5 with increasing temperature.
- (b) Uptake experiment on a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3} . The cold aqueous solution of H_2SO_4 (40–75%, $T = 215$ – 230 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(\text{H}_2\text{O})$ was generally around 1 mTorr. Owing to diffusion limitations a correction had to be applied to γ taking into account the estimated diffusion coefficients of N_2O_5 in He. The temperature dependence of γ was measured for the 60% and 70% solution: none was found within the reported error limits.
- (c) Uptake experiment on a fast droplet train (200 μm diameter 73% H_2SO_4 - H_2O droplets) traversing a flow tube coupled to a multiple pass IR diode laser absorption cell of 728 cm optical path at pressures of 10 Torr and droplet-gas interaction times of 1–2 ms. The prod-

uct branching ratio for the heterogeneous N_2O_5 - H_2O interaction was defined as the ratio of observable $\text{HNO}_3(\text{g})$ and twice the depletion of $\text{N}_2\text{O}_5(\text{g})$ [$\text{HNO}_3(\text{g})/2\Delta(\text{N}_2\text{O}_5(\text{g}))$], and varied between 0.25 and 0.37 for interaction times of 1.1 to 1.6 ms, respectively. The value for γ listed in the Table has been corrected for gas-phase diffusion and distortion of the Maxwellian velocity distribution near an adsorbing surface and is about 40% larger than in pure water. No saturation effects have been observed due to the high reactivity of the heterogeneous interaction.

- (d) Knudsen cell technique using electron-impact MS detection using modulated molecular beam phase-sensitive detection. N_2O_5 was detected at m/e 46 and HNO_3 detected at m/e 30, 46, and 63 (for high densities). The concentration of HNO_3 was in the range 4×10^{10} to 10^{12} molecule cm^{-3} . The uptake on 74 to 96% H_2SO_4 did not saturate around temperatures of 220 K for the duration of the experiment (1000 s) if the raw signal for N_2O_5 uptake was corrected for the formation of HNO_3 which increased slowly with time. The uptake experiments resulted in a temperature concentration (74 to 96% H_2SO_4) and time-independent γ value of 0.02–0.03. Saturation effects were thought to affect the measurement of γ even at low densities (2×10^{11} molecule cm^{-3}). Stirring the H_2SO_4 - H_2O solution increased γ by a factor of 2 to 3, resulting in a value displayed in the Table. At $\gamma = 0.1$ it takes a few seconds to saturate the sulfuric acid surface at the lowest densities used.
- (e) Uptake experiment in high-pressure (0.3–0.8 atm) flow tube using slow flow conditions and fine size-selected (classified) aerosol. The sulfuric acid aerosol size ranged from 60 to 250 nm diameter at 225 to 293 K, corresponding to a sulfuric acid content of 54% to 82%, and was generated by homogeneous nucleation from the reaction of $\text{SO}_3 + \text{H}_2\text{O}$. The N_2O_5 concentration ranged from 30 to 200 ppb at 333 to 800 mbar total pressure. The N_2O_5 detection was performed by observing the decrease in NO concentration after reaction in a heated quartz tube using tunable diode laser

absorption which was also used to monitor the partial pressure of H_2O vapor. Corrections to the decay curves of N_2O_5 as a function of reaction time amounted to less than 20% each and were principally due (i) to the presence of doubly charged aerosol particles in the aerosol classifier, (ii) to deviation from plug flow conditions and (iii) to gas-phase diffusion towards the aerosol surface. For each temperature and rh, N_2O_5 decays were obtained for several particle sizes and number densities of aerosol particles. No dependence of the N_2O_5 uptake coefficient on particle size was detected within the experimental conditions. At 293 and 273 K, γ_{ss} (see Table) was independent of the H_2SO_4 composition but seemed to depend on composition at lower temperatures. At 260 K, γ_{ss} is independent of composition for sulfuric acid concentrations up to, but excluding, 78% H_2SO_4 . At this composition and temperature there was an indication that $\gamma_{\text{ss}} = 4 \times 10^{-2}$ for a frozen aerosol and $\gamma_{\text{ss}} = 1.8 \times 10^{-1}$ for the aerosol in the supercooled state. At 230 K, γ_{ss} increased from 7.7×10^{-2} for compositions near 60% H_2SO_4 to 1.46×10^{-1} for compositions near 70% H_2SO_4 . Intermediate conditions resulted in intermediate results. A semiempirical model was put forward that explains the trends of γ_{ss} as a function of temperature and composition (rh). There were indications from this work that the sulfuric acid aerosol is in a supercooled state at $T \leq 260$ K.

- (f) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3} . The cryogenic deposits were characterized by their vapor pressure of H_2O , detected by an ion-molecule reaction with F_2^- , whose decrease with the H_2O vapor pressure was monitored. The sulfuric acid surfaces were prepared by freezing a small amount of 57.7% H_2SO_4 (tetrahydrate) or 60% H_2SO_4 on the inside of the flow tube wall. The results were obtained as a function of rh, which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.25 mTorr or by changing the H_2O flow rate at constant temperature to result in a range 10%–90% rh. The uptake coefficients were determined from the decrease of the N_2O_5 density ($\sim 10^{-7}$ Torr) with residence time. For 57.5% H_2SO_4 (tetrahydrate) they were almost independent of rh and were much lower than those found for liquid acid. The uptake coefficient determined for 60% H_2SO_4 at 192 K depended on rh (a decrease of a factor of 4 in going from 80% to 40% rh) whereas the one measured at 205 K was independent on rh within experimental error.
- (g) For experimental details, see Comment (l). A bulk solution of HNO_3 - H_2O corresponding to NAT stoichiometry was frozen to 188 K. The initial value for γ drops from the maximum given in the Table to a value of less than 0.01, typically 0.004 which is the steady-state asymptote for NAT. Uptake was studied on other cryo-

genic surfaces containing HNO_3 - H_2O in variable amounts. No consistent picture emerges as γ always goes through a maximum. There is concern that the bulk cryogenic phase did not correspond to NAT in those studies owing to the high reactant pressures used but was in fact a supercooled liquid glass.

- (h) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of N_2O_5 in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3} . NAT was prepared *in situ* by converting N_2O_5 into HNO_3 on the ice surface well past saturation. The steady-state HNO_3 vapor detected at the downstream end of the flow tube was consistent, within a factor of two, with the expected equilibrium vapor pressure over NAT- HNO_3 -in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate, a NAT layer 1 to 2 monolayers thick $[(2-4) \times 10^{14} \text{ HNO}_3 \text{ cm}^{-2}]$ was inferred. It was assumed that the saturated monolayer was at steady-state for the duration of the experiment. Saturation effects on pure ice were observed at N_2O_5 concentrations varying from 10^9 to 3×10^{10} molecule cm^{-3} . No saturation effects of γ on NAT have been reported. The relevant surface corresponds to the geometric area, as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ .
- (i) For experimental details see Comment (h). These experiments were designed to investigate the influence of the thickness of the substrate on γ . The values for γ given in the Table correspond to a thickness of 10 μm where one can expect a coherent film of substrate deposited from the vapor phase (see Kenner *et al.*¹³). The value for γ varied by a factor of no more than three and 1.5 for NAT and pure ice, respectively, when the thickness was varied from 1 to 100 nm. The conclusion is that there is no significant dependence of γ on thickness.
- (j) For experimental details see Comments (h) and (i). This study was undertaken to supplement the original work on ice and nitric-acid doped (NAT) surfaces to further confirm the independence of the measured uptake coefficients on the substrate thickness.
- (k) Uptake experiment in an ice-coated flow tube with MS detection in the ioncounting mode at m/e 30, 46, and 63. Characteristic N_2O_5 density of $(1-10) \times 10^{10}$ molecule cm^{-3} was used. Owing to the large difference between γ for ice and NAT, poisoning effects led to hysteresis behavior in the experimental data of N_2O_5 density vs. injector position as the injector was moved back and forth. The reaction product HNO_3 forms NAT in the course of the experiment. The results listed in the Table correspond to the initial value of γ . The geometric surface is the relevant area for the uptake experiment. Numerical modeling was used to interpret the experimental results. The simple model based on $\text{N}_2\text{O}_5(\text{g}) + \text{sf H}_2\text{O}(\text{s}) \rightarrow 2(\text{HNO}_3 \cdot 3\text{H}_2\text{O})(\text{s})$ satisfacto-

rily explained the major features of the data resulting in a modeled γ of 0.015 and $\text{sf}=7\pm3$ in accord with the hypothesis that initial reaction occurs on ice sites. A small negative temperature dependence for γ ($5\text{--}10\text{ kJ mol}^{-1}$) was noted. The poisoning effect consists in blocking free available water sites on which the reaction takes place by converting them into NAT. The model results were independent of the thickness of the ice (d) for $d>9\text{ }\mu\text{m}$ which seems to be the minimum thickness which still gave a coherent ice coat on the wall of the flow tube.

- (l) Uptake experiment in a low pressure Knudsen cell flow reactor monitored by modulated molecular beam electron-impact MS. The ice was condensed from the vapor phase, and the uptake experiment was performed at typical pressures of N_2O_5 of 1.0 mTorr. The uptake coefficient γ was monitored using the MS signal at m/e 46, where HNO_3 also contributed significantly; due to the high pressure of N_2O_5 used the vapor pressure of bulk HNO_3 (multilayers) significantly perturbed the quantitative measurement of γ so that only a lower limit could be given. The reaction was also followed by observing the identity of the reaction product (HNO_3) through its thermal desorption behavior when the cryogenic phase was allowed to warm up after the reaction. HNO_3 monitored at m/e 63 desorbed both at 203 (bulk or "overlayer") and around 230 K (unspecified hydrate). The corresponding H_2O signal recorded at m/e 18 showed two characteristic desorption temperatures, 209 K and 230 K; the former corresponds to free (bulk) H_2O whereas the latter corresponds to the dissociation of the HNO_3 hydrate (a temperature also found from reference experiments by co-condensing HNO_3 and H_2O). The yield of HNO_3 with respect to N_2O_5 was 1.3 (the expected value is 2.0 if the only reaction product is HNO_3 and if all HNO_3 formed desorbed into the gas phase).
- (m) Ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor and the typical N_2O_5 concentration was $1\times10^{13}\text{ molecule cm}^{-3}$. The kinetics were measured by monitoring the disappearance of N_2O_5 at m/e 46 under conditions where HNO_3 remained on the ice film. Corrections of γ due to diffusion limitations were performed using estimated diffusion coefficients scaled to 195 K. A fresh ice film was prepared for every uptake experiment.
- (n) Uptake experiment in a low pressure Knudsen cell flow reactor monitored by modulated molecular beam electron-impact MS. Pure ice from freezing liquid water (bulk) and condensed from the vapor phase (film, 5000 monolayers). No HNO_3 was observed. Monitored N_2O_5 using m/e 46. Characteristic pressure was on the order of $10^{11}\text{ molecule cm}^{-3}$. Unusual behavior of γ with time of exposure was observed: Uptake started at 0.01, then increased with time (maximum values given in Table) and subsequently tended towards a steady state at 0.004 (characteristic of NAT at long exposure times). This behavior was interpreted qualitatively as a combination of autocatalytic and saturation behavior. The number of N_2O_5 taken up to maximum γ was constant for all the experiments performed (4.6×10^{16} molecule or twice that in HNO_3). The geometric surface of ice seems to be the relevant area for uptake. Bulk and film values for γ are identical within the experimental uncertainty.
- (o) Uptake experiment on a fast droplet train (200 μm diameter) crossing a flow tube in transverse geometry. Trace gas analysis was by IR diode laser absorption in a multiple pass cell of 728 cm optical path at total pressures of 5–20 Torr. Values listed are corrected for gas-phase diffusion and distortion of velocity vector owing to rapid uptake.
- (p) Uptake experiment involving the interaction of N_2O_5 in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics was studied by analyzing the liquid water content for NO_3^- or Cl^- using ion chromatography. The jet diameter was 90 μm and the jet length between 0.2 and 6 mm leading to contact times of 0.03–1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The N_2O_5 concentration detected by UV absorption in the 200 to 224 nm range was about 100 ppm and the 10% HNO_3 impurity was taken into account in the fitting procedure. Less than 2 ppm of NO_2 was detected using LIF excited at 442 nm and a measurement of γ relative to the one for HCl ($\gamma=1.0\times10^{-2}$) resulted in a γ value larger by a factor of two with respect to the absolute determination.
- (q) Uptake experiment on a fast droplet train (80–150 μm diameter) inside a flow tube at total pressures of 20–60 Torr synthetic air with 4–16 ms contact time. The temperature of the droplet was controlled by the metered partial pressure of H_2O in the synthetic air carrier gas which was varied between 1.9 to 6.2 Torr (262–277 K). The N_2O_5 contained less than 8% HNO_3 and its partial pressure monitored by FTIR absorption ranged from 20 to 2000 ppm in the flow tube. The extent of reaction was followed by measuring the NO_3^- concentration in the collected droplets using HPLC. It was found that negligible loss of N_2O_5 occurred when the relative humidity was kept below 30% in the Teflon FEP tubing. The uptake coefficients were corrected for gaseous diffusion of N_2O_5 to the droplet surface. It is thought that the uptake coefficient is reaction controlled with a pseudo-first-order rate constant of $\sim10^5\text{ s}^{-1}$.
- (r) Uptake experiment in a low pressure Knudsen cell

monitored by electron-impact MS. The substrate was commercially available charcoal material with a BET surface area of $37 \text{ m}^2 \text{ g}^{-1}$. The first entry in the table refers to uptake of N_2O_5 on charcoal in the absence of added H_2O at a characteristic N_2O_5 concentration of $15.1 \times 10^{14} \text{ molecule cm}^{-3}$. Main reaction product was NO from redox reaction on charcoal, HNO_3 was observed at m/e 63 as a minor product. The second entry refers to N_2O_5 uptake in the presence of H_2O after steady state regarding N_2O_5 adsorption had been attained. Physisorption, redox reaction, and hydrolysis are all taking place with the added complication of secondary heterogeneous reaction of the hydrolysis product HNO_3 on the carbon surface. Therefore, the value for γ in the second entry has to be regarded as a lower limit for the uptake coefficient of N_2O_5 . In the initial stages of the uptake the redox reaction dominates, and after saturation of the reaction sites HNO_3 starts desorbing after about 20 min. Mass balance data indicate that 30% of the N_2O_5 undergoes redox reaction and/or physisorption at steady state at H_2O concentrations that maintain constant water coverage on the substrate. With increasing H_2O concentration an increased rate of HNO_3 formation is observed. In the later stages of the interaction the hydrolysis gains in importance in relation to the redox chemistry. This is apparent in an increase of both the rate of H_2O consumption and HNO_3 formation at the expense of the rate of NO formation. At steady state the rate law for HNO_3 formation is linear in $[\text{HNO}_3]$ and $[\text{H}_2\text{O}]$ under excess conditions of the other reaction partner.

Preferred Values

The uptake coefficient of N_2O_5 on *liquid* sulfuric acid substrates at temperatures around 220 K seems to fall between 5×10^{-2} to 1×10^{-1} for surfaces of bulk substrates. The results obtained on fine sulfuric acid *aerosols* at comparable temperatures seem to lie on the upper bound of the range and may have gone through a maximum around 250 K ($\gamma_{\text{max}} = 0.15$). The uptake coefficient on *frozen* bulk sulfuric acid at slightly lower temperatures (200 K) is 5×10^{-3} which is roughly an order of magnitude lower than the one for the bulk liquid. Although most of the measurements suggest that

this reaction is largely independent of the sulfuric acid content (water activity) and fairly insensitive to temperature changes, both of which cannot easily be varied independently in most experiments, the most recent experiments of Fried *et al.*⁷ reveal dependencies on both temperature and composition.

On NAT-like substrates the uptake coefficient attains a value on the order of 5×10^{-4} which is the result of several determinations using the same technique (flowing gas). The experiments seem to be prone to saturation effects.

The uptake on a water ice film at 190 K results in $\gamma = 2 \times 10^{-2}$, both for ice films deposited from the vapor phase as well as for bulk ice. This value is smaller than the one for uptake on liquid H_2SO_4 - H_2O at comparable temperatures, by a factor of three. A γ value of 4×10^{-2} is obtained for the uptake on supercooled and liquid water droplets at sub-ambient temperatures (260 to 280 K).

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\geq 3 \times 10^{-3}$	ice film, 15–32% HCl	185	Tolbert, Rossi, and Golden, 1988 ¹	(a)
γ_{ss}	$(2.7 \pm 1.0) \times 10^{-2}$	ice film, $p_{\text{HCl}} \rightarrow 0.0$	195	Leu, 1988 ²	(b)
γ_{ss}	$(3.2 \pm 1.0) \times 10^{-3}$	NAT film	200	Hanson and Ravishankara, 1991 ³	(c)

Comments

- (a) Uptake experiment in a low pressure Knudsen cell flow reactor monitored by modulated molecular beam electron-impact MS. The ice phase was condensed from H₂O vapor prior to the uptake experiment, and a HCl-H₂O ice (7 and 14% on a per mole basis) was prepared by co-condensation of both components. The characteristic N₂O₅ pressure was 12 mTorr. The uptake coefficient was measured at m/e 46 assuming only N₂O₅ and ClNO₂ in the Knudsen cell effluent. Therefore, γ given in the Table is a lower limit. Nitryl chloride, NO₂Cl, was confirmed as a gas-phase product together with condensed HNO₃, which was identified by thermal desorption experiments performed after the uptake experiment. No interaction of NO₂Cl with the solid solution of HCl-H₂O at 185 K was observed. An added complication in those experiments was the fast heterogeneous reaction of N₂O₅ with HCl on the cold reactor walls in the absence of a cryogenic H₂O film, resulting in identical reaction products. All but 5% of the originally co-condensed HCl was converted into ClNO₂.
- (b) Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The HCl-ice film was deposited from simultaneous condensation of H₂O and HCl vapor and the typical N₂O₅ concentration was 1×10^{13} molecule cm⁻³. The composition of the HCl-ice film was determined after each experiment: the HCl mole fraction ranged from 0.015–0.04. A fresh ice film was prepared for every uptake experiment. The kinetics were measured by monitoring the disappearance of N₂O₅ at m/e 46 under conditions where HNO₃ remained on the ice film. ClNO₂ or ClONO was observed at m/e 49/51, and uptake coefficients measured using m/e 46 signals were corrected for the contribution of those two (volatile) products. Corrections of γ for diffusion limitations were performed using estimated diffusion coefficients scaled to 195 K. The value of γ listed corresponds to a limiting value for the mole fraction of HCl in the ice (f_{HCl}) approaching zero: $\gamma=0.051$ at $f_{\text{HCl}}=0.015$, $\gamma=0.063$ at $f_{\text{HCl}}=0.04$.
- (c) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of N₂O₅ in the presence of HNO₃ and other reactants at characteristic densities of 10^9 – 10^{11} molecule cm⁻³. NAT was prepared *in situ* by converting N₂O₅ into HNO₃ well past saturation of the ice surface. The steady state HNO₃ vapor detected at the downstream end of the flow tube was consistent within a factor of two with the equilibrium vapor pressure over NAT-HNO₃-in-ice solid solution near 201 K. From the N₂O₅ taken up by the cryogenic substrate a NAT layer 1 to 2 monolayers thick [$(2-4) \times 10^{14}$ HNO₃ molecule cm⁻²] was inferred. It is assumed that the saturated monolayer is at steady-state over the duration of the experiment. The experiments were performed under conditions of a steady state concentration of HCl twice that of N₂O₅, namely between $(2-6) \times 10^9$ molecule cm⁻³, because the reaction was controlled by the availability of HCl. When the reaction was performed on pure ice no effect of the added HCl could be detected, thus indicating no preference for reaction of N₂O₅ with HCl over that with H₂O. Since the uptake on ice is faster by a factor of eight, the reactive uptake of N₂O₅ in the presence of HCl was studied on a NAT surface. No information regarding the saturation of γ on the NAT surface is available. The relevant surface corresponds to the geometric area as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ .

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\sim 5 \times 10^{-3}$	H ₂ O-ice, NAT	201	Hanson and Ravishankara, 1992 ¹	(a)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO₃-treated ice was defined as NAT under the given experimental conditions. On cold Pyrex, γ_{ss} was found to be $< 10^{-4}$ whereas γ_{ss} based on the disappearance of N₂O₅ increased to $\sim 5 \times 10^{-3}$ at 50% rh at HBr concentrations of 5×10^9 to 10^{11} molecule cm⁻³. Without HBr the N₂O₅ loss is much smaller ($\gamma_{\text{ss}} \sim 1 \times 10^{-3}$, consistent with the small uptake coefficient for N₂O₅ on NAT) such that the difference to 5.0×10^{-3} is attributed to the reaction probability of the title reaction. At higher N₂O₅ and HBr concentrations a new distinct phase forms that is visible to the eye with $\gamma_{\text{ss}} \sim 4 \times 10^{-2}$ with no intermediate values observed. On

pure H₂O-ice and NAT the same results were obtained as on cold Pyrex at 50% rh. An alternative reaction path leading to BrONO₂ + HONO could not be excluded. It has to be noted that BrONO was not observed in these experiments as it is an inferred reaction product.

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$\geq 2.5 \times 10^{-3}$		300	Livingston and Finlayson-Pitts, 1991 ¹	(a)
γ_{ss}	$(3.2 \pm 0.3) \times 10^{-2}$	high rh	292	Zetzsch and Behnke, 1992 ²	(b)
				Behnke <i>et al.</i> , 1992 ² , 1994 ^{4,5}	
γ_{ss}	$(3.9 \pm 1.3) \times 10^{-2}$	H ₂ O droplet	263	George <i>et al.</i> , 1994 ⁶	(c)
	$(1.4 \pm 0.8) \times 10^{-2}$	H ₂ O droplet	278		

Comments

- (a) The N₂O₅ exposure experiments were conducted in a static salt-packed cylindrical cell whose content was monitored by long path FTIR absorption spectroscopy at 1 atm pressure. HNO₃, N₂O₅, and NO₂Cl were observed in the spectral range 700–1500 cm⁻¹ and the uptake coefficient was inferred from the fractional yield of NO₂Cl relative to N₂O₅ as a function of residence time and mass of the salt. The typical initial concentration of N₂O₅ in the vessel containing the salt was approximately 5.5×10^{13} molecule cm⁻³. The salt had a surface area of 33 cm² g⁻¹ and small amounts of water vapor did not affect the results. Large amounts of HNO₃ (HNO₃/N₂O₅ = 0.55 ± 0.16) originating from the heterogeneous reaction of N₂O₅ with residual water resulted in the formation of HCl.
- (b) The N₂O₅ uptake experiments were performed in an aerosol smog chamber with Teflon coated walls in a mixture of hydrocarbons, NO_x, and O₃ and in the presence of a well characterized NaCl aerosol with known size distribution. Typical conditions were 60 ppb of N₂O₅ in air, 80 mg m⁻³ of NaCl and relative humidities of 71–92% (292 K). The extent of the reaction was followed by monitoring the decrease of the hydrocarbons, O₃, HCl, and NO₂ as a function of time. The amount of N₂O₅ taken up was assessed using the NO_x mass balance and ClNO₂ was derived from the hydrocarbon consumption with time in the presence of light (arising from the reaction Cl + hydrocarbon). The uptake coefficient γ based on the disappearance of N₂O₅ was independent of relative humidity for the range given above, whereas the yield of ClNO₂ varied strongly with relative humidity. The results on ClNO₂ were discussed in terms of a branching ratio k_a/k_b between N₂O₅(ads) + NaCl → NaNO₃ + ClNO₂ (k_a) and N₂O₅(ads) + H₂O → 2HNO₃ (k_b). The yields were 100%, 75%, 50%, and 33% ClNO₂ for rh of 50%, 71%, 76% (deliquescence point of NaCl), and 92%

based on N₂O₅ taken up. Recent results point towards a constant ClNO₂ yield of 70%, corresponding to a branching ratio of 2.5:1 independent of the relative humidities between 50 and 92% (corresponding to [NaCl] of 6 to 2.2 M). The yields were corrected for the formation of alkyl nitrates that were calculated from a standard photochemical model. The chlorinated hydrocarbons 1,1-dichloroacetone, chloroacetone, and phosgene probably resulted from the heterogeneous interaction of Cl with the hydrocarbons and were detected by GC. The ClNO₂ yields observed from experiments in a wetted-wall flow tube decreased continuously for [NaCl] ≤ 2 M corresponding to 94% rh but were still at 20% at [NaCl] = 1.7×10^{-2} M. The results from the smog chamber and wetted-wall flow tube experiments agree well in the overlapping range.

- (c) Uptake experiment on a fast droplet train (80–150 μm diameter) inside a flow tube at total pressures of 20–60 Torr synthetic air with 4–16 ms contact time containing 1 M NaCl. The temperature of the droplet was controlled by the metered partial pressure of H₂O in the synthetic air carrier gas which was varied between 2.1–6.2 Torr (263–278 K). The N₂O₅ contained less than 8 HNO₃ and its partial pressure monitored by FTIR absorption ranged from 20 to 2000 ppm in the flow tube. The extent of reaction was followed by measuring the NO₃⁻ concentration in the collected droplets using HPLC. It was found that negligible loss of N₂O₅ occurred when the rh was kept below 30% in the Teflon FEP tubing. The measured uptake coefficients were corrected for gaseous diffusion of N₂O₅ to the droplet surface and the NO₂Cl yield ($67 \pm 7\%$) obtained from independent wetted-wall flow tube experiments. The reactive uptake coefficients on droplets containing NaCl are slightly larger than those for droplets without NaCl. It is thought that the uptake coefficient is reaction controlled rather than given by mass accommodation.

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(including uptake studies)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
<i>Sulfate/H₂SO₄ (liquid) Substrates</i>					
γ_{ss}	$(3.2 \pm 0.8) \times 10^{-4}$	95.6% H ₂ SO ₄	300	Rossi, Malhotra, and Golden, 1987 ¹	(a)
γ_{ss}	2.6×10^{-3}	65% H ₂ SO ₄	210	Tolbert, Rossi, and Golden, 1988 ²	(b)
γ_{ss}	3.0×10^{-4}	75% H ₂ SO ₄	230	Hanson and Ravishankara, 1991 ³	(c)
	$(6.4 \pm 1.0) \times 10^{-2}$	40% H ₂ SO ₄	218 ± 3		
	$(3.1 \pm 0.5) \times 10^{-3}$	60% H ₂ SO ₄	215		
	$(1.2 \pm 0.2) \times 10^{-3}$	65% H ₂ SO ₄	215		
	$(3.9 \pm 0.7) \times 10^{-4}$	70% H ₂ SO ₄	220		
γ_{ss}	$(1.9 \pm 0.3) \times 10^{-4}$	75% H ₂ SO ₄	230	Golden <i>et al.</i> , 1992 ⁴ ; Williams <i>et al.</i> , 1994 ⁵ ; Manion <i>et al.</i> , 1994 ⁶	(d)
	$(8.1 \pm 1.3) \times 10^{-2}$	40% H ₂ SO ₄	220 ± 5		
	$(4.1 \pm 0.7) \times 10^{-3}$	57.5% H ₂ SO ₄	220 ± 5		
	$(2.1 \pm 0.35) \times 10^{-4}$	75% H ₂ SO ₄	220 ± 5		
	γ_{ss}	$(3.8 \pm 1.2) \times 10^{-2}$	46.6% H ₂ SO ₄ , liquid		
$(6.1 \pm 2.0) \times 10^{-3}$		57.5% H ₂ SO ₄ , liquid	202		
$(9.3 \pm 3.0) \times 10^{-4}$		65% H ₂ SO ₄ , liquid	202		
<i>Sulfate/H₂SO₄ (solid) Substrates</i>					
γ_{ss}	2.0×10^{-3}	57.7% H ₂ SO ₄ , 90% rh	191.5	Hanson and Ravishankara, 1993 ⁸	(f)
	2.0×10^{-3}	57.7% H ₂ SO ₄ , 30% rh	196		
	5.0×10^{-4}	57.7% H ₂ SO ₄ , 16% rh	200		
	1.0×10^{-4}	57.7% H ₂ SO ₄ , 7% rh	205		
γ_{ss}	$(1.6 \pm 0.4) \times 10^{-2}$	SAT, H ₂ O-rich, 100% rh	195	Zhang, Jayne and Molina, 1994 ⁹	(g)
	$(5.0 \pm 1.3) \times 10^{-4}$	SAT, H ₂ SO ₄ -rich, 0.8% rh	195		
<i>HNO₃–H₂O Substrates</i>					
γ_{ss}	$(6.0 \pm 2.0) \times 10^{-3}$	NAT film	201	Hanson and Ravishankara, 1991 ¹⁰	(h)
γ_{ss}	1.0×10^{-5}	NAT film	196	Leu, Moore, and Keyser, 1991 ¹¹	(i)
γ_{ss}	$(2.0 \pm 0.8) \times 10^{-3}$	NAT film	191	Hanson and Ravishankara, 1992 ¹²	(j)
γ_{ss}	$(4.0 \pm 1.6) \times 10^{-3}$	NAT film	201		
	$(8.0 \pm 3.2) \times 10^{-3}$	NAT film	211	Abbatt and Molina, 1992 ¹³	(k)
	$(2.0 \pm 1.0) \times 10^{-3}$	NAT film, H ₂ O-rich	202		
	$(5.0 \pm 2.5) \times 10^{-3}$	NAT film, HNO ₃ -rich	202		
	γ_{ss}	$(1.0 \pm 0.3) \times 10^{-3}$	NAT film	191	Hanson and Ravishankara, 1993 ¹⁴
γ_{ss}	2.0×10^{-3}	NAT, 90% rh	191	Hanson and Ravishankara, 1993 ⁸	(f)
	5.0×10^{-4}	NAT, 50% rh	194		
	3.0×10^{-4}	NAT, 25% rh	198		
γ_{ss}	$(2.0 \pm 0.3) \times 10^{-3}$	NAT, H ₂ O-rich, 100% rh	195	Zhang, Jayne, and Molina, 1994 ⁹	
<i>H₂O (solid) Substrates</i>					
γ_{ss}	$(9.0 \pm 2.0) \times 10^{-3}$	ice film	185	Tolbert <i>et al.</i> , 1987 ¹⁵	(m)
γ_{ss}	$(6.0 \pm 3.0) \times 10^{-2}$	ice film	200	Leu, 1988 ¹⁶	(n)
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	201	Hanson and Ravishankara, 1991 ³	(h)
γ_{ss}	$(5.0^{+5.0}_{-4.0}) \times 10^{-3}$	ice film	196	Leu, Moore, and Keyser, 1991 ¹¹	(i)
γ_{ss}	$0.8^{+0.2}_{-0.3}$	ice film	191	Hanson and Ravishankara, 1992 ¹²	(j)
γ_{ss}	0.30 ± 0.10	ice film	191	Hanson and Ravishankara, 1993 ¹⁴	(l)
γ_{ss}	3.0×10^{-2}	thin ice film	188	Chu, Leu, and Keyser, 1993 ¹⁷	(o)
	1.3×10^{-1}	thick ice film	188		
γ_{ss}	$(8.0 \pm 2.0) \times 10^{-2}$	ice film	195	Zhang, Jayne, and Molina, 1994 ⁹	(g)

Comments

- (a) Uptake experiment in a two-chamber Knudsen cell using molecular beam modulated electron-impact MS. Simultaneous flows of H₂O (1.5×10^{13} molecule cm⁻³) and ClONO₂ (9.4×10^{11} – 4.5×10^{13} molecule cm⁻³) were exposed to bulk 95.6% H₂SO₄ at ambient temperature. The uptake kinetics were monitored at m/e 46

(ClONO₂) and HOCl was measured at m/e 51/53 as the sole product released into the gas phase. The uptake coefficient was independent of the density of ClONO₂ and thus first order. The γ value listed in the Table corresponds to a steady-state value and was approximately a factor of three higher in the beginning of the experiment. In the absence of a continuous H₂O flow the HOCl signal decreased only by 25%, and the for-

mation of Cl_2O was detected under conditions of prolonged exposure of ClONO_2 to H_2SO_4 and thus prolonged generation of HOCl . No measurable uptake ($\gamma \leq 10^{-5}$) was reported for ClONO_2 uptake on 95.6% H_2SO_4 at 185 K (Tolbert *et al.*¹⁵).

- (b) Uptake experiment in a Knudsen cell flow reactor coupled to a modulated molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210–230 K. The H_2SO_4 concentration in the bulk was obtained by dilution from 96.5% H_2SO_4 and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is, in the temperature range 210–230 K and a vapor pressure of 4×10^{-4} Torr ($\pm 30\%$) which was the measured steady-state vapor pressure in the Knudsen cell. The measured values were measured under steady-state conditions with ClONO_2 monitored at m/e 46. The corresponding rate coefficient for uptake of ClONO_2 followed a first-order rate law and both HOCl and some Cl_2O reaction products were observed. The desorption behavior of HNO_3 incorporated into bulk 75% H_2SO_4 as a result of uptake of ClONO_2 at 230 K was very similar to that from HNO_3 interaction on the same substrate: apparent peak of HNO_3 desorption (almost certainly an artifact) was at 251 K and approximately 20% recovery.
- (c) Uptake experiment in a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of ClONO_2 in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3} , for product studies it was of the order of 10^{12} molecule cm^{-3} . The cold aqueous solution of H_2SO_4 (40 to 75% by weight, $T=215$ to 230 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(\text{H}_2\text{O})$ was generally around 1 mTorr. The ClONO_2 reaction seems to be a reactive process as HOCl was observed over the 40% and 60% H_2SO_4 solutions (large value of γ). For the 60% H_2SO_4 solution at 263 K the yield of HOCl was estimated to be about one half of the consumed ClONO_2 , with the remainder presumably dissolved in the solution. Temperature-dependent uptake experiments of ClONO_2 over 60%, 65%, 70%, and 75% solutions up to 260 K resulted in essentially no temperature dependence of γ outside the reported error limits.
- (d) Knudsen cell flow reactor technique with electron-impact MS detection using modulated molecular beam phase sensitive detection. ClONO_2 detected at m/e 46 and HOCl detected at m/e 51/53. p_{ClONO_2} was in the range 10^{12} to 10^{13} molecule cm^{-3} . The uptake on 40–75% H_2SO_4 did not saturate around temperatures of 220 K for the duration of the experiment (1000 s), and HOCl formation was delayed and increased on the same time scale. The following analytical expression for the uptake/reaction probability (γ) of ClONO_2 at

220 K was obtained: $\log \gamma = \{1.87 - 0.074 (\% \text{H}_2\text{SO}_4)\}$ ($\pm 15\%$) which is valid for the range of 40% to 80% $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ mixtures.

- (e) Uptake experiment in a laminar-flow tube of gas-phase ClONO_2 onto a quiescent liquid surface with chemical ionization detection MS as a partial pressure monitor. H_2SO_4 (46.6% to 65%) was applied as a cold liquid to the inner wall of the flow tube. The liquid H_2SO_4 with a residual HCl content of less than 10^{-4} mol dm^{-3} was back-titrated after the uptake experiment, and the product HOCl was only qualitatively detected. The first-order loss rate coefficients were based on the disappearance of ClONO_2 and were $\geq 10 \text{ s}^{-1}$. No significant temperature dependence of the uptake coefficient in the temperature range 200–220 K was observed. A simultaneous fit using two adjustable parameters resulted in fitted values for γ_{ss} that were less than 10% of the measured values. The second order rate coefficient $k_{\text{HCl}}^{\text{II}}$ for the title reaction in the bulk liquid has been estimated to be $\sim 3 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The natural variable to represent the dependence of γ_{ss} on the acid content of H_2SO_4 is the activity of H_2O over the liquid at temperature ($a_{\text{H}_2\text{O}}$) resulting in a smooth curve of γ_{ss} as a function of $a_{\text{H}_2\text{O}}$ given by $\gamma_{\text{ss}} = 0.5(a_{\text{H}_2\text{O}})^2$, where $a_{\text{H}_2\text{O}}$ is defined as the ratio of the equilibrium H_2O vapor pressure over the given $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ liquid and the vapor pressure of supercooled water at the same temperature. This simple relationship has been shown to hold for $a_{\text{H}_2\text{O}} \geq 0.05$.
- (f) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of ClONO_2 in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3} . The cryogenic deposits were characterized by their vapor pressures of H_2O and HNO_3 detected by an ion-molecule reaction with F_2^- for H_2O and with F^- or SF_6^- for HNO_3 , respectively. The frozen sulfuric acid surfaces were prepared by freezing a small amount of 57.7% H_2SO_4 (tetrahydrate) on the inside of the flow tube wall. The NAT layer was grown on a $0.5 \mu\text{m}$ thick H_2O ice undercoat on which a $0.05 \mu\text{m}$ thick NAT layer was deposited by flowing HNO_3 at 10^{-6} Torr. Subsequently the ice undercoat was sublimed off. The uptake coefficients were measured by monitoring the decrease of ClONO_2 with residence time. The results were obtained as a function of rh which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.25 mTorr or by changing the H_2O flow rate at constant temperature to result in a range 10–90% rh . The uptake coefficients were strongly dependent on rh and were lower compared to uptake by liquid sulfuric acid.
- (g) Fast flow reactor experiment coupled to a differentially pumped electron impact quadrupole MS using modulated molecular beam sampling. Two different flow tubes of 2.2 and 2.8 cm inner diameter were used, and

the pressure was in the range 0.5–2 Torr. Corrections to the uptake coefficients owing to competitive gas phase diffusion amounted to 10% for $\gamma < 1 \times 10^{-2}$ and up to a factor of four for $\gamma > 0.2$. The liquid solution of SAT (57.5% $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$) was applied to the inner wall of the flow tube as a film of ≥ 0.1 mm thickness and was quickly cooled to temperatures around 195 K. The thermodynamic state of the SAT sample was controlled by setting the vapor pressure of H_2O , either H_2O -rich (approaching 100% rh) or H_2SO_4 -rich at constant temperature or selecting the temperature at constant $p(\text{H}_2\text{O})$. Ice films were deposited from the vapor phase at 195 K and attained a thickness of 15–25 mm. The rate law for both the decrease of ClONO_2 and the increase of HOCl were unimolecular in the range of concentrations examined and resulted in identical γ values. A fraction of HOCl remained adsorbed on the SAT surface so that a lower limit of the HOCl yield of 0.5 could be obtained. The uptake coefficient decreases from a value of 1.6×10^{-2} at close to 100% rh by almost two orders of magnitude to 5×10^{-4} at low rh as a function of decreasing $p(\text{H}_2\text{O})$. The dependence of γ on $p(\text{H}_2\text{O})$ (Torr) and on temperature (K) is conveniently expressed in parametric form: $\log \gamma = \{10.12 + 5.75 \log [p(\text{H}_2\text{O})] + 0.62 \log^2 [p(\text{H}_2\text{O})]\}$ for $T = 195$ K, $p_{\text{ClONO}_2} = (3\text{--}5) \times 10^{-8}$ Torr, $p(\text{H}_2\text{O}) = 4 \times 10^{-5}$ to 5.6×10^{-4} Torr; $\log \gamma = \{318.67 - 3.13 \log T + 0.0076 \log T\}$ for T in the range 192–206 K, $p_{\text{ClONO}_2} = (2\text{--}4) \times 10^{-8}$ Torr and $p(\text{H}_2\text{O}) = 3.4 \times 10^{-4}$ Torr. The latter expression includes the change in the thermodynamic state of the SAT surface.

- (h) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of ClONO_2 in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3} . At high values of the uptake coefficient ($\gamma \geq 0.1$) significant corrections for diffusion had to be made using calculated diffusion coefficients for the reactants in He. The primary observable is a first-order loss rate coefficient from which γ is calculated taking into account the diffusion correction and the corrected gas-wall collision frequency in the presence of a reactive surface. Rapid saturation of the ice surface for ClONO_2 uptake was observed, usually within minutes at concentrations as low as 2×10^9 molecule cm^{-3} . NAT was prepared *in situ* by converting N_2O_5 into HNO_3 on the ice surface well past saturation. The HNO_3 vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT- HNO_3 -in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate a 1 to 2 monolayer [$(2\text{--}4) \times 10^{14}$ HNO_3 cm^{-2}] thick NAT layer was inferred. No information regarding the saturation behavior of γ on the NAT surface is available. The

relevant surface corresponds to the geometric area as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ .

- (i) Ice-coated flow tube using electron-impact MS with ion-counting. The substrates were prepared by bubbling He through a $\text{HNO}_3\text{-H}_2\text{O}$ solution and subsequently condensing the mixture (NAT films) at 196 K, resulting in film thicknesses of 70 μm . The surface areas and bulk densities of condensed films were measured *ex situ* in addition to the measurement of their FTIR absorption spectra. The reported data were corrected for external diffusion (important for large values of γ) using estimated diffusion coefficients in He as well as for pore diffusion (important for small values of γ) using a (semiquantitative) two-site surface reaction model: ice and NAT films were weighted according to their corresponding mass fractions. The characteristic pressures of ClONO_2 were in the range 8×10^{-5} Torr and the values given in the Table correspond to the fitted parameters for the pure phases of ice and stoichiometric NAT even though only NAT samples of varying compositions were used (37.6%–55.2% $\text{HNO}_3\text{-H}_2\text{O}$). The measured values of γ on samples of varying HNO_3 -NAT composition, corrected for external diffusion, were in the range 10^{-3} – 10^{-5} . Under the given experimental conditions the cryogenic surface saturated within a few minutes so that the results obtained within the first minute were retained. HOCl was detected as a reaction product although not used quantitatively.
- (j) For experimental details see under Comment (h). These experiments were designed to investigate the influence of the thickness of the substrate on γ . The values for γ given in the Table correspond to a thickness of 10 μm where one can expect a coherent coat of substrate deposited from the vapor phase. The value for γ varied by a factor of no more than three and 1.5 for NAT and pure ice, respectively, when the thickness was varied from 2 to 20 μm . The conclusion was that there is no significant dependence of γ on thickness. In these experiments the stoichiometry of the reaction was confirmed by direct observation of HOCl at densities of ClONO_2 ranging from 4×10^9 to 7×10^{10} molecule cm^{-3} (lower limit of 50% for HOCl with respect to ClONO_2 consumed). However, the HOCl signal did not appear instantaneously after exposure of ClONO_2 to the ice surface. It therefore arises from adsorption of HOCl on ice and subsequent desorption. No such adsorption of HOCl was detected on NAT surfaces. An upper limit of 5% was set for the formation of Cl_2O . The temperature dependence of γ for ClONO_2 uptake on NAT corresponds to an activation energy of 24 kJ mol^{-1} : the availability of the H_2O molecules that are bound to HNO_3 in NAT increases with increasing temperature so they more readily support the hydrolysis of ClONO_2 .
- (k) Uptake experiment in an ice-coated flow tube using

electron-impact quadrupole MS equipped with a closed ion-source. Uptake of ClONO_2 on NAT with careful control of the thermodynamic surface state of the cryogenic substrate with pressures of ClONO_2 ranging from $(2\text{--}20)\times 10^{-6}$ Torr. The NAT films were prepared starting from 10 mm thick ice films that were exposed to small pressures of HNO_3 over long periods of time resulting in a 0.1 mm thick NAT layer on top of the ice film. Both the decay of ClONO_2 monitored at m/e 46 and the generation of HOCl observed at m/e 52 gave identical results. The uptake was studied on a number of NAT films ranging from HNO_3 -rich [$p(\text{H}_2\text{O})=4\times 10^{-4}$ Torr, $\gamma=5\times 10^{-5}$] to H_2O -rich NAT [$p(\text{H}_2\text{O})=1.5\times 10^{-3}$ Torr, identical to the vapor pressure of ice at 202 K], $\gamma=2.0\times 10^{-3}$. The reaction probability expressed as γ is a strong function of the thermodynamic state of the NAT surface. However, the experiments were conducted at pressures of ClONO_2 high enough to saturate a pure ice surface within the observation period. For these reference experiments identical values for γ were obtained ($\gamma=2.0\times 10^{-3}$ at p_{ClONO_2} of 6×10^{-6} Torr).

- (l) For experimental details see under Comments (h) and (j). This study was undertaken to supplement the original work on ice and nitric-acid doped (NAT) surfaces to further confirm the independence of the measured uptake coefficients on the substrate thickness.
- (m) Uptake experiment in a two-chamber Knudsen cell using modulated molecular beam electron-impact MS. The uptake coefficient γ of ClONO_2 on pure ice prepared *in situ* by vapor deposition was measured at typical pressures $p_{\text{ClONO}_2}=0.02$ mTorr, $p(\text{H}_2\text{O})=1.4$ mTorr by monitoring the decrease of the MS signal at m/e 46. HOCl and Cl_2O were confirmed as gas phase products, and HNO_3 was detected after warming up the ice that had undergone reaction with ClONO_2 to at least 217 K. The ClONO_2 sample had a significant impurity of Cl_2 and a lesser one of Cl_2O . Similar qualitative results were reported for ClONO_2 uptake on HNO_3 - H_2O cryogenic surfaces that were co-condensed in the appropriate ratios before the uptake experiments. For HNO_3 : H_2O mole ratios of 2:1 and 1:2, no reaction (observation of HOCl) was reported. However, for a 1:4.5 mole ratio, "abundant" formation of HOCl was reported essentially pointing to an identical situation with respect to reaction on pure ice.
- (n) Fast flow tube reactor with electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). The standard deviation of γ shown in the Table represents the uncertainty in the estimation of the diffusion coefficient of ClONO_2 in He at 200 K. HOCl was confirmed as the sole reaction product released into the gas phase.
- (o) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure was 0.4 Torr He, the active (cooled)

surface was 183 cm^2 and the temperature was 188 ± 0.5 K. The ice film was deposited from water vapor saturated He to thicknesses ranging from 3.7 to $34.7\text{ }\mu\text{m}$, which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μm -sized granules whose internal surface was measured using BET gas adsorption measurements. In view of the buildup of HNO_3 on the ice substrate, minimum ClONO_2 concentrations were used ($p_{\text{ClONO}_2}=1.4\times 10^{-7}$ Torr). The observation of the ClONO_2 decay led to an average uptake coefficient of 0.03 on thin ice films ($\leq 4\text{ }\mu\text{m}$ thick) and of 0.13 on thick ice films ($\leq 34.1\text{ }\mu\text{m}$ thick). The results based on the observation of the HOCl growth corresponded to smaller values of γ_{ss} because of the possible surface deactivation by the product HNO_3 . Therefore the obtained values, which were corrected for gas-phase diffusion, are regarded as lower limits to the true uptake coefficients.

Preferred Values

The uptake coefficient on *liquid* H_2SO_4 - H_2O around 220 K depends on the H_2O activity of the mixture and can be described by the following expression: $\log \gamma=\{1.84-0.075(\%\text{H}_2\text{SO}_4)\} (\pm 20\%)$. This expression is valid for the range of 40 to 80% H_2SO_4 - H_2O mixtures and spans two and a half orders of magnitude in γ . Although this expression only applies to one temperature, there are indications that the temperature dependence of γ may be much weaker than the dependence on H_2O activity. This behavior is in marked contrast to that for the hydrolysis of N_2O_5 in sulfuric acid which is independent of sulfuric acid concentration over the same range. The γ values for *frozen* sulfuric acid corresponding to SAT (57.5% H_2SO_4 - H_2O) strongly depend on the thermodynamic state of the SAT surface. Typically, γ varies by almost two orders of magnitude at 195 K, namely from 1.6×10^{-2} to 5×10^{-4} when the rh is decreased from 100% to less than 1%. There are indications that γ increases with decreasing temperature at high rh. For frozen SAT samples at low relative humidity and $T=200$ K, the uptake is slowed down up to a factor of 40 relative to a liquid sample probably because of H_2O depletion or HNO_3 accumulation on the surface.

The uptake coefficient on NAT-like substrates at 190 K is on the order of 2×10^{-3} , similar to that for uptake on frozen SAT, and decreases by a factor of ten with decreasing rh from 90 to 25% probably due to H_2O depletion on the surface.

On water ice γ seems to be larger than on the other frozen surfaces, of the order of 0.1. This experiment seems to be prone to surface saturation effects.

The uptake coefficient for frozen surfaces seems to decrease in the following order: ice>SAT (H_2O -rich)>NAT (H_2O -rich). The thermodynamic state of the SAT and NAT surface corresponds to a high value of rh.

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
<i>Sulfate/H₂SO₄ (liquid) Substrates</i>					
γ_{ss}	3.0×10^{-3}	65% H ₂ SO ₄	210	Tolbert, Rossi, and Golden, 1988 ¹	(a)
γ_{ss}	2.0×10^{-2}	40% H ₂ SO ₄	218 ± 3	Hanson and Ravishankara, 1991 ²	(b)
	2.0×10^{-4}	60% H ₂ SO ₄	218 ± 3		
	$< 10^{-4}$	65% H ₂ SO ₄	218 ± 3		
	$< 2.0 \times 10^{-5}$	70% H ₂ SO ₄	218 ± 3		
	$< 2.0 \times 10^{-5}$	75% H ₂ SO ₄	218 ± 3		
γ_{ss}	3.8×10^{-2}	46.6% H ₂ SO ₄ , liquid, < 10 ⁻⁴ M HCl	202	Hanson and Ravishankara, 1994 ³	(c)
	1.1×10^{-1}	46.6% H ₂ SO ₄ , liquid, HCl = 10 ⁻³ M	202		
	3.0×10^{-1}	46.6% H ₂ SO ₄ , liquid, HCl = 6 × 10 ⁻³ M	202		
<i>Sulfate/H₂SO₄ (solid) Substrates</i>					
γ_{ss}	1.25×10^{-1}	57.5% H ₂ SO ₄	192	Hanson and Ravishankara, 1993 ⁴	
	2.4×10^{-4}	57.5% H ₂ SO ₄	205		(d)
γ_{ss}	$(1.2 \pm 0.3) \times 10^{-1}$	SAT, H ₂ O-rich, 100% rh	195	Zhang, Jayne, and Molina, 1994 ⁵	
	$(7.0 \pm 2.0) \times 10^{-4}$	SAT, H ₂ SO ₄ -rich, 0.7% rh	195		(e)
<i>HNO₃-H₂O Substrates</i>					
γ_{ss}	$0.3^{+0.7}_{-0.1}$	NAT film	200	Hanson and Ravishankara, 1991 ⁶	(f)
γ_{ss}	$(2.7 \pm 0.4) \times 10^{-1}$	NAT film	196	Leu, Moore, and Keyser, 1991 ⁷	(g)
γ_{ss}	$0.3^{+0.7}_{-0.1}$	NAT film	191	Hanson and Ravishankara, 1992 ⁸	(h)
γ_{ss}	$(3.0 \pm 1.0) \times 10^{-3}$	HNO ₃ -rich NAT	202	Abbatt and Molina, 1992 ⁹	(i)
	$\geq 2.0 \times 10^{-1}$	H ₂ O-rich NAT	202		
γ_{ss}	2.3×10^{-1}	NAT, $p_{\text{HCl}} = 5$ × 10 ⁻⁸ Torr, 90% rh	190	Hanson and Ravishankara, 1993 ⁴	(j)
	2.0×10^{-1}	NAT, $p_{\text{HCl}} = (3-4)$ × 10 ⁻⁷ Torr, 90% rh	190		
	3.0×10^{-2}	NAT, $p_{\text{HCl}} = (3-4)$ × 10 ⁻⁷ Torr, 30% rh	197		
<i>H₂O (solid)</i>					
γ_{ss}	$0.27^{+0.73}_{-0.13}$	HCl-H ₂ O film	200	Leu, 1988 ¹⁰	(k)
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	191	Hanson and Ravishankara, 1992 ⁸	(h)
γ_{ss}	$(2.7 \pm 1.9) \times 10^{-1}$	10.4 mm thick ice film	188	Chu, Leu, and Keyser, 1993 ¹¹	(l)

Comments

- (a) Uptake experiment in a Knudsen cell flow reactor coupled to a modulated molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210 to 230 K. The H₂SO₄ concentration in the bulk was obtained by

dilution from 96.5% H₂SO₄ and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is in the temperature range 210 to 230 K and a vapor pressure of 4 × 10⁻⁴ Torr (± 30%) which was the measured steady-state vapor pressure in the Knudsen cell. Before the ClONO₂ uptake experiment, the 65%

H₂SO₄-H₂O solution was exposed to 1.3 mTorr of HCl for an hour (estimated mole fraction ratio HCl:H₂O=2×10⁻⁴) after which the bulk cryogenic phase was exposed to ClONO₂ at typical pressures of 4.8 mTorr. The measured γ values were measured under steady-state conditions with ClONO₂ (monitored at m/e 46) and are very similar to the ones measured in uptake experiments without HCl by the same authors (see Data Sheet for ClONO₂ + H₂O). Gaseous reaction products HOCl (m/e 51/53), Cl₂ (m/e 70/72/74), and Cl₂O (m/e 86/88/90) were observed as was condensed phase HNO₃ through desorption experiments. More than 85% of the HCl was recoverable as Cl₂ from the 65% H₂SO₄ solution at 210 K. It is obvious that in addition to the title reaction, the reaction ClONO₂ + H₂O is occurring simultaneously.

- (b) Uptake experiment on a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of ClONO₂ in the presence of HNO₃ and other reactants at characteristic densities of 10¹⁰ to 10¹¹ molecule cm⁻³. The cold aqueous solution of H₂SO₄ (40 to 75%, $T=215-230$ K) was flowed down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(\text{H}_2\text{O})$ was generally around 1 mTorr. The HCl concentration for the experiments on the 40% solution was 2×10¹¹ molecule cm⁻³, that for the 60 to 75% solution was in the range (1–3)×10¹⁰ molecule cm⁻³. The error limits are reported to be (+100/-50%) except for the 40 and the 60% solution, and Cl₂ was confirmed as a reaction product. The uptake of ClONO₂ in the presence of HCl was not accelerated compared to experiments without HCl. The authors suggest that this reaction occurs in the liquid phase with the rates controlled by the solubilities of the reactants. The reaction probability (γ) for the title reaction is suggested to be at most 10% of the value of γ for the reaction ClONO₂ + H₂O → HNO₃ + HOCl. A number of experiments were performed at high HCl concentrations, with the result that γ was significantly enhanced at comparable ClONO₂ concentrations: for a 60% solution γ was 2×10⁻⁴ (215 K), 0.006 (215 K), and ~0.01 (238 K) for HCl concentrations of 2×10¹⁰, 7×10¹², and ~5×10¹² molecule cm⁻³, respectively.
- (c) Uptake experiment in a laminar-flow tube of gas-phase ClONO₂ onto a quiescent liquid surface with chemical ionization detection MS as a partial pressure monitor. H₂SO₄ (46.6% to 65%) was applied as a cold liquid to the inner wall of the flow tube. The liquid H₂SO₄ was back-titrated after the uptake experiment, and the product HOCl was qualitatively detected only for the case of no added HCl. The HCl was either added to the liquid (46.6% and 51% H₂SO₄) or taken up from the gas phase (55.6, 57.5, 58.5, 59.8, and 65% H₂SO₄). The first-order loss rate coefficients were based on the disappearance of ClONO₂ and were ≥10 s⁻¹. No significant temperature dependence of the uptake coefficient

in the temperature range 192 to 208 K was observed. The uptake coefficient increased with increasing p_{HCl} and increasing H₂O activity. The results can be summarized as follows: 1.0×10⁻³ ≤ γ_{ss} ≤ 0.30 at 46.6 to 65% H₂SO₄, 8×10⁻⁹ to 8×10⁻⁵ Torr HCl and at $T=202$ K. ClONO₂ undergoes a competitive reaction with both HCl ($k_{\text{HCl}}^{\text{II}}$) and H₂O (hydrolysis, k_0^{I}). It was found from curve fitting that a surface-mediated reaction between Cl⁻ and ClONO₂ scaling with p_{HCl} had to be invoked in addition to the competitive bulk reactions. A two-parameter fit to the global data set revealed a slow hydrolysis reaction ($k_0^{\text{I}} \sim 300$ dm³ mol⁻¹ s⁻¹) with $k_{\text{HCl}}^{\text{II}}$ estimated to be at or close to its diffusion limit of (1–3)×10⁷ dm³ mol⁻¹ s⁻¹ at 202 K and for 50% H₂SO₄-H₂O. The ClONO₂ uptake therefore does not vary linearly with p_{HCl} . An estimate within a factor of three is given for the solubility of ClONO₂ at 202 K and 60% acid ($H=1000$ mol dm⁻³ atm⁻¹).

- (d) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of ClONO₂ in the presence of HNO₃ and other reactants at characteristic densities of 10¹⁰ to 10¹¹ molecule cm⁻³. The cryogenic deposits were characterized by their vapor pressure of H₂O detected by an ion-molecule reaction with F₂⁻, whose decrease was monitored as a function of H₂O pressure. The sulfuric acid surfaces were prepared by freezing a small amount of 57.7% H₂SO₄ (tetrahydrate) on the inside of the flow tube wall. The results were obtained as a function of rh which was varied by adjusting the temperature of the frozen phase at a constant H₂O flow rate of 0.2 mTorr or by changing the H₂O flow rate at constant temperature to result in a range 10–90% rh. The HCl partial pressure was held at approximately 1.5×10⁻⁷ Torr, corresponding to 2–3 ppbv at 17 km and the water vapor pressure for the γ values given in the Table was 5×10⁻⁴ Torr. The uptake coefficients decreased markedly with decreasing rh and could be expressed as $\ln \gamma = (-0.636 - 0.4802\Delta T)$, where $\Delta T = T - 189$. ΔT can be approximated by $T - T_{\text{ice}}$ where T_{ice} is the temperature of the ice point at a given partial pressure of water vapor and where $p(\text{H}_2\text{O}) < p_{\text{ice}}$. Because the uptake coefficient over frozen sulfate is identical to within experimental error to that over NAT [see Comment (k)], it is believed that rh is the dominant controlling factor for ClONO₂ uptake.
- (e) Fast flow reactor experiment coupled to a differentially pumped electron impact quadrupole MS with molecular beam sampling. Two different flow tubes of 2.2 and 2.8 cm inner diameter were used, and the pressure was in the range 0.5–2 Torr. Corrections to the uptake coefficients arising from competitive gas-phase diffusion amounted to 10% for $\gamma < 1 \times 10^{-2}$ and up to a factor of four for $\gamma > 0.2$. The liquid solution of SAT (57.5% H₂SO₄-H₂O) was applied to the inner wall of the flow

tube as a film of ≥ 0.1 mm thickness and was quickly cooled to temperatures around 195 K. The thermodynamic state of the SAT sample was controlled by setting the vapor pressure of H_2O , either H_2O -rich (approaching 100% rh) or H_2SO_4 -rich at constant temperature or selecting the temperature at constant $p(\text{H}_2\text{O})$. Ice films were deposited from the vapor phase at 195 K and attained a thickness of between 15–25 μm . The rate law for both the decrease of ClONO_2 and the increase of Cl_2 , whose yield was measured to be 0.9 ± 0.1 , were unimolecular in the range of concentrations examined and resulted in identical γ values. The HCl was always in excess of ClONO_2 and no HOCl was detected. The uptake coefficient decreases from a value of 1.2×10^{-1} at close to 100% rh by more than two orders of magnitude to 7×10^{-4} at low rh as a function of decreasing $p(\text{H}_2\text{O})$. The dependence of γ on $p(\text{H}_2\text{O})$ (Torr) and on temperature (K) is conveniently expressed in parametric form: $\log \gamma = [5.25 + 1.91 \log p(\text{H}_2\text{O})]$ for $T = 195$ K, $p_{\text{ClONO}_2} = (3-5) \times 10^{-8}$ Torr, $p_{\text{HCl}} = (4-8) \times 10^{-7}$ Torr, $p(\text{H}_2\text{O}) = 4 \times 10^{-5}$ to 5.6×10^{-4} Torr; $\log \gamma = (175.74 - 1.59 \log T + 0.0035 \log^2 T)$ for T in the range 195–206 K, $p_{\text{ClONO}_2} = (3-5) \times 10^{-8}$ Torr, $p_{\text{HCl}} = (4-8) \times 10^{-7}$ Torr, and $p(\text{H}_2\text{O}) = 5.6 \times 10^{-4}$ Torr. The latter expression includes the change in the thermodynamic state of the SAT surface.

- (f) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of ClONO_2 in the presence of HNO_3 and other reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3} . At high values for the uptake coefficient ($\gamma \geq 0.1$), significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. The primary observable was a first-order loss rate coefficient from which γ was calculated taking into account the diffusion correction and the corrected gas-wall collision frequency in the presence of a reactive surface. NAT was prepared *in situ* by converting N_2O_5 into HNO_3 on the ice surface well past saturation. The HNO_3 vapor detected at the downstream end of the flow tube was consistent within a factor of two with the expected vapor pressure over NAT- HNO_3 in-ice solid solution near 201 K. From the N_2O_5 taken up by the cryogenic substrate a NAT film 1 to 2 monolayers thick $[(2-4) \times 10^{14} \text{ HNO}_3 \text{ cm}^{-2}]$ was inferred. The first-order loss rate coefficient of ClONO_2 on pure ice in the presence of HCl was identical to that measured in the absence of HCl , thus indicating no preference for reaction of ClONO_2 with HCl over that with H_2O , presumably because γ is already close to one. For the uptake experiments on NAT the HCl concentration was set to twice that for ClONO_2 , namely $(2-6) \times 10^9$ molecule cm^{-3} . The reaction is limited by the availability of HCl as excess conditions must be maintained. However, no information on the possible saturation of γ is available. The relevant sur-

face corresponds to the geometric area, as an increase of the ice mass by a factor of 5 to 10 had no noticeable effect on γ .

- (g) Ice-coated flow tube using electron-impact MS with ion-counting as a diagnostic. The substrates were prepared by bubbling He through a HNO_3 - H_2O solution and subsequently condensing the mixture (NAT films) at 196 K, resulting in film thicknesses of 70 μm . The surface areas and bulk densities of condensed films were measured *ex situ* in addition to the measurement of their FTIR absorption spectra. The reported data were corrected for external diffusion (important for large values of γ) using estimated diffusion coefficients in He. The characteristic pressures were: $p_{\text{HCl}} = 0.2$ to 2 mTorr, $p_{\text{ClONO}_2} = 8 \times 10^{-5}$ Torr. The measured values of γ were independent of the composition of HNO_3 - H_2O in the range 41.8–60.4% and of the HCl content (0.0375%–3.91% HCl). The experiments were conducted at excess HCl over ClONO_2 , no surface deactivation was observed and both ClONO_2 loss as well as Cl_2 appearance were used in the measurement of γ . The scatter in the data is largely given by the diffusion correction, and the authors give a corrected value of $\gamma = 0.10 \pm 0.02$ if pore diffusion is taken into account.
- (h) For experimental details see under Comment (f). Characteristic reactant concentrations were from 2×10^9 to 10^{10} molecule cm^{-3} . The experiments were designed to verify the identity of the reaction products. ClONO_2 , HCl , and Cl_2 were monitored albeit not simultaneously. Under conditions of $[\text{HCl}] > [\text{ClONO}_2]$, no saturation of the uptake of ClONO_2 and no HOCl were detected. It is suggested that the HOCl intermediate that is adsorbed on the ice undergoes a fast reaction with HCl . For the experiments on NAT the uptake of ClONO_2 , HCl , and the formation of the reaction product Cl_2 were studied at constant HCl concentration (2×10^{10} molecule cm^{-3}) and varying ClONO_2 concentration ranging from 6×10^9 to 3×10^{10} molecule cm^{-3} . A first-order rate law for uptake of HCl and ClONO_2 , as well as for the formation of Cl_2 , were found. The authors argue in favor of a direct reaction between ClONO_2 and HCl rather than a reaction via the intermediate HOCl in view of the high value for γ . The low value for γ found for the reaction of $\text{ClONO}_2 + \text{H}_2\text{O}$ on NAT would virtually preclude the present result if this reaction were part of the overall reaction mechanism: $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$, and $\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ (net reaction is the title reaction).
- (i) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. Uptake of ClONO_2 on NAT in the presence of a slight excess of HCl with careful control of the thermodynamic surface state of the cryogenic substrate with pressure of ClONO_2 ranging from $(1-9) \times 10^{-6}$ Torr and HCl ranging from $(4-10) \times 10^{-6}$ Torr. The NAT films were prepared starting from 10 μm thick

ice films that were exposed to small pressures of HNO_3 over long periods of time resulting in a 0.1 μm thick NAT layer on top of the ice film. Both the Cl_2 product formation as well as the ClONO_2 decay was observed in order to measure the reaction probability (γ). Under conditions of slight excess of HCl , γ was measured as a function of $p(\text{H}_2\text{O})$ from HNO_3 -rich NAT to H_2O -rich NAT: for $p(\text{H}_2\text{O})=2\times 10^{-4}$ Torr (HNO_3 -rich NAT), $\gamma=0.003$; and at the other extreme of the NAT existence curve [$p(\text{H}_2\text{O})=1.5\times 10^{-3}$ Torr, H_2O -rich], $\gamma=0.2$ was found. Additional experiments of the dependence of γ on p_{HCl} for HNO_3 -rich NAT [$p(\text{H}_2\text{O})=2.5\times 10^{-4}$ Torr] resulted in a factor of four increase in γ (from 0.01 to 0.04) when p_{HCl} was increased from 1.5×10^{-5} to 8×10^{-5} Torr. At even higher pressures of HCl [$(1-2)\times 10^{-4}$ Torr], $\gamma>0.5$ was measured due to the unlimited uptake of HCl into the molten surface phase of $\text{HCl-H}_2\text{O}$. Little HCl is taken up by HNO_3 -rich NAT so that the resulting low surface concentration of HCl leads to small reaction probabilities.

- (j) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of ClONO_2 and HCl in the presence of HNO_3 and other reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3} . The cryogenic deposits were characterized by their vapor pressures of H_2O and HNO_3 detected by an ion-molecule reaction with F_2^- for H_2O and with F^- or SF_6^- for HNO_3 , respectively. The NAT layer was grown on a 0.5 mm thick H_2O ice undercoat on which a 0.05 μm thick NAT layer was deposited by flowing HNO_3 at 10^{-6} Torr. Subsequently the ice undercoat was sublimed off. The results were obtained as a function of relative humidity which was varied by adjusting the temperature of the frozen phase at a constant H_2O flow rate of 0.25 mTorr. In some instances NAD deposits were obtained that converted to NAT within an hour. The uptake coefficients on NAD were similar if not slightly higher than on NAT under identical conditions. The partial pressure of HCl was about twice that of ClONO_2 and the loss rate of ClONO_2 on NAT followed a first-order rate law. The uptake coefficients were only slightly dependent on the temperature and p_{HCl} but strongly decreasing with decreasing rh. The expression $1/\gamma=1/\gamma_{\text{max}}+1/A\exp(B\Delta T)$ described well the dependence of the uptake coefficients on temperature, and thus relative humidity. ΔT is defined as $T-190$, the departure of the temperature of interest from the ice point temperature at which rh is 100% at the chosen flow rate of H_2O [$\text{rh}=100p(\text{H}_2\text{O})/p_{\text{ice}}(T)$], $A=0.7022$ and 2.2543 , $B=-0.518$ and -0.558 for $p_{\text{HCl}}=5\times 10^{-8}$ Torr and $(3-4)\times 10^{-7}$ Torr, respectively.
- (k) Fast flow tube reactor with electron-impact mass spectrometric sampling as a diagnostic. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total) together with HCl vapor to obtain

mole fractions f_{HCl} in the range 0.37 to 7.1% relative to H_2O . The reaction probability γ increased from 0.06, the value obtained for the reaction $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}$ to a constant value of 0.27 independent of f_{HCl} for the range 1.5 to 7.1% (see Table). The standard deviation of the γ value shown in the Table represents the uncertainty in the estimation of the diffusion coefficient of ClONO_2 and HCl in He at 200 K. Cl_2 was confirmed as the sole reaction product released into the gas phase. For $f_{\text{HCl}}=0.37\%$, both Cl_2 and HOCl were observed. Moreover, evidence for fast diffusion of HCl across an amorphous ice layer has been obtained.

- (l) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure was 0.4 Torr He, the active (cooled) surface was 183 cm^2 and the temperature was 188 ± 0.5 K. The ice film was deposited from water vapor saturated He to thicknesses ranging from 3.7 to 34.7 μm , which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μm -sized granules whose internal surface was measured using BET gas adsorption measurements. A typical experimental sequence included conditioning of the ice film by a constant flow of HCl after which a flow of ClONO_2 -saturated He was added to the flow tube. The concentration of HCl was always larger than that for ClONO_2 such that pseudo-first-order conditions prevailed. p_{ClONO_2} ranged from 6.5×10^{-8} to $\sim 10^{-6}$ Torr and p_{HCl} from 1.6×10^{-7} to 2.3×10^{-6} Torr. The observation of the ClONO_2 decay led to an average uptake coefficient of 0.26 ± 0.19 , and the monitoring of the growth of Cl_2 led to a value for γ_{ss} of 0.28 ± 0.18 , the median of which is given in the Table. The results were independent of p_{ClONO_2} , p_{HCl} , and temperature within experimental variability, and all were corrected for gas-phase diffusion. This correction amounted to a factor exceeding ten in some cases. Taking into account a structural model for the ice substrate, a value of $\gamma_{\text{ss}}=0.10 \pm 0.08$ was obtained which is approximately a factor of 2.6 smaller than the value based on the geometrical (external) surface. The surface roughness rather than the porosity of the film is seen as the principal parameter being responsible for the reduction of the measured γ_{ss} . The Cl_2 yield based on the ClONO_2 reacted was measured as 1.2 ± 0.2 under excess HCl condition.

Preferred Values

The uptake coefficient for liquid $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ at $T=220$ K is a strong function of the water activity in analogy to the results for the reaction $\text{ClONO}_2 + \text{H}_2\text{O}$. For 40% $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ γ is lower by a factor of four and for 75% $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ lower by a factor of 10 in comparison to the reaction with H_2O on the same bulk substrates. The total variation of γ with water activity spans a range of three orders of mag-

nitide. The uptake coefficient scales with the HCl partial pressure attaining a γ value of 0.3 at 10^{-4} Torr HCl at 202 K. On *frozen* SAT, γ seems to be similar to the one for liquid sulfuric acid. However, γ strongly depends on the thermodynamic state of the SAT surface: Its value decreases by more than two orders of magnitude at 195 K, from 1.2×10^{-1} at 100% rh to 7×10^{-4} at low rh. There are indications of an increase of γ with decreasing temperature for H₂O-rich SAT surfaces (high rh).

On NAT-like and H₂O-rich NAT substrates the uptake coefficient is found to be large, on the order of 0.3 at $T = 190$ K. It decreases significantly for substrates at low rh or correspondingly for HNO₃-rich conditions by up to two orders of magnitude.

On a water ice substrate the uptake coefficient is found to be large, on the order of 0.1 to 0.3 at 190 K.

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\sim 1.0 \times 10^{-2}$	cold Pyrex	201	Hanson and Ravishankara, 1992 ¹	(a)
	$\geq 3.0 \times 10^{-1}$	cold Pyrex at 50% rh, H ₂ O-ice, NAT	201		

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO₃-treated ice was defined as NAT under the used experimental conditions. On cold Pyrex both the decrease of ClONO₂ and HBr as well as the increase in BrCl were observed. The reactive uptake coefficient scales with the amount of adsorbed HBr: no reaction was observed at 220 K, and no uptake of ClONO₂ could be observed in the absence of HBr. On cold Pyrex at 50% rh an efficient reaction with $\gamma_{\text{ss}} \geq 0.3$ could be observed under conditions of excess ClONO₂. However, a smaller yield of BrCl was observed owing to the fast secondary reaction BrCl

+ HBr $\rightarrow$ HCl + Br₂. The authors do not exclude the possibility that the title reaction might occur through formation of BrONO₂ + HCl with a subsequent rapid formation of Br₂ + HNO₃. No difference in reactivity was found between pure ice and “NAT,” presumably because the former was rapidly converted into NAT owing to the deposition of HNO₃ from the title reaction. The reaction did not show any signs of saturation, and identical results were obtained for γ_{ss} measured from the disappearance of either ClONO₂ or HBr. At excess HBr no BrCl was observed due to the fast secondary reaction between BrCl and HBr.

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- ¹D. R. Hanson and A. R. Ravishankara, *J. Phys. Chem.* **96**, 9441 (1992).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\leq 1.0 \times 10^{-2}$	H ₂ O-ice, NAT	201	Hanson and Ravishankara, 1992 ¹	(a)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and prod-

ucts. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO₃-treated ice was defined as NAT under the experimental conditions used. On pure H₂O-ice or NAT

into which the pure ice substrate was converted only the known reaction of $\text{ClONO}_2 + \text{H}_2\text{O}$ was observed with $\gamma_{\text{ss}}=0.015$ as measured from the formation of HOCl . It accounted for 50%–75% of the ClONO_2 lost. Even at high initial HF concentrations of the order of 2×10^{13} molecule cm^{-3} no new products were detected. The listed value for γ_{ss} represents a conservative upper limit with the most probable value being a factor of

10^4 lower under stratospheric conditions. HF itself was not observed to interact measurably with the ice substrate.

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¹D. R. Hanson and A. R. Ravishankara, *J. Phys. Chem.* **96**, 9441 (1994).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(4.6 \pm 3.1) \times 10^{-3}$ $(6.7 \pm 3.2) \times 10^{-3}$	dry salt, baked	296 225	Timonen <i>et al.</i> , 1994 ¹	(a)

Comments

- (a) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure in the flow tube was 0.3 Torr He. Both the decrease of ClONO_2 monitored at m/e 46 as well as the increase of Cl_2 monitored at m/e 70 were used to calculate the uptake coefficient. The internal surface of the dry NaCl sample ground to an average size of $4 \mu\text{m}$ was determined in separate experiments and agrees with the internal surface calculated from average dimensions observed in SEM pictures. The measured uptake coefficient was corrected for radial diffusion (% level) and for the uptake on the external surface of deeper layers of NaCl exposed to the gas phase according to a chemical engineering model applied by the authors. This latter correction decreases the observed value for γ_{ss} by a factor of 7 to 8, with a global uncertainty of a factor of 2 associated with uncertainties in the model parameters used to reduce the

raw values of γ_{ss} . The values displayed in the above Table do not correspond to the measured uptake coefficients, but reflect the results after theoretical treatment. The ClONO_2 concentration varied from 2.5×10^{-8} to 1.9×10^{-6} Torr and the uptake coefficient was independent of the ClONO_2 pressure. The dose of ClONO_2 to saturation corresponds to adsorption of 18 monolayers at 296 K and to one monolayer at 225 K. The addition of H_2O vapor in the range 5.7×10^{-5} – 3×10^{-4} Torr decreased γ_{ss} by approximately 10% at both temperatures. With increasing H_2O concentration, increasing amounts of HNO_3 and HOCl but no HCl were observed.

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
<i>Sulfate/H₂SO₄ (liquid) Substrates</i>					
γ_{HCl}	6.0×10^{-3}	60% H_2SO_4	215	Hanson and Ravishankara, 1991 ¹	(a)
γ_{HOCl}	1.0×10^{-3}	60% H_2SO_4	263		
γ_{HOCl}	$(2.0 \pm 0.5) \times 10^{-2} \leq \gamma \leq (1.8 \pm 0.8) \times 10^{-1}$	60% H_2SO_4	200–220	Hanson and Ravishankara, 1993 ²	(b)
<i>HNO₃–H₂O Substrates</i>					
γ_{ss}	$(1.0 \pm 0.25) \times 10^{-1}$	NAT	191	Hanson and Ravishankara, 1992 ³	(c)
γ_{ss}	1.7×10^{-1}	H_2O -rich NAT, 100% rh	202	Abbatt and Molina, 1992 ⁴	(d)
γ_{ss}	2.0×10^{-3}	HNO_3 -rich NAT, 17.8% rh	202		
<i>H₂O (solid) Substrates</i>					
γ_{ss}	$\geq 0.3^{+0.7}_{-0.1}$	ice film	191	Hanson and Ravishankara, 1992 ³	(c)
γ_{ss}	$(1.6 \pm 1.0) \times 10^{-1}$	ice film	202	Abbatt and Molina, 1992 ⁴	(d)
γ_{ss}	$0.24^{+0.5}_{-0.15}$	ice film	195		
γ_{ss}	$(3.4 \pm 2.0) \times 10^{-1}$	19.4 μm thick ice film	188	Chu, Leu, and Keyser, 1993 ⁵	(e)

Comments

- (a) Uptake experiment in a wetted-wall flow tube using chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^{10} to 10^{11} molecule cm^{-3} . The cold aqueous solution of H_2SO_4 (60%, $T=215$ and 263 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(\text{H}_2\text{O})$ was generally around 1 mTorr. HOCl was generated through the reaction $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}$ over 60% H_2SO_4 . The uptake coefficient for HCl in the presence of HOCl was significantly larger than that in the absence of HOCl (see HCl data sheet, $\gamma=4\times 10^{-4}$) in part due to the large reactant concentrations: $[\text{ClONO}_2]=10^{12}$ molecule cm^{-3} and $[\text{HCl}]=3\times 10^{11}$ molecule cm^{-3} . The uptake coefficient γ_{HOCl} has been measured at $[\text{ClONO}_2]=10^{11}$ molecule cm^{-3} and $[\text{HCl}]=2\times 10^{11}$ molecule cm^{-3} , Cl_2 has been confirmed as a reaction product. It is thought that the title reaction is a condensed phase reaction with a rate coefficient of 10^4 to 10^5 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.
- (b) Time-dependent uptake experiment in a flow tube (0.4 to 2 Torr He) coupled to a chemical ionization MS. The liquid H_2SO_4 was either applied to the internal wall of the flow tube with subsequent determination of the acid content by titration (59.6%), or the liquid sample was in a boat container lying on the bottom of the horizontal flow tube. H_2O vapor was added to the He carrier to control the H_2SO_4 concentration. HOCl came from three sources: (1) entrainment from a solid $\text{Ca}(\text{OCl})_2$ sample exposed to H_2O and HCl, (2) from the heterogeneous reaction of ClONO_2 on the substrate to be studied, and (3) from an equilibrium mixture of Cl_2O (1 Torr) and H_2O (15 Torr). Pseudo-first-order conditions prevailed during the time-dependent uptake measurements performed in the temperature range 200–220 K with $[\text{HCl}]_0 \gg [\text{HOCl}]_0$. The values for γ increase with p_{HCl} ranging from 2.3×10^{-7} to 3.6×10^{-5} Torr. The experimental conditions were chosen such that the chloride concentrations in the liquid phase were $\geq 10^{-5}$ mol dm^{-3} and the HOCl uptake coefficient was independent of $[\text{HOCl}]_0$. The bimolecular rate coefficient for the title reaction in 60% H_2SO_4 and for the temperature range 200–220 K was found to be 1.6×10^5 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ with a factor of two uncertainty. Solubilities (effective Henry's law constants for HCl, H_{HCl}^* , and H_{HOCl}) and diffusion constants for the liquid phase of HCl (D_1) were obtained from time dependent uptake measurements of HCl and HOCl and "direct" determinations of solubilities for HCl from pseudostatic, that is low flow rate experiments. The separation of the factors in $H^*(D_1)^{1/2}$ resulting from time-dependent uptake experiments was obtained through direct measurement of H_{HCl}^* for some cases thus obtaining temperature-dependent values for both H_{HCl}^* and D_1 . It was assumed D_1 was identical for both HCl and HOCl and that it was independent of acid concentration in the range 45–60%.
- (c) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3} . At high values of the uptake coefficient ($\gamma \geq 0.1$) significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. The source of HOCl was the reaction $\text{HCl} + \text{Ca}(\text{ClO})_2$ for the ice experiments, and an equilibrium mixture of $\text{Cl}_2\text{O} + \text{H}_2\text{O}$. The decay of HCl and HOCl resulted in identical decay rates for $[\text{HOCl}]=2\times 10^9$ molecule cm^{-3} and $[\text{HCl}]$ ranging from 2×10^9 to 2×10^{10} molecule cm^{-3} . In separate experiments, Cl_2 was identified as a reaction product. No saturation effects were observed in keeping with the volatility of Cl_2 over ice surfaces. For the NAT experiments the concentrations were $[\text{HOCl}]=[\text{HCl}]=10^{10}$ molecule cm^{-3} .
- (d) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source as a probe. The uptake of HOCl in the presence of HCl (in excess by a factor of two or so) was time-independent and therefore not saturable. The reaction product on ice and NAT has been confirmed to be Cl_2 , with a yield of 0.87 ± 0.20 . On ice and for $[\text{HCl}] > [\text{HOCl}]$ a negative temperature dependence of γ has been observed: γ increases from 0.16 to 0.24 when the temperature drops from 202 to 195 K (see Table). There is an indication that γ increases slightly with increasing HCl pressure (preliminary finding). As the H_2O partial pressure drops from 1.7 mTorr at 202 K (the equilibrium vapor pressure for pure H_2O ice) to 0.8 mTorr and 0.3 mTorr, γ drops precipitously from 0.13 to 0.07 and reaching a value of 0.002 for HNO_3 -rich NAT. At 195 K, γ was found to be 0.18 ± 0.10 at H_2O pressures greater than 0.2 mTorr. (The equilibrium vapor pressure of H_2O over ice at 195 K is 0.56 mTorr.) This last value for γ is at least somewhat unexpected as the water vapor pressure of 0.2 mTorr should favor the formation of NAT in the midrange between H_2O -rich and HNO_3 rich and we therefore expect a smaller value for γ .
- (e) Uptake experiment in a flow reactor coupled to a differentially pumped electron-impact quadrupole MS. The total pressure was 0.4 Torr He, the active (cooled) surface was 183 cm^2 , and the temperature was 188 ± 0.5 K. The ice film was deposited from water vapor saturated He to thicknesses ranging from 3.7 to 34.7 μm , which were both calculated and calibrated gravimetrically. The morphology of the ice films were layers of μ -sized granules whose internal surface was measured using BET gas adsorption measurements. A typical experimental sequence included conditioning of the ice film by a constant flow of He-HCl after which a flow of HOCl-saturated He was added to the flow tube.

The concentration of HCl was always larger than that for ClONO₂ such that pseudo-first-order conditions prevailed. p_{HOCl} ranged from 1.3×10^{-7} to 1.8×10^{-6} Torr and p_{HCl} from 9×10^{-7} to 8×10^{-6} Torr. The observation of the HOCl decay led to an average uptake coefficient of 0.30 ± 0.18 , and the monitoring of the growth of Cl₂ led to a value for γ_{ss} of 0.38 ± 0.24 , the median of which is given in the Table. The results were independent of p_{HOCl} , p_{HCl} , and temperature within experimental variability, and all were corrected for gas-phase diffusion. This correction amounted to a factor exceeding ten in some cases. Taking into account a structural model for the ice substrate, a value of $\gamma_{\text{ss}} = 0.13 \pm 0.08$ was obtained which is approximately a factor of 2.6 smaller than the value based on the geometrical (external) surface. The surface roughness rather than the porosity of the film is seen as the principal parameter being responsible for the reduction of the measured γ_{ss} . The Cl₂ yield based on HOCl reacted was measured as 0.80 ± 0.20 .

Preferred Values

The uptake coefficient for HOCl in the presence of an excess of HCl on 60% liquid sulfuric acid was found to vary between 0.02 and 0.2 with temperature in the range 200–220 K. The uptake of HOCl is rate limiting in view of the faster uptake of HCl by approximately a factor of 6.

On NAT-like or water-rich substrates γ has been measured to be approximately 0.2 at 200 K. This value decreases by two orders of magnitude for conditions of low rh or correspondingly for HNO₃-rich NAT substrates.

Values of $\gamma = 0.3$ are observed on water ice substrates at 190 K.

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\geq 3.0 \times 10^{-1}$	H ₂ O-ice	200	Hanson and Ravishankara, 1993 ¹	(a)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS. Both the loss of BrONO₂ as well as the generation of HOBr were monitored. The uptake coefficient based on the loss of BrONO₂ and that based on the generation of the prod-

uct HOBr were identical within the experimental uncertainty.

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Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\sim 2.5 \times 10^{-1}$	H ₂ O-ice	200	Hanson and Ravishankara, 1993 ¹	(a)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS. Both the decrease in BrONO₂ and HCl as well as the formation of the products BrCl and HOBr were detected. There was, however, a monotonous decrease of HOBr with increasing injector distance which points to a competitive reaction between hydrolysis and halogen metathesis (title reaction). Analogous to the reaction ClONO₂ + HCl, the

efficient secondary reaction between HOBr generated from the hydrolysis of BrONO₂ and HCl results in BrCl + H₂O.

References

- ¹D. R. Hanson and A. R. Ravishankara, NATO ASI Series (17), 281, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker (Springer-Verlag, Berlin, 1993).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	3.0×10^{-1} $\sim 2.0 \times 10^{-1}$	cold Pyrex at 50% rh H ₂ O-ice	221 221	Hanson and Ravishankara, 1992 ¹	(a)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO₃-treated ice was defined as NAT under the used experimental conditions. On cold Pyrex at 50% rh the stoichiometry of the reaction was observed as $2\text{HBr} + \text{Cl}_2 \rightarrow \text{Br}_2 + 2\text{HCl}$ because the quantity of HCl produced was equal to the amount of HBr and to twice the amount of Cl₂ lost. The reaction most likely pro-

ceeds through formation of BrCl that is consumed in a fast secondary reaction by excess HBr. On pure ice efficient loss of HBr and Cl₂ was observed where the loss of HBr was due to uptake by the ice substrate as well as due to the title reaction. In the absence of HBr a reactive uptake coefficient for loss of Cl₂ of $\leq 7 \times 10^{-4}$ was measured.

References

- ¹D. R. Hanson and A. R. Ravishankara, J. Phys. Chem. **96**, 9441 (1992).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(1.2 \pm 0.3) \times 10^{-1}$	ice film	228	Abbatt, 1994 ¹	(a)

Comments

- (a) Flow tube study at a total pressure of 1 Torr He using a moveable injector and quadrupole MS sampling (HOBr at m/e 96, 98) at a slight excess of HBr. The HOBr was generated *in situ* inside a moveable injector tube by reaction of Br₂ with OH that was produced from NO₂ + H from a microwave discharge of H₂ in He. The ice film was prepared by wetting the flow tube wall and rapidly cooling to 228 K. The characteristic

concentrations were $[\text{HBr}] \sim (6-15) \times 10^{12}$ molecule cm⁻³, $[\text{HOBr}] \sim (25) \times 10^{12}$ molecule cm⁻³ and the uptake coefficient was measured by observation of the HOBr disappearance with injector position.

References

- ¹J. P. D. Abbatt, Geophys. Res. Lett. **21**, 665 (1994).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$0.25^{+0.10}_{-0.05}$	ice film	228	Abbatt, 1994 ¹	(a)

Comments

- (a) Flow tube study at a total pressure of 1 Torr He using a moveable injector and quadrupole MS sampling (HOBr at m/e 96, 98) at a slight excess of HCl. The HOBr was generated *in situ* inside a moveable injector tube by reaction of Br₂ with OH that was produced from NO₂ + H from a microwave discharge of H₂ in He. The ice film was prepared by wetting the flow tube wall and rapidly cooling to 228 K. The characteristic concentrations were $[\text{HCl}] \sim (1-2) \times 10^{12}$ molecule

cm⁻³ (about a factor of four lower than the vapor pressure at which melting of the ice phase was previously observed) and $[\text{HOBr}] \sim 10^{12}$ molecule cm⁻³. An uptake coefficient of $0.3^{+0.7}_{-0.1}$ was measured by observing the increase of the product BrCl, consistent with the above measurement made by the observation of the HOBr disappearance.

References

- ¹J. P. D. Abbatt, Geophys. Res. Lett. **21**, 665 (1994).

$$\text{O}_3 + \text{Substrate (C}_{\text{am}}) \rightarrow \text{products (O}_2, \text{CO, CO}_2, \{\text{C}_{\text{am}} \text{O}\})$$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_0	$(3.2 \pm 1.0) \times 10^{-3}$	amorphous carbon	300	Stephens, Rossi, and Golden, 1986 ¹	(a)
γ_{ss}	$(4.8 \pm 1.2) \times 10^{-5}$ at $[\text{O}_3] = 4.7 \times 10^{13}$ molecule cm^{-3}		300		
γ_{ss}	$> 2.2 \times 10^{-3}$	carbon aerosol	300	Fendel and Schmidt Ott, 1993 ²	(b)

Comments

- (a) Low pressure reactor study (Knudsen cell) with modulated molecular-beam sampling electron-impact MS detection. The solid substrate was bulk commercial-grade charcoal (Norit) of varying quantities (10–50 mg). Rapid poisoning of the surface took place with concomitant saturation of the uptake kinetics, usually within a few minutes. The decrease of the uptake coefficient in going from the initial to steady state uptake varied from a factor of eight at $[\text{O}_3] = 2.8 \times 10^{14}$ molecule cm^{-3} to a factor of sixty at $[\text{O}_3] = 3.2 \times 10^{13}$ molecule cm^{-3} . The rate law was not first order and could be represented by a fractional reaction order of $m = 0.633$ on the average. The sample could be restored close to its original state as measured by its uptake coefficient by heating in vacuum: CO_2 , CO , and H_2O were observed as desorption products. The mass balance resulted in a CO_2/CO ratio of 2.5–4.0, depending on the O_3 density. For every molecule of O_3 adsorbed, one molecule of O_2 was detected. Between 12% and 23% of the adsorbed O_3 turned up as volatile carbon (CO_2 , CO). With respect to odd oxygen, 20% to 35%

left the carbon surface as CO_2 and CO with the balance staying on the carbon as some unidentified surface oxide.

- (b) Flowing gas experiment of carbon aerosol in air exposed to ozone monitored using an electrochemical analyzer. The spark generator produced soot-like material of 10–100 nm radius, corresponding to agglomerates of fractal structure. The dimension of the carbon particulates corresponds to mobility-equivalent geometrical parameters. The collision cross sections derived from these mobility-equivalent parameters are thought to correspond to the gas kinetic collision cross section. Typically, an initial ozone concentration of 4×10^{12} molecule cm^{-3} decayed to 50% in the presence of 2.5 ng cm^{-3} of carbon aerosol after a reaction time of 30 s. Assuming an average diameter of 100 nm, one obtains a lower limit for the uptake coefficient of 2.2×10^{-3} .

References

- ¹ S. Stephens, M. J. Rossi, and D. M. Golden, *Int. J. Chem. Kinet.* **18**, 1133 (1986).
² W. Fendel and A. Schmidt Ott, *J. Aerosol. Sci.* **24**, Suppl. 1, S317 (1993).

$$\text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$$

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(8.0 \pm 2.0) \times 10^{-3}$	pH=0.25, 1M H_2O_2 droplets	283	Jayne <i>et al.</i> , 1990 ¹	(a)
	$(2.0 \pm 0.6) \times 10^{-2}$	pH=2.0, 1M H_2O_2 droplets	283		
	$(3.5 \pm 0.4) \times 10^{-2}$	pH=4.0, 1M H_2O_2 droplets	283		

Comments

- (a) Uptake experiment on a fast moving droplet train traversing a flow tube coupled to tunable diode laser absorption of SO_2 in a multiple pass absorption cell (728 cm optical path). The measurement consists of monitoring the gas density in the flow tube with the droplet train switched on and off. The droplet size was 120 μm and the interaction time of the droplets with SO_2 was 2 and 10 ms. The SO_2 density was 4×10^{12} molecule cm^{-3} at a total pressure of 10 Torr ($\text{He} + \text{H}_2\text{O}$). A small admixture of CH_4 was used to control the degree of water saturation (=100%) of the carrier gas in order to prevent evaporation/condensation of the water droplets. The listed value has been corrected for gas-phase diffusion of SO_2 towards the droplet surface. The measured uptake coefficient is a composite of

liquid diffusion limited uptake of S(IV) , chemical reaction depending on the pH and saturation of the diffusion thickness layer (Henry's law saturation). These competing processes are all strongly pH dependent and lead to a complex pH dependence of γ . The presence of H_2O_2 induces significant uptake of SO_2 into the aqueous phase in the pH range 0–2 compared to the situation in the absence of H_2O_2 where reevaporation of SO_2 is dominant. The results are consistent with a maximum uptake coefficient of 0.11 which is a hypothetical value obtained in the absence of any surface saturation, diffusion, and chemical reaction rate limitation.

References

- ¹ J. T. Jayne, J. A. Gardner, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *J. Geophys. Res.* **95**, 20559 (1990).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\leq 3 \times 10^{-6}$	ice, HNO ₃ -treated ice	192	Hanson and Ravishankara, 1991 ¹	(a)
	$3.0^{+2}_{-3} \times 10^{-6}$	60% H ₂ SO ₄	215–230		
	6.0×10^{-5}	40% H ₂ SO ₄	215–230		
γ	$< 5 \times 10^{-4}$	water droplets, pH=1–14	275	De Bruyn <i>et al.</i> , 1992 ²	(b)
γ_{obs}	$(8 \pm 4) \times 10^{-3}$	water droplets, pH=6	273	George <i>et al.</i> , 1994 ³	(c)

Comments

- (a) Uptake experiment of COF₂ gas onto the walls of a coated flow tube. The kinetics were measured using a chemical ionization MS, observing CF₃O[−] after reaction of CF₂O with SF₆[−] or F[−]. Typical densities of COF₂ used in the present study were between 10¹² and 10¹³ molecule cm^{−3}. The ice and simulated NAT surfaces were stationary solid coatings at 192 K, whereas the 40% and 60% sulfuric acid flowed down the vertically mounted flow tube at $T=215\text{--}230$ K. On ice and simulated NAT surfaces no COF₂ uptake was observed, and the value given in the Table corresponds to an upper limit. Owing to the high densities of COF₂, experiments were performed to check the saturation behavior of COF₂. None was observed. It is thought that the uptake on 40% H₂SO₄ is due to chemical reaction rather than physical condensation.
- (b) Uptake experiment on a fast monodisperse droplet train moving coaxially down a low pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase-sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm , and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H₂O to result in a droplet temperature of 275 K. No uptake was detected for the droplet pH in the range 1–14 so that the value given in the Table represents an upper limit to the uptake coefficient.

- (c) Uptake experiment of COF₂ gas in a reduced pressure flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N₂, the diameter of the droplets lied between 100–110 μm , the droplet pH was varied between 3 and 10, and the contact times between 4 and 16 ms. The uptake kinetics were monitored using HPLC detection of the halogenide using conductometric (F[−]) and UV detection (CF₃COOH). The temperature of the droplets was controlled by the H₂O vapor pressure in the flow tube and corresponded to $T=273\text{--}294$ K. Using the weak time- and temperature-dependence of γ_{obs} one obtains a Henry's law solubility of 35 and 22 mol dm^{−3} atm^{−1} and a hydrolysis rate constant of <1 and 30 s^{−1} at $T=273$ and 294 K, respectively. No pH dependence was detected.

References

- ¹D. R. Hanson and A. R. Ravishankara, *Geophys. Res. Lett.* **18**, 1699 (1991).
- ²W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **19**, 1939 (1992).
- ³C. George, J. Y. Saison, J. L. Ponche, and P. Mirabel, *J. Phys. Chem.* **98**, 10857 (1994).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$< 5 \times 10^{-4}$	water droplets, pH=1–14	275	De Bruyn <i>et al.</i> , 1992 ¹	(a)

Comments

- (a) Uptake experiment on a fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm , and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H₂O to re-

sult in a droplet temperature of 275 K. No uptake was detected for the droplet pH in the range 1–14 so that the value given in the Table represents an upper limit to the uptake coefficient.

References

- ¹W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **19**, 1939 (1992).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	4.0×10^{-5} to 8.0×10^{-3}	water droplets, pH=6	275	De Bruyn <i>et al.</i> , 1992 ¹	(a)
γ_{obs}	$(8 \pm 3) \times 10^{-4}$	water droplets, pH=3.4	272–294	George <i>et al.</i> , 1994 ²	(b)

Comments

- (a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm , and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. Reactivity limited uptake of the title compound was observed at pH = 13 and 14. The values given in the Table are obtained by extrapolation to pH=6. The lower limit is obtained by assuming the hydrolysis rate constant $k_{\text{hyd}} = k_p [\text{OH}^-]$ with $k_p = 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from phosgene hydrolysis, whereas the upper limit results from direct scaling of the rate of phosgene hydrolysis at pH=6. The upper limit is preferred.
- (b) Uptake experiment of CCl_3COCl gas in a reduced pressure flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2 , the diameter of the droplets between 100 and 110 μm , and the contact times between 4 and 16 ms. The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to $T=274\text{--}294$ K. The uptake was monitored by mea-

suring the concentration of Cl^- in the droplets after collection and HPLC analysis. The uptake process of CCl_3COCl is complex and can be reduced to two competing steps of comparable rate: diffusion/uptake of the gas onto the surface and bulk of the droplet (Henry's law constant H) and hydrolysis (k_h). The observed uptake coefficient (see Table) was weakly dependent on the contact time and independent of pH in the range 3–12. This together with an estimated diffusion coefficient for CCl_3COCl in aqueous solution resulted in $H = 2.0 \text{ mol dm}^{-3} \text{ atm}^{-1}$ and $k_h = 500 \text{ s}^{-1}$ for $T=274$ K with an uncertainty of a factor of two to three. The first-order rate constant k_h was also measured using the stopped flow technique in a dioxane-water solvent mixture and resulted in a value of $150 \pm 25 \text{ s}^{-1}$ after extrapolation to pure water. The reaction was found to be acid and base catalyzed and k_h depended strongly on the presence of dioxane in the range 9.1–75% v. It also depended on the temperature and the presence of the acetate buffer.

References

- W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **19**, 1939 (1992).
- C. George, J. Lagrange, P. Lagrange, P. Mirabel, C. Pallares, and J. L. Ponche, *J. Geophys. Res.* **99**, 1255 (1994).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	1.2×10^{-6} to 2.4×10^{-4}	water droplets, pH=6	275	De Bruyn <i>et al.</i> , 1992 ¹	(a)
γ_{obs}	$(7 \pm 2) \times 10^{-4}$	water droplets, pH=6	274	George <i>et al.</i> , 1994 ²	(b)

Comments

- (a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase-sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. Reactivity-limited uptake of the title compound was observed at pH=13 and 14. The values given in the Table are ob-

tained by extrapolation to pH=6. The lower limit is obtained by assuming the hydrolysis rate constant $k_{\text{hyd}} = k_p [\text{OH}^-]$ with $k_p = 1.6 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ from phosgene hydrolysis, whereas the upper limit results from direct scaling of the rate of phosgene hydrolysis at pH=6. The upper limit is preferred.

- (b) Uptake experiment of CF_3COF gas in a reduced pressure flow tube in the presence of a fast moving monodisperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2 , the diameter of the droplets was between 100–110 μm , the droplet pH was varied between 3 and 10 and the contact times between 4 and 16 ms. The uptake

kinetics were monitored using HPLC detection of the halogenide using conductometric (F^-) and UV detection (CF_3COOH). The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to $T=273-294$ K. Using the weak time- and temperature-dependence of γ_{obs} , one obtains a Henry's law solubility of 3 and $2.6 \text{ mol dm}^{-3} \text{ atm}^{-1}$ and a hydrolysis rate constant of 150 and

330 s^{-1} at $T=273$ and 294 K, respectively. No pH dependence was detected.

References

- ¹W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **19**, 1939 (1992).
²C. George, J. Y. Saison, J. L. Ponche, and P. Mirabel, *J. Phys. Chem.* **98**, 10857 (1994).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	3.0×10^{-5} to 6.0×10^{-3}	water droplets, pH=6	275	De Bruyn <i>et al.</i> , 1992 ¹	(a)
γ_{obs}	$(7 \pm 3) \times 10^{-4}$	water droplets, pH=6	274	George <i>et al.</i> , 1994 ²	(b)

Comments

- (a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He, the droplet diameter was 50–200 μm , and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O to result in a droplet temperature of 275 K. Reactivity limited uptake of the title compound was observed at pH = 13 and 14. The values given in the Table are obtained by extrapolation to pH=6. The lower limit is obtained by assuming the hydrolysis rate constant $k_{hyd} = k_p[OH^-]$ with $k_p = 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from phosgene hydrolysis, whereas the upper limit results from direct scaling of the rate of phosgene hydrolysis at pH=6. The upper limit is preferred.
- (b) Uptake experiment of CF_3COCl gas in a reduced pressure flow tube in the presence of a fast moving mono-

disperse droplet train originating from a vibrating orifice. The pressure inside the flow tube was 20–25 Torr N_2 , the diameter of the droplets was between 100–110 μm , the droplet pH was varied between 3 and 10, and the contact times between 4 and 16 ms. The uptake kinetics were monitored using HPLC detection of the halogenide using conductometric (Cl^-) and UV detection (CF_3COOH). The temperature of the droplets was controlled by the H_2O vapor pressure in the flow tube and corresponded to $T=273-294$ K. No pH or temperature dependence of γ_{obs} was detected. Using the weak time and temperature dependence of γ_{obs} one obtains a Henry's law solubility of $4 \text{ mol dm}^{-3} \text{ atm}^{-1}$ and a hydrolysis rate constant of 50 s^{-1} at $T=273$ K.

References

- ¹W. J. De Bruyn, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *Geophys. Res. Lett.* **19**, 1939 (1992).
²C. George, J. Y. Saison, J. L. Ponche, and P. Mirabel, *J. Phys. Chem.* **98**, 10857 (1994).

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_0	$(6.4 \pm 2.0) \times 10^{-2}$	amorphous carbon	300	Tabor, Gutzwiller, and Rossi, 1993 ¹ , 1994 ²	(a)
γ_3	$(6.0 \pm 2.0) \times 10^{-5}$	$N_2O_4 + NaCl$, dry	300	Vogt and Finlayson-Pitts, 1994 ³	(b)

Comments

- (a) Uptake experiment in a low-pressure reactor (Knudsen cell) monitored by modulated molecular beam sampling electron-impact MS and *in situ* laser-induced fluorescence. In addition to steady-state uptake experiments of NO_2 on three different samples of amorphous carbon, each characterized by its BET surface area (20, 115, and $460 \text{ m}^2 \text{ g}^{-1}$), pulsed valve experiments limited the NO_2 dose to the solid carbon sample and re-

sulted in real-time measurements of the NO_2 lifetime in the presence of the carbon surface. The initial adsorption kinetics were identical for all three amorphous carbon samples within the experimental uncertainty, indicating that the uptake is independent of the microscopic details of the surface. Chemical kinetic modeling was used to explain the pulsed as well as the steady-state uptake curves obtained over a range of two orders of magnitude in NO_2 flow rates (2×10^{14} to 2

$\times 10^{16}$ molecule s^{-1}) and a factor of 15 in residence time. The reaction mechanism was complex and included surface saturation as well as competitive adsorption to nonreactive adsorption sites leading to inhibition effects at higher pressures. The pressure in the Knudsen cell was sufficiently low to exclude the participation of N_2O_4 in the uptake. NO was the only major product and was formed in decreasing yields with decreasing BET surface area, starting at 100%. Repetitively exposed carbon samples were subject to severe poisoning effects that were partially reversible upon prolonged pumping or heat treatment under vacuum.

- (b) The reaction resulted in the formation of NOCl and solid NaNO_3 and was followed by monitoring the formation of nitrate on the surface of the ground NaCl sample as a function of time using diffuse reflectance FTIR. The rate of nitrate formation was obtained from the integrated area of all absorptions in the region of the antisymmetric NO_3^- stretch (1390 cm^{-1} band). The cell residence time was on the order of 3 s, the NO_2 concentration was in the range $(1.8\text{--}29) \times 10^{14}$ molecule cm^{-3} at 30 mbar total pressure, and the extent of reaction was kept small. The rate law was obtained and

resulted in a second-order dependence of the rate of nitrate formation on NO_2 concentration. The heterogeneous reaction was interpreted using a mechanism wherein N_2O_4 directly reacted with NaCl resulting in NOCl (not observed) and NaNO_3 . The γ value listed in the Table therefore refers to the uptake of N_2O_4 in equilibrium with NO_2 , as the dimer seems to be the active species under the given pressure and temperature conditions of the uptake experiment. Complicating factors found in the course of the diffuse reflectance FTIR spectroscopic study were uncertainties regarding the penetration depth of the IR radiation, nitrate concentration gradients, and H_2O adsorption. Two different kinds of adsorbed nitrate were observed and the interconversion between the two forms was facilitated by adsorbed H_2O forming a quasi-liquid layer.

References

- ¹ K. Tabor, L. Gutzwiller, and M. J. Rossi, *Geophys. Res. Lett.* **20**, 1431 (1993).
- ² K. Tabor, L. Gutzwiller, and M. J. Rossi, *J. Phys. Chem.* **98**, 6172 (1994).
- ³ R. Vogt and B. J. Finlayson-Pitts, *J. Phys. Chem.* **98**, 3747 (1994).

5.2.2. Uptake Kinetics without Chemical Reaction

HO_2 + Substrate (SiO_2 , H_2O -Aerosol)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_0	$(5.3 \pm 4.5) \times 10^{-1}$	$r=0.055\text{ mm NH}_4\text{HSO}_4$	300	Mozurkewich <i>et al.</i> , 1987 ³	(a)
	$(3.4 \pm 1.0) \times 10^{-1}$	$r=0.081\text{ mm NH}_4\text{HSO}_4$	300		
γ_{ss}	$(1\text{--}3) \times 10^{-3}$	SiO_2	300–369	Antsupov, Ksandopulo, and Gershenzon, 1990 ²	(b)
γ_{ss}	$> 1.0 \times 10^{-2}$	fluid film	275	Hanson <i>et al.</i> , 1992 ³	(c)
	$> 5.0 \times 10^{-2}$	28% H_2SO_4	249		

Comments

- (a) Atmospheric pressure flow tube experiment with chemical detection of HO_2 using a fast chain chemical amplification of HO_2 coupled to NO_2 chemiluminescence detection. The HO_2 was generated by thermal dissociation of $\text{H}_2\text{--H}_2\text{O}$ over a hot NiCr wire with estimated HO_2 densities of 10^8 to 10^9 molecule cm^{-3} . The aerosol was produced from atomizing salt solutions and size selected by a Differential Mobility Analyzer. The fraction selected was monodisperse (particle radii within $\pm 14\%$) and contained typically $(2\text{--}3) \times 10^5$ particles cm^{-3} . A Cu(II) salt was added to the solution in order to oxidize HO_2 to H_2O_2 in solution thus preventing reevaporation of HO_2 . The uptake efficiency has therefore to be interpreted as the kinetics of HO_2 accommodation on the surface of fine aqueous aerosol particles. The pseudo-first-order rate coefficient for loss of HO_2 , k_1 , was interpreted in terms of HO_2 wall loss (k_w) and a second-order rate coefficient (k_{II})

for the loss of HO_2 on the surface of the aerosol: $k_1 = k_w + k_{\text{II}} N$ (N =number of particles). The authors conclude that the Cu(II) concentration used in their experiments (up to 0.0063 mole kg^{-1} solution) may have been only marginally sufficient to trap the HO_2 . The uptake coefficient of HO_2 on LiNO_3 aerosol ($r=0.054\text{ }\mu\text{m}$) was 0.57 ± 0.16 .

- (b) Flowing gas experiment in an all-quartz flow tube reactor using a microwave sustained cool flame of 100:1 oxygen and ethanol or allyl alcohol at pressures of 5.3–12.8 Torr. HO_2 was detected by LMR and γ was found to be independent of the total pressure in the range 5.3–12.8 Torr. At higher pressure the homogeneous disproportionation reaction becomes increasingly important. It was observed that γ has a strong negative temperature dependence, which was interpreted in terms of increasing passivation of the quartz surface by alcohol combustion products. However, reference experiments with added H_2O led to a decrease in γ , reportedly because of blocking of active surface sites for

adsorption of HO₂ on quartz. The specific-temperature dependent values of γ were $\gamma = 1.5 \times 10^{-5} \exp[(1430 \pm 50)/T]$ for ethanol and $\gamma = 1.6 \times 10^{-5} \exp[(1540 \pm 120)/T]$ for allyl alcohol.

- (c) Uptake experiment in a wetted-wall flow tube reactor. The HO₂ free radical was generated through the reaction $F + H_2O_2 \rightarrow HO_2 + HF$ using a microwave discharge. The HO₂ density was measured by titration with NO, and the resulting OH was monitored using pulsed LIF excited at 282 nm and detected at 308 ± 4 nm. The HO₂ density was between $(0.5-3) \times 10^{11}$ molecule cm⁻³ and no homogeneous self-reaction was expected. Deionized water was flowing down the vertical flow tube at 274.5 K in one series of experiments (9 Torr total pressure), and a fluid 28% H₂SO₄-H₂O mixture in another series of experiments at 249.5 K (1.6 Torr total pressure). Precautions were taken to achieve complete saturation of the He flow with H₂O,

and the analysis included full treatment of gas-phase (radial) diffusion. The measured first-order rate coefficients for the HO₂ reaction on the fluid H₂O film were extrapolated to zero carrier flow speed in order to approach the limit of vanishing Reynolds number. The listed γ values for both the fluid water film and the aqueous H₂SO₄ experiment are very sensitive to uncertainties in the diffusion coefficient and the measured k_w because the kinetics is close to the diffusion limit. Therefore only lower limits for γ are given.

References

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OH + Substrate (H₂O, SiO₂, H₂SO₄)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(10.0 \pm 3.0) \times 10^{-3}$	acid-washed SiO ₂	300	Gershenzon <i>et al.</i> , 1985 ¹	(a)
	$(5.0 \pm 2.0) \times 10^{-3}$	HF-etched SiO ₂	300		
	$\geq 4.0 \times 10^{-1}$	H ₂ O-ice	253		
	≤ 1.0	96% H ₂ SO ₄	298	Hanson <i>et al.</i> , 1992 ²	(b)
γ_{ss}	3.5×10^{-3}	fluid H ₂ O film	275		
	$> 8.0 \times 10^{-2}$	28% H ₂ SO ₄	249		

Comments

- (a) Flowing gas experiment in an all-quartz flow tube reactor coupled to a combined EPR/LMR detector for OH radicals at pressures in the range 1–4.5 Torr and residence times up to 200 ms. The all-quartz flow tube reactor was coated either with fluorinated Teflon or with the material of interest (96% H₂SO₄, water-ice) and was equipped with a jacket for circulation of a temperature controlled fluid used in the temperature range 253–348 K. The OH radical was generated from the reaction $H + NO_2 \rightarrow OH + NO$ using a microwave discharge of a 0.1% H₂-He mixture. Typical densities were $[H] = (1-3) \times 10^{13}$ molecule cm⁻³, $[NO_2] = (1-2) \times 10^{12}$ molecule cm⁻³ and $[OH] \leq 2 \times 10^{12}$ molecule cm⁻³. At those densities no homogeneous OH self-reactions were important, and no correction for diffusive transport was deemed necessary. For the Teflon surface a strong negative temperature dependence was noted: $\gamma = 3.9 \times 10^{-6} \exp[(1610 \pm 554)/T]$, and there was a significant difference in γ for single and double Teflon-coatings (the expression applies to a triply Teflon coated surface). In contrast, CrO₃-treated quartz surfaces showed a positive temperature dependence with $\gamma = 8.3 \times 10^{-2} \exp[(-654 \pm 151)/T]$, whereas results for a HF-treated quartz surface did not

show a significant temperature dependence. The γ value for ice (253 K) was measured at 1.5 Torr of He, and that for 96% H₂SO₄ at 4.5 Torr.

- (b) Uptake experiment in a wetted-wall flow tube reactor. The OH free radical was generated through the reaction $H + NO_2 \rightarrow OH + NO$ under conditions of excess H, and OH radicals were monitored using pulsed LIF excited at 282 nm and detection at 308 ± 4 nm. The OH radical density was between $(0.5-3) \times 10^{11}$ molecule cm⁻³ at H atom densities of 10^{11} – 10^{12} molecule cm⁻³. Deionized water was flowing down the vertical flow tube at 274.5 K in one series of experiments (9 Torr total pressure), and a fluid 28% H₂SO₄-H₂O mixture in another series of experiments at 249.5 K (1.6 Torr total pressure). Precautions were taken to achieve complete saturation of the He flow with H₂O, and the analysis included full treatment of gas-phase (radial) diffusion. The measured first-order rate constants for the OH radical reaction on the fluid H₂O film were extrapolated to zero carrier flow speed in order to approach the limit of vanishing Reynolds number. The listed γ value for the aqueous H₂SO₄ experiment is very sensitive to uncertainties in the diffusion coefficient and the measured k_w because the kinetics is close to the diffusion limit. Therefore only lower limits for γ are given.

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H₂O + Substrate (water ice, NAT, NaCl)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	195	Leu, 1988 ¹	(a)
γ_{ss}	1.06 ± 0.10	ice film	20	Haynes, Tro, and George, 1992 ²	(b)
	$(6.5 \pm 0.8) \times 10^{-1}$	ice film	185		
γ_{ss}	$2.0 \times 10^{-3} \leq \gamma \leq 1.0 \times 10^{-2}$	NAT	197	Middlebrook <i>et al.</i> , 1992 ³	(c)
γ_{ss}	$< 2.0 \times 10^{-4}$	dry NaCl, rh $\leq 1\%$	300	Fenter, Caloz, and Rossi, 1994 ⁴	(d)

Comments

- (a) Fast flow tube reactor with electron-impact MS sampling as a diagnostic. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). Owing to the large value of γ a diffusion correction had to be applied to the uptake rate coefficient using the measured diffusion coefficient of H₂O in He scaled to 195 K.
- (b) Ultra-high vacuum interferometric observation of the growth and evaporation of H₂O as a function of temperature. Three different types of experiments were performed: measurement of the thickness of the H₂O multilayer (sub μm) as a function of time at a given static pressure of H₂O, isothermal evaporation into the vacuum, and quasiequilibrium studies at constant temperature by setting the water vapor pressure to balance condensation and evaporation. The "evaporation coefficient" is numerically equal to the condensation coefficient in the temperature where it could be measured (175–205 K) and was found to have an activation energy of $49.8 \pm 0.8 \text{ kJ mol}^{-1}$ using a zero-order rate law appropriate for multilayer desorption. A precursor-mediated adsorption/desorption model was used to explain the negative temperature dependence of the condensation coefficient. A sublimation enthalpy of H₂O ice has been obtained from the quasiequilibrium measurement of the vapor pressure as a function of temperature. $\Delta H_{\text{sub}} = 49.4 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{sub}} = 129.7 \text{ J K}^{-1} \text{ mol}^{-1}$ have been obtained, in excellent agreement with the kinetic results of the activation energy for evaporation. Therefore, no barrier exists for

adsorption and desorption of H₂O onto itself. No dependence of the kinetic parameters on the various ice modifications has been observed.

- (c) Isothermal film growth experiment in a static chamber with time-dependent FTIR monitoring of optical density of depositing NAT film at 3371 cm^{-1} in absorption. Absolute calibration of the thickness of the NAT deposited film was performed by observing the optical interference (fringes) in the range $4000\text{--}7000 \text{ cm}^{-1}$ assuming a refractive index of 1.45 for NAT. The pressures were chosen to simulate stratospheric conditions with $p(\text{H}_2\text{O}) = 1.5 \times 10^{-4} \text{ Torr}$ and $p_{\text{HNO}_3} = (4\text{--}10) \times 10^{-7} \text{ Torr}$. The spread of the γ values given in the Table corresponds to the range in the HNO₃ pressure. A doubling of the H₂O and the upper limit of the HNO₃ pressure left the uptake coefficient unchanged.
- (d) Transient uptake experiment of H₂O on dry NaCl in a low-pressure reactor (Knudsen cell) with modulated molecular-beam sampling and phase sensitive detection using an electron-impact quadrupole MS. The H₂O was dosed onto the salt surface using a pulsed valve and gave rise to a transient H₂O pressure on the order of a mTorr. No significant uptake of H₂O vapor by NaCl could be observed.

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HCl + Substrate (water ice, NAT, H₂SO₄/H₂O, NaCl)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
<i>Sulfate/H₂SO₄ (liquid) Substrates</i>					
γ_{ss}	1.5×10^{-3}	65% H ₂ SO ₄	210	Tolbert, Rossi, and Golden, 1988 ¹	(a)
	2.6×10^{-4}	70% H ₂ SO ₄	220		
	$\geq 8.5 \times 10^{-5}$	75% H ₂ SO ₄	230		
γ	$(1.5 \pm 0.3) \times 10^{-1}$	0–40% H ₂ SO ₄ droplet	300	Watson <i>et al.</i> , 1990 ²	(b)
	$(1.04 \pm 0.12) \times 10^{-1}$	47% H ₂ SO ₄ droplet	300		
	$(7.8 \pm 0.6) \times 10^{-2}$	52% H ₂ SO ₄ droplet	300		
	$(1.0 \pm 0.4) \times 10^{-2}$	73% H ₂ SO ₄ droplet	300		
γ_{ss}	$\geq 5.0 \times 10^{-2}$	40% H ₂ SO ₄	218 ± 3	Hanson and Ravishankara, 1991 ³	(c)
	4.0×10^{-4}	60% H ₂ SO ₄	215		
	$< 3.0 \times 10^{-5}$	65% H ₂ SO ₄	215		
	$< 1.0 \times 10^{-5}$	70% H ₂ SO ₄	220		
<i>HNO₃–H₂O Substrates</i>					
γ_{ss}	$\geq 2.0 \times 10^{-1}$	NAT film	202	Abbatt and Molina, 1992 ⁴	(d)
γ_{ss}	$> 2.0 \times 10^{-1}$	NAT film	188, 193	Chu, Leu, and Keyser, 1993 ⁵	(e)
<i>H₂O (solid) Substrates</i>					
γ_{ss}	$0.4^{+0.6}_{-0.2}$	ice film	197	Leu, 1988 ⁶	(f)
γ_{ss}	$(4.0 \pm 2.0) \times 10^{-2}$	ice film	196	Leu, Moore, and Keyser, 1991 ⁷	(g)
γ_{ss}	$\geq 0.3^{+0.7}_{-0.1}$	ice film	190	Hanson and Ravishankara, 1992 ⁸	(h)
γ_{ss}	$> 2.0 \times 10^{-1}$	H ₂ O-ice film	188, 193	Chu, Leu, and Keyser, 1993 ⁵	(e)
<i>H₂O (liquid) Substrates</i>					
γ	$(6.4^{+1.2}_{-0.8}) \times 10^{-2}$	H ₂ O droplet	294	Van Doren <i>et al.</i> , 1990 ⁹	(i)
	$(1.77^{+0.24}_{-0.17}) \times 10^{-1}$	H ₂ O droplet	274		
γ	$2.0 \times 10^{-2} \geq \gamma \geq 1.0 \times 10^{-2}$	liquid jet	296.7	Kirchner <i>et al.</i> , 1990 ¹⁰	(j)
<i>Other Substrates</i>					
γ_0	3.0×10^{-3}	dry NaCl, rh ≤ 1%	300	Fenter, Caloz, and Rossi, 1994 ¹¹	(k)

Comments

- (a) Uptake experiment in a Knudsen cell flow reactor coupled to a molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210–230 K. The H₂SO₄ concentration in the bulk was obtained by dilution from 96.5% H₂SO₄ and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is in the temperature range 210–230 K. The measured steady-state H₂O vapor pressure in the Knudsen cell was 4×10^{-4} Torr ($\pm 30\%$). The listed γ values in the Table were measured under steady-state conditions, and the value for 75% H₂SO₄ is thought to be a lower limit to the uptake efficiency owing to diffusion limitation of HCl in the sulfuric acid. Less than 5% of HCl was desorbed from a 65% H₂SO₄-H₂O solution at 253 K.
- (b) Uptake experiment in a gas-droplet flow tube apparatus of transverse geometry coupled to a multiple path IR diode laser absorption cell of 728 cm optical path. The droplet diameter ranged from 110 to 280 nm and the interaction time of the sulfuric acid droplets with the HCl was varied from 2 to 0.7 ms. The HCl density was kept below 8×10^{12} molecule cm⁻³ and the total pressure (H₂O + He) ranged from 4 to 10 Torr. The γ values listed in the Table are corrected for gas-phase diffusion. Saturation phenomena became apparent at high acidities (pH = -3) and long interaction times.

- (c) Uptake experiment in a wetted-wall flow tube with chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^{10} to 10^{11} molecule cm⁻³. The cold aqueous solution of H₂SO₄ (40 to 75% by weight, $T = 215$ to 230 K) was flowing down the walls of the flow tube with a liquid film residence time of 20–30 s. $p(\text{H}_2\text{O})$ was generally around 1 mTorr. In general, there is very little uptake of HCl on liquid aqueous solutions except for 40% H₂SO₄. The error limits were reported as $^{+100}_{-50}\%$.
- (d) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. Uptake study of HCl on NAT with careful control of the thermodynamic surface state of the cryogenic substrate with characteristic pressures of HCl of $\sim 10^{-6}$ Torr. The NAT films were prepared starting from 10 μm thick ice films that were exposed to small pressures of HNO₃ over long periods of time resulting in a 0.1 μm thick NAT layer on top of the ice film. On HNO₃-rich NAT only small amounts of HCl were taken up, usually $< 10^{13}$ molecule cm⁻² except at high p_{HCl} . On H₂O-rich NAT the HCl reached monolayer coverage, 10^{15} molecule cm⁻² ($10 \text{ \AA}^2$ cross-section) already at low p_{HCl} (5×10^{-6} Torr). There were two regimes for HCl adsorption separated by a threshold pressure p_{HCl} depending on $p(\text{H}_2\text{O})$ in an inverse manner: For $p(\text{H}_2\text{O}) = (2-5) \times 10^{-4}$ Torr leading to

HNO₃-rich NAT, $p_{\text{HCl}}=10^{-4}$ Torr; for $p(\text{H}_2\text{O})=10^{-3}$ Torr, $p_{\text{HCl}}=3\times 10^{-5}$ Torr; for $p(\text{H}_2\text{O})=1.5\times 10^{-3}$ Torr leading to H₂O-rich NAT, $p_{\text{HCl}}=10^{-5}$ Torr. Below p_{HCl} the HCl adsorption was weak, reversible, and saturable. The adsorption of HCl at pressures greater than the corresponding threshold value was unlimited in time and thus not saturable. It is thought that this situation corresponds to uptake of HCl by a molten liquid phase on the surface of the cryogenic substrate resulting in a H₂O-HNO₃-HCl solution at 202 K. The measured vapor pressure of H₂O corresponds to the one for pure ice at 202 K (1.7 mTorr) and is apparently controlled by the underlying solid ice phase. Sizeable amounts of HCl can apparently be adsorbed only above a molten surface phase whose stability is given by the composition of the cryogenic phase (HNO₃-H₂O) and p_{HCl} .

- (e) Uptake experiment performed in an ice- and HNO₃-doped ice-coated flow tube coupled to a differentially pumped electron-impact quadrupole MS in the ioncounting mode. Characteristic pressures of HCl and other reactants were of the order of 10^{-7} Torr. No explicit uptake kinetics are reported owing to the rapid uptake of HCl on both ice and HNO₃-doped ice. The cryogenic surfaces were deposited onto the cold walls of the flow tube from the vapors entrained in He from the corresponding liquids. The HNO₃ content was verified using acid-base titration. The mole fraction taken up by pure water ice was in the range 3.3×10^{-5} to 6.4×10^{-4} at p_{HCl} of 7×10^{-8} to 6×10^{-6} Torr in the temperature range 188–193 K. The amount taken up by ice increased with p_{HCl} and decreasing temperature. For an increase in ice thickness from 0.5 to 15.7 μm a factor of five increase of the HCl taken up by the ice was observed at $p_{\text{HCl}}=(2.1\pm 0.1)\times 10^{-7}$ Torr and $T=188$ K. The HCl uptake on HNO₃-doped ice ranged from $(2.8\text{--}24)\times 10^{-6}$ mole fraction at $p_{\text{HCl}}=4.5\times 10^{-5}$ Torr at 188 K and 1.6 μm substrate thickness. A fast HCl adsorption was followed by an isothermal desorption of HCl for a HNO₃-H₂O composition of 47.1%. Curiously, concomitantly with HCl desorption an increase of HNO₃ and a decrease of H₂O vapor pressure were observed perhaps indicating transient formation of NAD upon exposure of NAT to HCl.
- (f) Uptake experiment performed in a fast flow tube reactor with electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). Owing to the large value of γ a diffusion correction had to be applied to the uptake rate coefficient using estimated diffusion coefficients scaled to 197 K.
- (g) Uptake experiment in an ice-coated flow tube using electron-impact MS with ion-counting. The substrates were prepared by bubbling He through a HNO₃-H₂O solution and subsequently condensing the mixture (NAT films) at 196 K resulting in film thicknesses of 70 μm . The surface areas and bulk densities of con-

densed films were measured *ex situ* in addition to the measurement of their FTIR absorption spectra. The reported data were corrected for external diffusion (important for large values of γ) using estimated diffusion coefficients in He as well as for pore diffusion (important for small values of γ) using a (semiquantitative) two-site surface reaction model: ice and NAT films were weighted according to their corresponding mass fractions. The characteristic pressures of HCl were in the mTorr range ($\pm$ one decade) and γ given in the Table corresponds to the fitted parameters for the pure phases of ice and stoichiometric NAT even though only NAT samples of varying compositions were used (44.2 to 57.4% HNO₃ H₂O). The measured values for γ on samples of varying HNO₃-NAT composition, corrected for external diffusion, were in the range $0.01\text{--}10^{-6}$. The authors note an "induction" period of several minutes during which the uptake coefficient increased up to a factor of five.

- (h) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of reactants at characteristic densities of 10^9 to 10^{11} molecule cm^{-3} . At high values of the uptake coefficient ($\gamma\geq 0.1$) significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. At low HCl concentrations (10^{10} molecule cm^{-3}) rapid saturation of the pure ice surface was observed within one minute and γ decreased from ≥ 0.3 to <0.01 . The dose to saturation was essentially a monolayer or so: 5×10^{14} molecule cm^{-2} for pure ice, half that value for NAT. HCl is thought to remain adsorbed onto the surface: the diffusion into the bulk is extremely slow at 190 K. Only 50% of the HCl can be recovered. At high HCl concentrations (2×10^{12} molecule cm^{-3}) there was unlimited uptake at $\gamma>0.3$. At those high HCl densities either a stable hexahydrate (HCl.6H₂O) or a metastable supercooled liquid is formed. Whatever the new phase, the uptake coefficient is independent of the condensed phase and controlled by the steady-state pressure of water (2×10^{-4} Torr at 191 K).
- (i) Uptake experiment on a fast droplet train (200 μm diameter) crossing a flow tube in transverse geometry. Trace gas analysis was by IR diode laser absorption in a multiple pass cell of 728 cm optical path at total pressures of 5–20 Torr. Values listed are corrected for gas-phase diffusion and distortion of velocity vector owing to rapid uptake.
- (j) Uptake experiment involving the interaction of HCl in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for Cl[−] using ion chromatography. The jet diameter was 90 μm , the jet length between 0.2 and 6 mm leading to contact times of 0.03–1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with

the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The HCl concentration was about 223 ppm. The mass accommodation coefficient showed a weak dependence on the mean speed of the jet ($10\text{--}750\text{ cm s}^{-1}$) and was independent of the relative humidity (0–48%) of the gas phase.

- (k) Uptake experiment involving HCl on dry NaCl in a low-pressure reactor (Knudsen cell) with modulated molecular-beam sampling and phase sensitive detection using an electron-impact quadrupole MS. The initial uptake at a flow of $5 \times 10^{14}\text{ molecule s}^{-1}$ depended only on the external (geometric) sample surface and was independent of the mass and grain size of the salt sample.

Preferred Values

The uptake coefficient of HCl on bulk substrates of *liquid* sulfuric acid at $T=220\text{ K}$ is strongly anticorrelated with the H_2O activity of these mixtures and is comparable in magnitude and behavior with γ for $\text{ClONO}_2 + \text{H}_2\text{O}$ and $\text{ClONO}_2 + \text{HCl}$. It spans the range of γ values of 0.1 to 10^{-5} . The solubility of HCl in those mixtures seems to be the controlling factor. This drop in γ with decreasing H_2O activity is less pronounced for *droplets* interacting with HCl at 300 K. The uptake coefficient is 0.15 for 0 to 40% sulfuric

acid at ambient temperature and is interpreted as accommodation coefficient. This behavior confirms a trend where the accommodation coefficient on droplets seems to be larger than the limiting uptake coefficient on the corresponding bulk phase after suitable correction for saturation and temperature.

On NAT-like substrates and on water ices γ has been found to be large, of the order of 0.2. On water ice γ has been found to be large, of the order of 0.3. On liquid water droplets the uptake coefficient is significantly smaller of the order of ≤ 0.1 at ambient temperature. On lowering the temperature by 20 K, γ increases to 0.2.

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HOCl + Substrate (water ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\geq (0.3^{+0.7}_{-0.1})$	ice film	191–211	Hanson and Ravishankara, 1992 ¹	(a)
γ_{ss}	$\geq 3.0 \times 10^{-1}$	ice film	195–208	Abbatt and Molina, 1992 ²	(b)

Comments

- (a) Uptake experiment in an ice-coated flow tube with chemical ionization MS detection. This method allows selective detection of HOCl at characteristic densities of 10^9 to $10^{11}\text{ molecule cm}^{-3}$. At high values of the uptake coefficient ($\gamma \geq 0.1$) significant diffusion corrections had to be made using calculated diffusion coefficients for the reactants in He. The primary observable was a first-order loss rate coefficient from which γ was calculated taking into account the diffusion correction and the corrected gas-wall collision frequency in the presence of a reactive surface. The source of HOCl was either from the reaction $\text{HCl} + \text{Ca}(\text{ClO})_2$ or from the *in situ* reaction of $\text{ClONO}_2 + \text{H}_2\text{O}$ (ice). The thermodynamics of adsorption were measured from the integrated (relative) HOCl signal over the temperature range 191–211 K and resulted in the following values: $\Delta H_{\text{ads}} = -(58.6 \pm 8.4)\text{ kJ mol}^{-1}$, $\Delta S_{\text{ads}} = -(167.3$

$\pm 41.8)\text{ J mol}^{-1}\text{ K}^{-1}$ (estimated). The fractional surface coverage in all the reported experiments did not exceed 0.01. HOCl does not adsorb on NAT nor is it formed from the reaction $\text{ClONO}_2 + \text{H}_2\text{O}$ on NAT under the given experimental conditions.

- (b) Uptake experiment in an ice-coated flow tube using electron-impact quadrupole MS equipped with a closed ion-source. No specific value for the uptake kinetics was given. A surface coverage estimate yields $3.2 \times 10^{13}\text{ molecule cm}^{-2}$ at a HOCl pressure of $3 \times 10^{-6}\text{ Torr}$, representing 5% of a monolayer on ice with 0.15 nm^2 of (estimated) cross-sectional area. The heat of adsorption was determined to be $(43.9 \pm 8.4)\text{ kJ mol}^{-1}$.

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HBr + Substrate (water ice, NAT)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	0.3–1.0	water-ice, NAT	201	Hanson and Ravishankara, 1992 ¹	(a)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to a chemical ionization MS with selective detection of HBr and other halogen containing reactants and products. Ice layers 2–10 μm thick were condensed from the vapor phase onto the cold flow tube wall and HNO_3 -treated ice was defined as NAT under the used experimental conditions. The uptake of HBr on pure ice is very efficient with no signs of saturation up to 10 monolayers of HBr on ice (5×10^{15} molecule cm^{-2}) at HBr concentrations as low as 2×10^{10} molecule cm^{-3} . It is thought that a new fluid binary phase HBr- H_2O forms at HBr pressures as low as 6×10^{-9} Torr explaining the unlimited HBr uptake, rather than

being due to a physical uptake process. No significant uptake of HBr on cold Pyrex was observed ($\gamma_{ss}=1.0 \times 10^3$), however, the uptake was significantly enhanced on HF-treated cold Pyrex reaching values up to 0.10. In contrast, significant uptake of HBr was observed when HBr was introduced into the tube concomitantly with H_2O vapor at 50% relative humidity at 201 K. Again, a binary fluid mixture HBr- H_2O is thought to form at HBr pressures $\geq 5 \times 10^{-7}$ Torr.

References

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HOBr + Substrate (Pyrex, water ice, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(2-4) \times 10^{-4}$	Pyrex	228	Abbatt, 1994 ¹	(a)
	$(2.0 \pm 1.0) \times 10^{-3}$	water-ice	228		
	$> (6.0 \pm 2.0) \times 10^{-2}$	60% H_2SO_4	228		

Comments

- (a) Flow tube study (1 Torr He) using moveable injector and quadrupole MS sampling (HOBr at m/e 96, 98). The HOBr was generated *in situ* inside a moveable injector tube by reaction of Br_2 with OH that was produced from $\text{NO}_2 + \text{H}$ from a microwave discharge of H_2 in He. The ice film was prepared by wetting the flow tube wall and rapidly cooling to 228 K. The uptake coefficient was measured by observation of the HOBr disappearance with injector position. The characteristic HOBr concentration for the uptake study on

pure ice was $< 5 \times 10^{11}$ molecule cm^{-3} . For concentrations exceeding 10^{12} molecule cm^{-3} a bimolecular rate law for HOBr disappearance was observed with no gas-phase products observed. There was no evidence for reversible adsorption of HOBr on ice. For the uptake on 60% H_2SO_4 the HOBr concentration was $< 5 \times 10^{12}$ molecule cm^{-3} .

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HNO₃ + Substrate (water ice, water droplets, H₂SO₄/H₂O, salt surfaces)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
<i>Sulfate/H₂SO₄ (liquid) Substrates</i>					
γ_{ss}	2.0×10^{-3}	75% H ₂ SO ₄	230	Tolbert, Rossi, and Golden, 1988 ¹	(a)
	4×10^{-3}	96.5% H ₂ SO ₄	295		
γ_0	$(2.5 \pm 0.5) \times 10^{-1}$	15–87% H ₂ SO ₄	188	Reihs, Golden, and Tolbert, 1990 ²	(b)
	$(7.0 \pm 1.0) \times 10^{-2}$	15–87% H ₂ SO ₄	223		
γ	$(1.1 \pm 0.1) \times 10^{-1}$	73% H ₂ SO ₄ droplets	283	Van Doren <i>et al.</i> , 1991 ³	(c)
<i>Sulfate/H₂SO₄ (solid) Substrates</i>					
γ_{ss}	$\geq 3.0 \times 10^{-1}$	57.7% H ₂ SO ₄	191.5	Hanson, 1992 ⁴	(d)
	$\geq 2.0 \times 10^{-1}$	57.7% H ₂ SO ₄	200		
<i>HNO₃-H₂O Substrates</i>					
γ_{ss}	$\geq 3.0 \times 10^{-1}$	ice film, HNO ₃ coverage ≤ 0.3	191.5	Hanson, 1992 ⁴	(e)
	$\geq 2.0 \times 10^{-1}$	ice film, HNO ₃ coverage ≤ 0.2	200		
γ_{ss}	$4.0 \times 10^{-1} \leq \gamma \leq 1.0$	NAT	197	Middlebrook <i>et al.</i> , 1992 ⁵	(f)
<i>H₂O (solid) Substrates</i>					
γ_{ss}	$0.3^{+0.7}_{-0.1}$	ice film	197	Leu, 1988 ⁶	(g)
<i>H₂O (liquid) Substrates</i>					
γ	$(7.1^{+2.0}_{-1.0}) \times 10^{-2}$	H ₂ O droplets	293	Van Doren <i>et al.</i> , 1990 ⁷	(h)
γ	$(1.93^{+0.21}_{-0.15}) \times 10^{-1}$	H ₂ O droplets	268		
γ	$\leq 1.0 \times 10^{-2}$	liquid jet	298	Kirchner <i>et al.</i> , 1990 ⁸	(i)
γ	$(1.1 \pm 0.1) \times 10^{-1}$	H ₂ O droplets	298	Ponche, George, and Mirabel, 1993 ⁹	(j)
<i>Other Substrates</i>					
γ_0	$(2.8 \pm 0.3) \times 10^{-2}$	dry NaCl, KCl, NaBr, KBr, NaNO ₃	300	Fenter, Caloz, and Rossi, 1994 ¹⁰	(k)
γ_0	$(1.0 \pm 0.2) \times 10^{-2}$	dry CaCO ₃ , Na ₂ CO ₃ , rh $\leq 1\%$	300	Fenter, Caloz, and Rossi, 1995 ¹¹	(l)
γ_0	$(4.0 \pm 2.0) \times 10^{-4}$	single crystal NaCl, dry	300	Laux, Hemminger, and Finlayson-Pitts, 1994 ¹²	(m)

Comments

- (a) Uptake experiment in a Knudsen cell flow reactor coupled to a modulated molecular beam sampled electron-impact MS. The bulk substrate (1–5 mL) was cooled slowly to temperatures of 210–230 K. The H₂SO₄ concentration in the bulk was obtained by dilution from 96.5% H₂SO₄ and was chosen to reflect the sulfuric acid aerosol concentration under stratospheric conditions, that is in the temperature range 210–230 K. The measured steady-state vapor pressure in the Knudsen cell was 4×10^{-4} Torr ($\pm 30\%$). The listed γ values in the Table were measured under steady-state conditions. The apparent desorption temperature (probably an artifact) and yield of evaporated HNO₃ that was condensed on 75% H₂SO₄ at 230 K were measured to be 251 K and approximately 20%, respectively, in contrast to pure ice (230 K, 100%).
- (b) The uptake was measured using the Knudsen cell technique with modulated electron-impact MS detection of HNO₃ vapor effusing out of the Knudsen cell. The sulfuric acid substrate was prepared from bulk solutions and cooled down to the temperature range 188–240 K. The values in the Table refer to γ measured at time zero (γ_0) before the uptake kinetics reaches steady state at the interfacial layer and thus become time independent. The time dependence of γ could be described by $1/\gamma(t) = \{1/\gamma_0 + c(t)^{0.5}/4RTH^*(D)^{0.5}\}$ where D was the diffusion coefficient of HNO₃ in

H₂SO₄ at temperature T . It results essentially from two competing factors: the solubility (Henry's law coefficient) of HNO₃ in sulfuric acid solution increases with decreasing temperature and H₂SO₄ concentration, and liquid diffusion of HNO₃ decreases with decreasing temperature. Accordingly, γ becomes time dependent for a H₂SO₄ concentration $\geq 58\%$ at $T=223$ K and $\geq 74\%$ at 188 K due to the fact that H^*D becomes sufficiently small. Effective Henry's law solubilities H^* were calculated whose temperature dependence resulted in heats of solvation and standard entropies of solvation. For H₂SO₄ concentrations $> 58\%$ HNO₃ was dissolved in molecular form, thus $H=H^*$. For 58% H₂SO₄ the solubility data show a possible influence of ionic dissociation of HNO₃.

- (c) Uptake experiment on fast droplet train (200 μ m diameter 73% H₂SO₄ H₂O droplets) traversing a flow tube coupled to a multiple pass IR diode laser absorption cell of 728 cm optical path at pressures of 10 Torr and droplet-gas interaction times of 1–2 ms. HNO₃ is a confirmed reaction product of the heterogeneous N₂O₅-H₂O interaction and the product branching ratio defined as the ratio of observable HNO₃(g) and twice the depletion of N₂O₅(g) $[(\text{HNO}_3(\text{g}))/2\Delta(\text{N}_2\text{O}_5(\text{g}))]$ varies between 0.25 and 0.37 for interaction times of 1.1 to 1.6 ms, respectively. The value for γ listed in the Table has been corrected for gas phase diffusion and distortion of the Maxwellian velocity distribution near

an adsorbing surface. Both the reduction in the HNO_3 uptake coefficient relative to that on water and the HNO_3 gaseous evolution from N_2O_5 uptake can be explained by the limited HNO_3 solubility in aqueous sulfuric acid.

- (d) Uptake experiment in a frozen liquid-coated flow tube (~ 0.45 Torr He) coupled to a chemical ionization MS. Both the H_2O and HNO_3 signals were calibrated, and the volumetrically prepared 57.7% H_2SO_4 solution was applied on the inside of the flow tube wall at 205 K as a liquid. The $p(\text{H}_2\text{O})$ corresponded to the ice point, and the pressure of HNO_3 was 8×10^{-8} Torr at 191.5 K and 3×10^{-7} Torr at 200 K. A correction was applied to the signal taking into account the steady state vapor pressure of p_{HNO_3} of $\sim 10^{-8}$ Torr at 191.5 K and 200 K for HNO_3 coverages of 0.06 and 0.03, respectively. In the former case p_{HNO_3} was higher by a factor of three relative to the vapor pressure of NAT, in the latter case it was a factor of three lower than the NAT vapor pressure. With increasing coverage up to several monolayers the uptake coefficient stayed unchanged whereas the steady-state p_{HNO_3} increased by a factor of 10–20 relative to what is expected for NAT. With the HNO_3 and H_2O sources turned off, p_{HNO_3} slowly decreased from 5×10^{-8} Torr to 1.5×10^{-8} Torr over 40 minutes.
- (e) Uptake experiment in an ice-coated flow tube (~ 0.45 Torr He) coupled to a chemical ionization MS. Both the H_2O and HNO_3 signals were calibrated with the $p(\text{H}_2\text{O})$ at the ice point, and the pressure of HNO_3 set to 8×10^{-8} Torr at 191.5 K and 3×10^{-7} Torr at 200 K. A correction was applied to the signal taking into account the steady-state vapor pressure of p_{HNO_3} of $\sim 10^{-9}$ Torr at 191.5 K and of $\sim 10^{-8}$ Torr at 200 K for HNO_3 coverages of <0.3 and <0.2 , respectively. In both cases p_{HNO_3} was lower by a factor of three relative to the vapor pressure of NAT. With increasing surface coverage of HNO_3 the HNO_3 uptake decreased and the steady-state p_{HNO_3} increased significantly as the ice surface became coated with HNO_3 . The steady-state p_{HNO_3} over an ice surface with a coverage of approximately 1 monolayer of HNO_3 was about a factor of five higher than the vapor pressure over NAT. With the sources of HNO_3 and H_2O turned off, p_{HNO_3} at steady state decreased steadily with time to a value close to the vapor pressure of NAT at 191.5 K and to approximately a factor of two below p_{NAT} at 200 K.
- (f) Isothermal film growth experiment in a static chamber with time-dependent FTIR monitoring of optical density of depositing NAT film at 3371 cm^{-1} . Absolute calibration of the thickness of the NAT deposited film was performed by observing the optical interference (fringes) in the range 4000 to 7000 cm^{-1} assuming a refractive index of 1.45 for NAT. The pressures were chosen so as to simulate stratospheric conditions with $p(\text{H}_2\text{O}) = 1.5 \times 10^{-4}$ Torr and $p_{\text{HNO}_3} = (4\text{--}10) \times 10^{-7}$

Torr. The spread of the γ values given in the Table corresponds to the range in the HNO_3 pressure. A doubling of the H_2O and the upper limit of the HNO_3 pressure left the uptake coefficient unchanged.

- (g) Uptake experiment performed in a fast flow tube reactor with electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). Owing to the large value of γ a diffusion correction had to be applied to the uptake rate coefficient using estimated diffusion coefficients of HNO_3 in He scaled to 197 K.
- (h) Uptake experiment on a fast droplet train (200 μm diameter) crossing a flow tube in transverse geometry. Trace gas analysis is by IR diode laser absorption in a multiple pass cell of 728 cm optical path at total pressures of 5–20 Torr. Values listed are corrected for gas-phase diffusion and distortion of velocity vector owing to rapid uptake.
- (i) Uptake experiment involving the interaction of HNO_3 in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for NO_3^- or Cl^- using ion chromatography. The jet diameter was 90 μm , the jet length between 0.2 and 6 mm leading to contact times of 0.03 to 1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The HNO_3 concentration was about 60 ppm and a measurement of γ relative to the one for HCl ($\gamma = 1.0 \times 10^{-2}$) agreed with the absolute measurement of γ .
- (j) Uptake experiment on a monodisperse (70–110 μm diameter droplets) and fast moving (480–2000 cm s^{-1}) droplet train propagating axially in a low-pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake is determined by chemical analysis (ion chromatography) of collected aqueous phase. The uptake coefficient has been found to be independent of pH in the basic range, of the contact time and of the HNO_3 concentration in the range 10–100 ppm. The value listed in the Table has been corrected for gas phase diffusion as the experimentally determined uptake coefficient has been found to depend on pressure. The measured average uptake coefficient γ_{obs} is $(5.0 \pm 0.9) \times 10^{-2}$ at 50 Torr N_2 and 298 K.
- (k) Uptake experiment of HNO_3 on dry alkali salt powders (NaCl , NaBr , KCl , KBr) and NaNO_3 in a two-chamber low-pressure reactor (Knudsen cell) with modulated molecular beam sampling and phase sensitive detection using an electron-impact quadrupole MS. Both steady-

state experiments with HNO_3 flows ranging from 10^{13} to 2×10^{15} molecule s^{-1} as well as transient dosing experiments ($\sim 10^{14}$ molecules per pulse representing a few percent of a monolayer on the geometric surface of the sample) using a pulsed valve were performed. Both types of experiments were interpreted using a simple chemical kinetic model. The initial uptake coefficient γ_0 was measured in the low dose limit and was found to be dependent only on the external (geometric) surface, but independent of the nature of the salt, whereas the rate of HCl and HBr generation as well as the yield were found to be sensitive to several experimental parameters such as the nature, mass and grain size of the salt. The yields of HCl were in general higher than the yields of HBr . No synergistic effect in the HNO_3 uptake was observed in the presence of water vapor in the mTorr range. The adsorbed product hydrohalogenic acids are efficiently displaced from their sites of generation by HNO_3 .

- (l) Uptake experiment of HNO_3 on dry carbonate powders including a "natural" limestone in a two-chamber low pressure reactor (Knudsen cell) with modulated molecular beam sampling and phase sensitive detection using an electron-impact quadrupole MS. Both the uptake of HNO_3 as well as the generation of CO_2 and H_2O were measured for the heterogeneous chemical reaction $\text{CaCO}_3 + 2\text{HNO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O}$ at flow rates of HNO_3 in the range 5×10^{14} to 6×10^{15} molecule s^{-1} . The uptake of HNO_3 shows an onset of saturation on the time scale of several minutes. The time evolution for all of the observed species points to a complex mechanism on the surface of or within the powder sample. The interaction of H_2O vapor on dry calcite powder is surprisingly strong and corresponds to an uptake coefficient γ_0 of 0.05 ± 0.02 for a flow rate of 1.7×10^{15} molecule s^{-1} with some signs of saturation on the time scale of a few minutes. The adsorption of HNO_3 on calcite seems to be independent of the H_2O partial pressure whereas the formation of H_2O and CO_2 seem to be enhanced by a factor of two in the presence of a flow of H_2O comparable to HNO_3 .
- (m) The reaction was followed by using x-ray photoelectron spectroscopic signals (XPS) quantifying the surface Cl^- and NO_3^- concentration as a function of exposure of a single crystal NaCl sample (100 face) to dry HNO_3 dispensed from a capillary mounted 1 mm in front of the dry salt sample under UHV conditions. The average sticking coefficient was obtained by dividing the number of nitrate species on the surface at satu-

ration by the number of HNO_3 molecules incident on the sample. The assumption was made that at saturation, that is when the XPS signal due to N and O stopped changing with exposure time, the sample had acquired one monolayer of nitrate at the expense of the chloride. At saturation the Cl signal also reached a constant value having decreased by 50% compared to the original clean NaCl sample. The XPS signals (peak areas) were corrected for charging effects, properly background subtracted and scaled using standard XPS sensitivity factors.

Preferred Values

The uptake coefficient γ interpreted as mass accommodation coefficient α on *liquid* sulfuric acid at 200 K is found to be large, of the order of 0.2. It is weakly dependent on temperature over the range 188–223 K but independent of the sulfuric acid concentration in the range 15–87%. On sulfuric acid *droplets* γ (or α) attains similar values (0.1) at 283 K on 73% sulfuric acid. This confirms a trend where the accommodation coefficient on droplets seems to be larger than the limiting uptake coefficient for the corresponding bulk phase after suitable correction for saturation and temperature, where applicable. An equally large γ of 0.2 has been observed for *frozen* substrates of H_2SO_4 .

On water ice γ is ≥ 0.3 at 200 K. This also seems to hold for NAT-like surfaces. On liquid water γ is interpreted as a mass accommodation coefficient and seems to be 0.1 at ambient temperature.

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HONO + Substrate (water droplets and liquid jet)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	5.0×10^{-3}	liquid jet	299	Kirchner <i>et al.</i> , 1994 ¹	(a)
γ	$0.05^{+0.02}_{-0.01}$	liquid jet	297	Bongartz <i>et al.</i> , 1994 ²	(b)
	$0.05^{+0.04}_{-0.01}$	droplets	245		

Comments

- (a) Uptake experiment involving the interaction of HONO in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for NO_2^- using ion chromatography. The jet diameter was $90\ \mu\text{m}$, the jet length between 0.2 and 6 mm leading to contact times of 0.03 to 1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The gas phase interacting with the liquid jet consisted of approximately 130 ppm of HONO detected using UV absorption, 170 ppm of NO_2 detected using LIF excited at 442 nm and an unknown amount of NO. Similar amounts of pure NO_2 in air do not lead to detectable amounts of NO_2^- after liquid jet interaction. Using an effective Henry's law constant that takes into account the pK_a of HONO and an acid dissociation constant of $k_a = 5.0 \times 10^6\ \text{s}^{-1}$ results in satisfactory fits to the NO_2^- concentration vs. time curves if the UV absorption cross section of HONO is reduced by 30%.
- (b) This work on HONO uptake on liquid condensed surfaces comprised two experimental techniques related to flowing gas experiments: an improved version of the

liquid jet and the droplet train technique. The liquid jet technique involved the measurement of the concentration of NO_2^- in the collected jet. The jet diameter was $110\ \mu\text{m}$ at the orifice leading to contact times between 0.1 to 0.8 ms at one atmosphere of N_2 . The droplet train technique involved exposing gasphase HONO at pressures of 30–60 Torr to a fast moving train of droplets of $100\text{--}110\ \mu\text{m}$ diameter at residence times of 3.7–16 ms. The small partial pressure of H_2O of 0.25 Torr corresponded to a droplet surface temperature of $245 \pm 5\ \text{K}$. The first value of the uptake coefficient in the Table corresponds to the measurement using the liquid jet technique where the error limits have been estimated from a sensitivity analysis of the input parameters used to fit the concentration in the collected liquid vs. contact time data. The principal source of uncertainty is the evaluation of the binary gas-phase diffusion coefficient of HONO (D_p). The second value of the uptake coefficient in the Table pertains to the application of the fast droplet train method. The observed uptake coefficient was independent of reaction time but dependent on total pressure. Again, a 20% uncertainty in D_p leads to the stated error intervals.

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NO + Substrate (water ice, 70% $\text{H}_2\text{SO}_4\text{-H}_2\text{O-ice}$)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$< 1.0 \times 10^{-4}$	$\text{H}_2\text{O-ice}$	195	Leu, 1988 ¹	(a)
γ_0	$\leq 5.0 \times 10^{-6}$	70% H_2SO_4	193–243	Saastad, Ellermann, and Nielsen, 1993 ²	(b)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor.
- (b) Measurement of the total pressure drop in a static system over bulk frozen 70% $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ monitored by MS. Visual inspection of the substrate indicated a supercooled glass even at the lowest temperatures. The values given represent conservative upper limits de-

rived in comparison with calculated signals. Three kinds of experiments were performed: uptake of NO, NO_2 , and a mixture of NO- NO_2 , all giving the same result.

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NO₂ + Substrate (water ice and droplets, 70% H₂SO₄-H₂O-ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$< 1.0 \times 10^{-4}$	H ₂ O-ice	195	Leu, 1988 ¹	(a)
γ_0	$(6.3 \pm 0.7) \times 10^{-4}$	H ₂ O droplets	273	Lee and Tang, 1988 ²	(b)
γ_0	$\leq 5.0 \times 10^{-6}$	70% H ₂ SO ₄	193–243	Saastad, Ellermann, and Nielsen, 1993 ³	(c)
γ_{obs}	$(1.5 \pm 0.8) \times 10^{-3}$	H ₂ O droplets	298	Ponche, George, and Mirabel, 1993 ⁴	(d)

Comments

- (a) Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor.
- (b) Uptake experiment involving a stopped flow of NO₂ in humidified He carrier gas exposed to a circulating fluid sample of water containing between 1×10^{-2} and 7×10^{-2} M of hydroquinone as a scavenger in basic solution. Total pressures of 25–50 Torr were used and the uptake coefficients were corrected for gas phase diffusion resulting in mass accommodation coefficients. A 10% change in the diffusion coefficient for NO₂ in He resulted in a variation between 2% and 20% of the accommodation coefficient.
- (c) Measurement of the total pressure drop in a static system over bulk frozen 70% H₂SO₄-H₂O monitored by MS. Visual inspection of the substrate indicated a supercooled glass even at the lowest temperatures. The values given represent conservative upper limits derived in comparison with calculated signals. Three kinds of experiments were performed: uptake of NO, NO₂, and a mixture of NO-NO₂, all giving the same result.

- (d) Uptake experiment on a monodisperse (70–110 μ m diameter droplets) and fast moving (480–2000 cm s⁻¹) droplet train propagating axially in a low-pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake is determined by chemical analysis (ion chromatography) of collected aqueous phase. A chemical scavenger H₂O₂ was added to the condensed phase in order to scavenge NO₂⁻ to nitrate. The uptake coefficient has been found to be independent of pH in the range 4–11 and of the contact time. The observed value of the uptake coefficient seems to exceed the value expected on the basis of published Henry's law coefficients by at least a factor of ten and is attributed to unknown chemical reactions.

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CH₃CO(O)₂NO₂ (PAN) + Substrate (water jet)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$1.0 \times 10^{-3} < \gamma < 5 \times 10^{-3}$	liquid jet	281.8	Kirchner <i>et al.</i> , 1990 ¹	(a)

Comments

- (a) Uptake experiment involving the interaction of PAN in an atmospheric pressure of synthetic air with a liquid jet of pure water. The uptake kinetics were studied by analyzing the liquid water content for the sum of NO₂⁻ + NO₃⁻ using ion chromatography. The jet diameter was 90 μ m, the jet length between 0.2 and 6 mm leading to contact times of 0.03–1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of anions in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The results are regarded as lower limits owing to uncertainties in the velocity distribution of the liquid jet. The PAN con-

centration was about 290 ppm detected by UV absorption in the range 200–250 nm with small impurities of NO₂ (250 ppb) detected using LIF excited at 442 nm and CH₃ONO₂ (>3 ppm) detected by GC. The poor agreement between the absolute measurement and the determination of γ relative to the one for HCl ($\gamma = 10^{-2}$) indicates a problem with the data reduction for low solubility gases.

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NH₃ + Substrate (liquid water jet, water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(4.0^{+3}_{-0.5}) \times 10^{-2}$	liquid jet	299 $\pm$ 1	Bongartz <i>et al.</i> , 1995 ¹	(a)
γ	$(9.7 \pm 0.9) \times 10^{-2}$	H ₂ O droplets	290	Ponche, George, and Mirabel, 1993 ²	(b)

Comments

- (a) Uptake experiment of NH₃ by a liquid jet of dilute HCl solution using a combination of a peristaltic pump/conductivity detector for the continuous on-line measurement of NH₄⁺ in the collected jet waters. The liquid jet diameter was 97 ± 2 μ m, the jet length could be varied from 0.2 to 4 mm corresponding to a contact time of 0.1–0.8 ms. Both synthetic air and He were used as a carrier gas at a total pressure of 1 atm. The NH₃ concentration was in the range 100–200 ppm for air and 50–100 ppm for He as a carrier gas. Despite a factor of three difference in the diffusion coefficient for NH₃ gas the γ values for air as a carrier gas were agreeing very well with the ones measured in He ($\gamma = 3.5 \times 10^{-2}$ in air vs. 4.0×10^{-2} in He). The results are extremely sensitive to the value of the diffusion coefficient for NH₃ gas and sensitive to Henry's constant for NH₃. Owing to the short contact times the method is virtually free of saturation effects in the liquid phase.
- (b) Uptake experiment on a monodisperse (70–110 μ m

diameter droplets) and fast moving (480–2000 cm s⁻¹) droplet train propagating axially in a low pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake is determined by chemical analysis (ion chromatography) of collected aqueous phase. The uptake coefficient has been found to be independent of pH in the range 4.2–11.5 but dependent on the contact time. The value listed in the Table has been corrected for gas phase diffusion as the experimentally determined uptake coefficient has been found to depend on pressure. The measured average uptake coefficient γ_{obs} is $(2.4 \pm 1.0) \times 10^{-2}$ at 70 Torr N₂ and 290 K.

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O₃ + Substrate (water ice, liquid, NAT, Pyrex)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$< 1.0 \times 10^{-4}$	ice film	195	Leu, 1988 ¹	(a)
γ_{ss}	$< 1.0 \times 10^{-6}$	ice film	195	Dlugokencky and Ravishankara, 1992 ²	(b)
	$< 1.0 \times 10^{-6}$	97% H ₂ SO ₄	196		
	$(1-5) \times 10^{-4}$	NAT	195		
γ_{ss}	$\geq 2 \times 10^{-3}$	liquid water	276	Utter <i>et al.</i> , 1992 ⁴	(c)
γ_{ss}	$< 6.0 \times 10^{-5}$	ice film, Pyrex	183	Kenner, Plumb, and Ryan, 1993 ⁴	(d)
	$< 8.0 \times 10^{-5}$	NAT	183		

Comments

- (a) Uptake experiment performed on an ice-coated flow tube coupled to electron impact MS. The ice film was deposited from water vapor.
- (b) Uptake experiment in a coated flow tube reactor using chemiluminescent ozone detection (via reaction of O₃ + NO $\rightarrow$ NO₂^{*} + O₂). The O₃ detection limit was $\sim 2 \times 10^7$ molecule cm⁻³ at S/N=1 and 1.5 min averaging time. Typical pressures were $p_{\text{O}_3} = 10^8$ – 10^{12} molecule cm⁻³ with 1 Torr of He carrier gas. The flow tube was coated with the appropriate solution at $T \sim 230$ K to result in a coating of approx. 2 mm thickness. No diffusion corrections were deemed necessary at the low vapor pressure of H₂O (0.65 mTorr). Satu-

ration phenomena were apparent in that use of low ozone concentrations ($\leq 2 \times 10^9$ molecule cm⁻³) resulted in the largest values of γ ($\sim 1.0 \times 10^{-2}$) and increasing sulfite concentrations obtained still larger values for reactive uptake (0.01 on 0.1 M Na₂SO₃ at 196 K).

- (c) Uptake experiment on wetted-wall flow tube reactor in which a film of liquid water (0.2 mm thickness) flowed down a vertical flow tube at a liquid flow velocity of 4–16 cm s⁻¹. The initial ozone concentration was 10^{11} molecule cm⁻³ and was detected at the exit of the flow tube using chemiluminescence. The gas flow characteristics was between laminar and turbulent and corrections had to be applied for significant radial O₃ concentrations gradients. The total pressure was between

10.2–11 Torr with half of it being H₂O vapor. No uptake was observed when ozone interacted with pure deionized water presumably owing to saturation effects. Adding a trapping agent for ozone such as Na₂SO₃, Na₂S₂O₃, or SnCl₂ increased γ as a function of the concentration of the trapping agent to values in the 10⁻² range. The uptake rate constant was independent of changes in the liquid flow velocity by a factor of four and of the gas flow velocity by a factor of three. A conservative lower limit for the accommodation coefficient of 2 × 10⁻² is obtained.

- (d) Uptake experiment in a fast flow tube reactor with electron-impact MS sampling and ion counting. The cryogenic phase was deposited from H₂O vapor and H₂O:HNO₃=3:1 vapor mixtures to obtain thicknesses

of 4–7 μm for ice and additional 2–3 μm thick films on top of already deposited ice layers. This limitation in terms of deposited material could lead to an increase of γ by a factor of two at most. Taking into account the porosity of the deposited layer would lead to a lowering of γ .

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Cl₂ + Substrate (water ice)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	< 10 ⁻⁴	ice film	200	Leu, 1988 ¹	(a)
γ_{ss}	< 5.0 × 10 ⁻⁵	ice film	183	Kenner, Plumb, and Ryan, 1993 ²	(b)

Comments

- (a) Uptake experiment performed in a fast flow tube reactor using electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). The value given in the Table is an upper limit.
- (b) Fast flow tube reactor study using electron-impact MS sampling and ion counting. The cryogenic phase was deposited from H₂O vapor to obtain thicknesses of 4–7

μm . This limitation in terms of deposited material could lead to an increase of γ by a factor of two at most. Taking into account the porosity of the deposited layer would lead to a lowering of γ .

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ClO + Substrate (water ice, H₂SO₄-H₂O, NAT, Pyrex)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	(8.0 ⁺¹⁴ ₋₅) × 10 ⁻⁴	70% H ₂ SO ₄	220	Martin, Judeikis, and Wun, 1980 ¹	(a)
γ_{ss}	> 1.0 × 10 ⁻²	ice film	190	Leu, 1988 ²	(b)
γ_{sss}	< 1.8 × 10 ⁻⁵	Pyrex	295	Kenner, Plumb, and Ryan, 1993 ³	(c)
	(8 ± 2) × 10 ⁻⁵	Pyrex, ice film, and NAT	183		

Comments

- (a) Measurement of the uptake kinetics in a fast flow tube with EPR detection of ClO. Pure Cl₂ at 0.5 Torr was discharged in a microwave cavity and combined downstream with an excess of O₃ in order to generate ClO. The quartz flow tube was coated with halocarbon wax and the discharge tube with solid B₂O₃ in order to minimize wall losses of ClO. The inside of the flow tube was coated with H₂SO₄ and the H₂O vapor pressure was held constant throughout the temperature range at 5 × 10⁻⁴ Torr leading to a changing composi-

tion of the H₂SO₄-H₂O mixture as the temperature was changed (96% at 300 K, 80% at 240 K). Therefore no separation between the effects of changing composition of the cryogenic phase (considered to be negligible) and the temperature dependence of γ could be achieved. All kinetic results were obtained from the full numerical integration of the parabolic flow system including axial diffusion and resulted in a pronounced negative temperature dependence of the uptake coefficient γ_{ss} represented by $\ln \gamma_{ss} = \{-9.361 + (3.22 \pm 1.34) \times (1000/T - 3.840)\}$ on H₂SO₄ at T = 240–295 K. The

product of the heterogeneous reaction was HCl and no effect on γ upon irradiation by simulated sunlight was found within a $\pm 20\%$ variation of γ .

- (b) Uptake experiment performed in a fast flow tube reactor using electron-impact MS sampling. The ice was condensed from the vapor phase onto the cold wall of the flow tube (1 g total). The value given in the Table is a lower limit.
- (c) Uptake experiment performed in a fast flow tube reactor using electron-impact MS sampling and ion counting at m/e 51. The cryogenic phase was deposited from H_2O vapor and $H_2O:HNO_3=3:1$ vapor mixtures to obtain thicknesses of 4–7 μm for ice and additional 2–3 μm thick films on top of already deposited ice layers. This limitation in terms of deposited material could

lead to an increase of γ by a factor of two at most. The ClO free radical was generated either from a microwave discharged mixture of $Cl_2 + O_2$ in He or from a discharged Cl_2 -He mixture in an excess of O_3 resulting in typical densities of $(2-3) \times 10^{11}$ molecule cm^{-3} . The kinetic results were independent of the ClO densities varied by a factor of ten. The error limit for γ on NAT is twice that for water-ice.

References

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Cl + Substrate (SiO_2 , H_2SO_4 - H_2O , Teflon)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	1.0×10^{-3}	acid-treated SiO_2	300	Martin, Judeikis, and Wun, 1980 ¹	(a)
	2.0×10^{-3}	base-treated SiO_2	300		
	1.0×10^{-4}	H_2SO_4 conc, 5.0×10^{-4} NH_4SO_4	300		
γ_{ss}	$(5.9_{-2.4}^{+3.1}) \times 10^{-4}$	70% H_2SO_4	220	Martin, Judeikis, and Wun, 1980 ¹	
γ_{ss}	$\leq 6.0 \times 10^{-6}$	PTFE-Teflon, for Cl, Cl^*	300	Müller-Markgraf and Rossi, 1990 ²	(b)

Comments

- (a) Measurement of the uptake kinetics in a fast flow tube with EPR detection of Cl. A 1% Cl_2 in He mixture at 1.5–2.0 Torr or pure Cl_2 at 0.25 Torr was discharged in a microwave cavity at 20 W in order to generate Cl. The quartz flow tube was coated with halocarbon wax and the discharge tube with solid B_2O_3 in order to minimize wall losses of Cl. The inside of the flow tube was coated with H_2SO_4 and the H_2O vapor pressure was held constant throughout the temperature range at 5×10^{-4} Torr leading to a changing composition of the H_2SO_4 - H_2O mixture as the temperature was changed (96% at 300 K, 71% at 221 K). Therefore no separation between the effects of changing composition of the cryogenic phase (considered negligible) and the temperature dependence of γ could be achieved. All kinetic results were obtained from the full numerical integration of the parabolic flow and the chemical mechanism including axial diffusion. It resulted in a slight negative temperature dependence of the uptake coefficient γ represented by $\ln \gamma_{ss} = \{-8.874 + (2.122 \pm 0.78) \times (1000/T - 3.867)\}$ on H_2SO_4 at $T=221-296$ K. The product of the heterogeneous reaction was HCl and no effect on γ upon irradiation by simulated sunlight was found within a $\pm 20\%$ variation of γ .

- (b) The uptake kinetics of both ground state $Cl(^2P_{3/2})$ and upper spin-state $Cl^*(^2P_{1/2})$ were studied in a low-pressure flow reactor (Knudsen cell) using Resonance-Enhanced Multiphoton Ionization ($[3 + 2]$ REMPI) detection at 404.02 and 405.3 nm for Cl and Cl^* detection, respectively. The Cl was added to the reactor through a pulsed valve-microwave discharge combination using Cl_2 -He gas mixtures (1:2) undergoing from 25 to 40% decomposition at 70 W absorbed power. The decomposition of the parent Cl_2 was monitored by electron-impact MS thus affording a quantitative calibration of the REMPI signal. Typically, 10^{15} molecules per pulse were obtained leading to densities of 5×10^{12} molecule cm^{-3} . Depending on the discharge conditions, comparable densities of Cl^* were generated showing identical (slow) uptake kinetics on laboratory Teflon surfaces. Thus the lifetime for both Cl and Cl^* at densities of 10^{12} molecule cm^{-3} is of the order of several seconds.

References

- ¹L. R. Martin, H. S. Judeikis, and M. Wun, *J. Geophys. Res.* **85**, 5511 (1980).
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Br + Substrate (Teflon)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$(5.6 \pm 1.5) \times 10^{-5}$	PTFE Teflon, for Br, Br*	300	Müller-Markgraf and Rossi, 1995 ¹	(a)

Comments

- (a) The uptake kinetics of both ground state Br ($^2P_{3/2}$) and upper spin-state Br* ($^2P_{1/2}$) has been studied in a low-pressure Knudsen cell using Resonance-Enhanced Multiphoton Ionization ([3+2] REMPI) detection at 461.9 and 459.1 nm, respectively. The Br was added to the reactor through a pulsed valve-microwave discharge combination using pure Br₂ undergoing 8% decomposition at 30 W absorbed power. The decomposition of the parent Br₂ was monitored at m/e 160 using electron-impact MS thus affording a quantitative cali-

bration of the REMPI signal. The detection limit for Br was estimated as $5 \times 10^{10} \text{ cm}^{-3}$ for a signal to noise ratio of 2:1. Depending on the discharge conditions, comparable densities of Br* were generated showing identical uptake kinetics on laboratory Teflon surfaces if a correction was made for the radiative lifetime of Br* (0.77 s).

References

- ¹ W. Müller-Markgraf and M. J. Rossi, *Int. J. Chem. Kinet.* **27**, 403 (1995).

SO₂ + Substrate (water droplets and jet)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(5.4 \pm 0.5) \times 10^{-2}$	water droplets, pH=11.5	295	Gardner <i>et al.</i> , 1987 ¹ , 1989 ²	(a)
γ	$(1.1 \pm 0.2) \times 10^{-1}$	water droplets	273	Worsnop <i>et al.</i> , 1989 ³	(b)
γ	8.0×10^{-3}	effective H ₂ O droplet, pH=1	283	Jayne <i>et al.</i> , 1990 ⁴	(c)
	1.1×10^{-1}	effective H ₂ O droplet, pH=6			
γ	$(6.0^{+1.4}_{-3}) \times 10^{-2}$	liquid jet	300	Welter, Schweighoefer, and Schurath, 1990 ⁵	(d)
γ	$(1.3 \pm 0.1) \times 10^{-1}$	water droplets	298	Ponche, George, and Mirabel, 1993 ⁶	(e)

Comments

- (a) Uptake experiment on a fast moving droplet train propagating in a flow tube coupled to tunable diode laser absorption of SO₂ in a multiple pass absorption cell (728 cm optical path). The measurement consisted of monitoring the gas density in the flow tube with the droplet train switched on and off. The droplet size varied from 80–180 μm and the residence time of the individual droplet ranged from 2.2 to 12.8 ms. The SO₂ density was $(1.5\text{--}15) \times 10^{12} \text{ molecule cm}^{-3}$ and the total pressure was 21 Torr (He + H₂O). A small admixture of CH₄ was used to control the degree of water saturation (100%) of the carrier gas in order to prevent evaporation/condensation of the water droplets. The listed value has been corrected for gas-phase diffusion of SO₂ towards the droplet surface. When mass transport limitations in the condensed phase due to liquid diffusion and boundary layer saturation (Henry's law) are taken into account, the observed value is consistent with a value of $\gamma=0.12$ for a 120 μm diameter droplet. This discrepancy is due to evaporation of initially adsorbed SO₂.
- (b) Uptake experiment on a fast moving neutral water droplet train propagating in a flow tube either in axial or transverse direction. The interaction time ranged from 2 to 12 ms (axial) or from 0.5 to 2 ms (trans-

verse), and the temperature was varied from 260 to 292 K at total pressures from 10 to 50 Torr (He + H₂O) for the axial configuration, and 2.3 to 10 Torr for the transverse geometry. A tunable diode laser was used to measure the absorption of SO₂ in a multiple pass absorption cell (728 cm optical path) which was appended to the droplet flow tube. Initial SO₂ densities were of the order of $10^{13} \text{ molecule cm}^{-3}$. The measurement consists of monitoring the gas density in the multiple path absorption cell with the droplet train switched on and off and calculating an observed value of γ . A slight negative temperature dependence for the SO₂ uptake was obtained with $E=(2 \pm 5) \text{ kJ mol}^{-1}$.

- (c) Uptake experiment on a fast moving droplet train propagating in a flow tube either in axial or transverse direction. The interaction time ranged from 2 to 12 ms (axial) or from 0.5 to 2 ms (transverse), and the temperature was varied from 275 to 285 K at total pressures from 5 to 10 Torr (He + H₂O). A tunable diode laser was used to measure the absorption of SO₂ in a multiple pass absorption cell (728 cm optical path) which was appended to the droplet flow tube. Initial densities of SO₂ in the range $10^{13}\text{--}10^{15} \text{ molecule cm}^{-3}$ were used. The measurement consists of monitoring the gas density in the multiple path absorption cell with the droplet train switched on and off. The pH in the

bulk droplets ranged from 0 to 12 and corrections for gas phase diffusion and additional acidification of the droplet owing to SO₂ adsorption were applied to the uptake kinetics. The results displayed in the Table were obtained at a minimal droplet gas interaction time and a minimal SO₂ density of 10¹³ molecule cm⁻³. Taking into account liquid diffusion of SO₂ and the kinetics of ionic dissociation of SO₂ in H₂O, a γ value of 0.11 is obtained at low (effective) pH. This value is observed at pH > 5 (effective pH within the diffusion depth) and is significantly smaller than 1, the assumed mass accommodation coefficient. The discrepancy is attributed to evaporation of initially adsorbed SO₂. The measured uptake kinetics are consistent only with a larger value of the rate constant for ionic solvation which is attributed to the formation of an incipient complex H⁺-HSO₃⁻ in the interface region.

- (d) Uptake experiment of SO₂ in an atmosphere of synthetic air with a liquid jet of pure water to which small amounts of H₂O₂ were added in order to afford rapid oxidation of SO₂ to sulfate. The uptake kinetics of typically 100 ppm SO₂ in synthetic air were measured by analyzing the sulfate concentration in the collected jet waters using ion chromatography. The jet was emerging out of a capillary of 100 μ m diameter and gas/jet contact times were between 0.03 to 1.0 ms. The uptake coefficient was interpreted as a mass accommodation coefficient after fitting of the concentration of sulfate in the collected sample with the jet length taking into account the diffusion coefficients for the gas and liquid phase as well as the Henry's law constants. The uptake was found to be dependent on SO₂ concentration owing to a change in surface pH. Addition of NH₃ to the SO₂-air mixture minimized the pH dependence. The true surface velocity of the liquid jet was taken from

analogous jets described in the literature and an extreme sensitivity of γ on the gas diffusion coefficient for SO₂ was noted.

- (e) Uptake experiment on a monodisperse (70–110 μ m diameter droplets) and fast moving (480–2000 cm s⁻¹) droplet train propagating within a low-pressure flow tube in the pressure range 35–70 Torr. The contact time of the flowing gas interacting with the droplet train over a length of 7.5 to 21.5 cm varied between 3.7 and 45 ms. The extent of the uptake was determined by chemical analysis (ion chromatography) of collected aqueous phase. A chemical scavenger H₂O₂ was added to the condensed phase in order to trap dissolved SO₂ by rapid chemical reaction to H₂SO₄. The observed uptake coefficient was strongly dependent on the pH of the droplet in the range 4–11 and on the interaction time. The average value of the uptake coefficient γ_{obs} is $(6.0 \pm 0.8) \times 10^{-2}$ at 38 Torr N₂, 298 K and pH 11, a value to which the others determined at lower pH converge. The value given in the Table has been corrected for gas-phase diffusion.

References

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H₂O₂ + Substrate (water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(3.2 \pm 0.2) \times 10^{-1}$	droplets	260	Worsnop <i>et al.</i> , 1989 ¹	(a)
	$(1.8 \pm 0.2) \times 10^{-1}$	droplets	273		
	$(8.0 \pm 0.2) \times 10^{-2}$	droplets	292		

Comments

- (a) Uptake experiment on a fast moving water (pH=7) droplet train propagating in a flow tube either in axial or transverse direction. The interaction time ranged from 2 to 12 ms (axial) or from 0.5 to 2 ms (transverse), and the temperature was varied from 260 to 292 K at total pressures from 10 to 50 Torr (He + H₂O) for the axial configuration, and 2.3 to 10 Torr for the transverse geometry. A tunable diode laser was used to measure the absorption of H₂O₂ in a multiple pass absorption cell (728 cm optical path) which was appended to the droplet flow tube. Initial H₂O₂ densities

were in the range $(1.5\text{--}15) \times 10^{12}$ molecule cm⁻³. The measurement consists of monitoring the gas density in the multiple path absorption cell with the droplet train switched on and off and calculating an observed value of γ . A negative temperature dependence for the H₂O₂ uptake was obtained with $E = -(26 \pm 7)$ kJ mol⁻¹.

References

- D. R. Worsnop, M. S. Zahniser, C. E. Kolb, J. A. Gardner, L. R. Watson, J. M. Van Doren, J. T. Jayne, and P. Davidovits, *J. Phys. Chem.* **93**, 1159 (1989).

CH₃COCH₃ + Substrate (water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(6.6 \pm 1.2) \times 10^{-1}$	droplets	263	Duan <i>et al.</i> , 1993 ¹	(a)
	$(1.3 \pm 0.2) \times 10^{-2}$	droplets	285		

Comments

- (a) Uptake experiment on a fast monodisperse droplet train moving on axis in a flow tube and sampled by a quadrupole MS. The droplet diameter ranged between 50 to 200 μm and the total pressure in the flow tube was between 6 and 20 Torr. The droplet-acetone interaction time was between 1.8 and 21 ms and the partial pressure of water in the flow tube was adjusted to result in droplets ranging from the supercooled state to liquid. The values listed in the Table were corrected both for gas-phase diffusion which corresponded to a 20% correction of γ_{obs} at most, and solubility saturation (Henry's law). After correction of those two processes the

experimental uptake coefficients were interpreted as mass accommodation coefficients α . The temperature dependence of α resulted in an enthalpy and entropy of solvation of 53.3 kJ mol⁻¹ and -224.3 J mol⁻¹ K⁻¹, respectively. A parametric representation of Henry's law constant for dissolution of acetone in pure water as a function of temperature was obtained ($H=30$ mol dm⁻³ atm⁻¹ at 273 K).

References

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H₂CO + Substrate (water droplets, H₂SO₄/H₂O solution)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$(2.0 \pm 0.3) \times 10^{-2}$	droplets	267	Jayne <i>et al.</i> , 1993 ¹	(a)
γ_{ss}	1×10^{-2}	67% H ₂ SO ₄ bulk	223	Tolbert <i>et al.</i> , 1993 ²	(b)
	8×10^{-2}	75% H ₂ SO ₄ bulk	223		

Comments

- (a) Uptake experiment on a fast monodisperse droplet train moving axially in a flow tube and sampled by a differentially pumped quadrupole MS. The droplet diameter ranged between 80 to 240 μm and the total pressure in the flow tube was between 6 and 20 Torr N₂ with the formaldehyde density being in the range 10¹³–10¹⁴ molecule cm⁻³. The droplet-formaldehyde interaction time was between 1.8 and 21 ms. The partial pressure of water vapor in the flow tube was adjusted to result in droplets ranging from the supercooled state at 260 K to near ambient temperature at 290 K. The observed uptake coefficient was time independent but depended strongly on pH at the high end of the scale reflecting the pH dependence of the formation of the gem-diol in a base-catalyzed reaction. The dependence of γ_{obs} on OH⁻ activity resulted in a rate coefficient of $(4.0 \pm 0.2) \times 10^7$ cm³ mol⁻¹ s⁻¹ at 267 K for the reaction H₂CO + H₂O → H₂C(OH)₂ and the dependence of γ_{obs} on sulfite activity at pH=10 obtained a rate coefficient of $(2.2 \pm 0.2) \times 10^7$ cm³ mol⁻¹ s⁻¹ at 267 K for the addition of SO₃²⁻ to H₂CO resulting in hydroxymethanesulfonate [CH₂(O⁻)SO₃⁻].
- (b) Uptake experiment of CH₂O on quiescent and stirred sulfuric acid solutions in a Knudsen cell flow reactor which is monitored by modulated molecular beam MS.

The decrease of the CH₂O steady-state vapor pressure upon exposure to the low-temperature sulfuric acid solution whose concentration was determined by titration was monitored at m/e 29 as a function of exposure time. The concentration of CH₂O ranged from 2 × 10¹⁰ to 2 × 10¹¹ molecule cm⁻³ and no new gas phase products were detected during the uptake. By analogy to known condensed phase kinetics CH₂O is both solvated to methyleneglycol as well as protonated. The uptake showed a negative temperature dependence over the range 205–234 K and a pronounced concentration dependence of increasing γ with increasing sulfuric acid concentration, starting from a concentration where formaldehyde protonation is thought to be the dominant solvation mechanism. The uptake seems to be irreversible in 10–20 ml sulfuric acid solutions.

References

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² M. A. Tolbert, J. Pfaff, I. Jayaweera, and M. J. Prather, *J. Geophys. Res.* **98**, 2957 (1993).

CH₃CHO + Substrate (water droplets)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ	$\geq 3.0 \times 10^{-2}$	droplets	267	Jayne <i>et al.</i> , 1993 ¹	(a)

Comments

- (a) Uptake experiment on a fast monodisperse droplet train moving axially in a flow tube and sampled by a differentially pumped quadrupole MS. The droplet diameter ranged between 80 and 240 μm and the total pressure in the flow tube was between 6 and 20 Torr N₂ with the acetaldehyde density being approximately 10^{13} molecule cm^{-3} . The droplet-acetaldehyde interaction time was between 1.8 and 21 ms. The partial pressure of water vapor in the flow tube was adjusted to result in droplets ranging from the supercooled state at 260 K to near ambient temperature at 290 K. The measured uptake coefficient γ_{obs} was time dependent both at pH = 6.1 and 14 at 267 K. The uptake kinetics were found

to be significantly faster than predicted from known bulk thermodynamic parameters, especially at short reaction times (2 ms). A plausible explanation would be the formation of enolate ion chemisorbed at the interface. The introduction of an additional fitting parameter into the model has the effect that the accommodation coefficient becomes insensitive to the experimental data, so that only a lower limit is presented (see Table).

References

- ¹J. T. Jayne, S. X. Duan, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *J. Phys. Chem.* **96**, 5452 (1992).

CHBr₃ + Substrate (water ice, H₂SO₄)

Uptake Coeff.	Value	Condensed Phase	Temp./K	Reference	Comments
γ_{ss}	$\leq 6.0 \times 10^{-5}$	H ₂ O ice film	200	Hanson and Ravishankara, 1993 ¹	(a)
γ_0	3.0×10^{-3}	58% H ₂ SO ₄ , liquid	200		

Comments

- (a) Uptake experiment in a wall coated flow tube coupled to a chemical ionization MS as a probe. On ice the reaction was found to be immeasurably slow, and thus the uptake coefficient is given as an upper limit. On 58% H₂SO₄ a reversible physical adsorption was observed with an initial uptake coefficient $\gamma=0.003$ (see above) and 0.5 s exposure time. For longer exposure

times (~ 20 s) γ decreases to 2×10^{-4} because of a probable acid-catalyzed hydrolysis reaction.

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Alcohols, Haloalcohols, HOC₂H₄OH + Substrate (H₂O droplets)

Uptake Coeff.	Value	Condensed Phase Chemical Species	Temp./K	Reference	Comments
γ	$(5.6 \pm 1.0) \times 10^{-2}$	methanol	273	Jayne <i>et al.</i> , 1991 ¹	(a)
	$(4.8 \pm 1.0) \times 10^{-2}$	ethanol	273		
	$(2.6 \pm 1.0) \times 10^{-2}$	1-propanol	273		
	$(3.2 \pm 1.0) \times 10^{-2}$	2-propanol	273		
	$(5.2 \pm 1.0) \times 10^{-2}$	2-methyl-2-propanol	273		
	$(5.7 \pm 1.0) \times 10^{-2}$	2-chloroethanol	273		
	$(6.9 \pm 1.0) \times 10^{-2}$	2-bromoethanol	273		
	$(9.9 \pm 1.0) \times 10^{-2}$	2-iodoethanol	273		
	$(7.1 \pm 1.0) \times 10^{-2}$	ethylene glycol	273		

Comments

- (a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He with densities of the title compounds of the order of 5×10^{13} molecule cm^{-3} , the droplet diameter was 110–230 μm and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O corresponding to a range of 260 (supercooled state) to 291 K. The uptake coefficients were corrected for gas phase diffusion using calculated or scaled diffusion coefficients in He and H_2O vapor. An additional correction owing to limited solubility was performed for methanol, ethanol, 1- and 2-propanol and 2-methyl-2-propanol because these substances

showed a time-dependent uptake coefficient. The remaining uptake coefficients were found to be time-independent. From the temperature dependence of the corrected uptake coefficient which is interpreted as mass accommodation coefficient, pairs of the thermodynamic parameters for solvation, ΔH_{obs}^0 and ΔS_{obs} are obtained. The pairs address the energy barrier for the transition state from gas to solution in terms of the Gibbs free energy for the transition. ΔH_{obs}^0 and ΔS_{obs} seem to be correlated and are in the range of -22.2 to -46.0 kJ mol^{-1} and -102.5 to -193.3 $\text{J mol}^{-1}\text{K}^{-1}$, respectively.

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HCOOH, CH_3COOH + Substrate (H_2O droplets)

Uptake Coeff.	Value	Condensed Phase Chemical Species	Temp./K	Reference	Comments
γ	$(4.7 \pm 1.0) \times 10^{-2}$	HCOOH	273	Jayne <i>et al.</i> , 1991 ¹	(a)
	$(6.7 \pm 1.0) \times 10^{-2}$	CH_3COOH	273		
γ	$(8.9 \pm 1.0) \times 10^{-2}$	CH_3COOH	273	Hu <i>et al.</i> , 1993 ²	(b)

Comments

- (a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He with densities of the title compounds on the order of 5×10^{13} molecule cm^{-3} , the droplet diameter was 110–230 μm and the contact times were in the range 1.8–21 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H_2O corresponding to a range of 260 (supercooled state) to 291 K. The uptake coefficients were corrected for gas phase diffusion using calculated or scaled diffusion coefficients in He and H_2O vapor. The uptake coefficients were found to be time-independent and thus not limited by solubility. From the temperature dependence of the corrected uptake coefficient which is interpreted as mass accommodation coefficient, pairs of the thermodynamic parameters for solvation, ΔH_{obs}^0 and ΔS_{obs} are obtained. The pairs address the energy barrier for the transition state from gas

to solution in terms of the Gibbs free energy of the transition. ΔH_{obs}^0 and ΔS_{obs} were measured as -33.1 and -33.9 kJ mol^{-1} and -146.0 and -146.0 $\text{J mol}^{-1}\text{K}^{-1}$ for formic and acetic acid, respectively.

- (b) This is a redetermination of the temperature-dependent uptake coefficient using the identical experimental technique described in comment (a). The diffusion coefficient of CH_3COOH in Ar was determined by measuring the uptake coefficient over a range of pressures (3–23 Torr). The diffusion coefficient for both CH_3COOH and H_2O in He were calculated using scaling laws based on experimental values for Ar and a data base of more than 20 compounds. ΔH_{obs}^0 and ΔS_{obs} were measured to be $-(35.1 \pm 3.3)$ kJ mol^{-1} and $-(148.1 \pm 12.1)$ $\text{J mol}^{-1}\text{K}^{-1}$, respectively.

References

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²J. H. Hu, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, *J. Phys. Chem.* **97**, 11037 (1993).

Haloacetic acids + Substrate (H₂O droplets)

Uptake Coeff.	Value	Condensed Phase Chemical Species	Temp./K	Reference	Comments
γ	$(1.32 \pm 0.20) \times 10^{-1}$	CCl ₃ COOH	273	Hu <i>et al.</i> , 1993 ¹	(a)
	$(1.35 \pm 0.20) \times 10^{-1}$	CCl ₂ HCOOH	273		
	$(1.39 \pm 0.20) \times 10^{-1}$	CClH ₂ COOH	273		
	$(1.54 \pm 0.20) \times 10^{-1}$	CF ₂ ClCOOH	273		
	$(1.39 \pm 0.20) \times 10^{-1}$	CF ₃ COOH	273		

Comments

- (a) Uptake experiment on fast monodisperse droplet train moving coaxially down a low-pressure flow tube. The extent of the uptake was monitored by a differentially pumped MS with phase sensitive detection. The total pressure was 6–20 Torr He with densities of the title compounds of the order of 5×10^{13} molecule cm⁻³, the droplet diameter was 120–250 μ m, and the contact times were in the range 1.8–15 ms. The temperature of the droplets was controlled by adjusting the partial pressure of H₂O corresponding to a range of 260 (supercooled state) to 288 K. The uptake coefficients were corrected for gas phase diffusion using scaled diffusion coefficients for the haloacetic acids in He and H₂O vapor using measured diffusion coefficients in Ar. The uptake coefficients were found to be time-independent

and thus not limited by solubility. From the temperature dependence of the corrected uptake coefficient which is interpreted as mass accommodation coefficient, pairs of the thermodynamic parameters for solvation, ΔH_{obs}^0 and ΔS_{obs} were obtained. The pairs address the energy barrier for the transition state from gas to solution in terms of the Gibbs free energy of the transition. ΔH_{obs}^0 and ΔS_{obs} were measured to be in the range from -18.8 to -41.4 kJ mol⁻¹ and from -84.1 to -167.3 J mol⁻¹ K⁻¹.

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6. Appendix 1

Enthalpy Data*—Continued

Enthalpy Data*			
Species	$\Delta_f H_{298}^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ} \cdot \text{mol}^{-1}$	Reference
H	217.998		20
H ₂	0	0	20
O	249.18	246.8	20
O(¹ D)	438.9	436.6	25
O ₂	0	0	20
O ₂ (¹ Δ)	94.3	94.3	25
O ₂ (¹ Σ)	156.9	156.9	25
O ₃	142.7	145.4	57
HO	39.3	39.0	30
HO ₂	14.6		30
H ₂ O	-241.826		20
H ₂ O ₂	-136.32	-130.04	57
N	472.68		20
N ₂	0	0	20
NH	352		49
NH ₂	185.4	188.4	30
NH ₃	-45.94		20
NO	90.25	89.75	57
NO ₂	33.2	36	57
NO ₃	73.7		21
N ₂ O	82.05	85.50	57
N ₂ O ₄	9.1	18.7	15
N ₂ O ₅	11.3		15,21
HNO	99.6	102.5	15
HNO ₂	-79.5	-74	57
HNO ₃	-135.06	-125.27	57
HO ₂ NO ₂	-57		47
CH	596.35		30
CH ₂ (³ B ₁)	392.5		30
CH ₂ (¹ A ₁)	430.1		30
CH ₃	146.0		30
CH ₄	-74.81	-66.82	57
CN	435		15,30
HCN	135		15
HCO	41.8		17
CH ₂ O	-108.6	-104.7	25
CH ₃ O	17.6		30
CH ₂ OH	-9		24
CH ₃ OH	-201.6		19
CO	-110.53		20
NCO	159		15
COOH	-223		30
HCOOH	-378.8	-371.6	19
CH ₃ O ₂	10.4		36
CH ₃ OOH	-131		15
HOCH ₂ O ₂	-162.1		36
CH ₃ ONO	-65.3		8
CH ₃ ONO ₂	-119.7		8
CH ₃ O ₂ NO ₂	-44		47
CO ₂	-393.51		20
C ₂ H	565		30
C ₂ H ₂	228.0		19
C ₂ H ₃	279.9		52
C ₂ H ₄	52.2		19
C ₂ H ₅	121.5		30
C ₂ H ₆	-84.0		19
CH ₂ CN	244.8		30
CH ₃ CN	64.3		54
CH ₂ CO	-47.7		45
CH ₃ CO	-24.3		30
CH ₂ CHO	12.6		30

Species	$\Delta_f H_{298}^\circ / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_0^\circ / \text{kJ} \cdot \text{mol}^{-1}$	Reference
CH=CHOH	115		53
CH ₃ CHO	-165.8		19,54
C ₂ H ₅ O	-17.2		30
C ₂ H ₄ OH	-34		8
CH ₃ CHOH	-63.6		30
C ₂ H ₅ OH	-234.8		19,54
(CHO) ₂	-211.9		19,54
CH ₃ CO ₂	-207.5		30
CH ₃ CO ₂ H	-432.04		19,54
C ₂ H ₅ O ₂	-28.7		36
CH ₃ OOCH ₃	-125.7		19,54
CH ₃ C(O)O ₂	-172		36
C ₂ H ₅ ONO	-103.8		19,54
C ₂ H ₅ ONO ₂	-154.0		19,54
C ₂ H ₅ O ₂ NO ₂	-63.2		23
CH ₂ =CHCH ₂	163.6		30
C ₃ H ₆	20.2		19,54
<i>n</i> -C ₃ H ₇	97.5		30
<i>i</i> -C ₃ H ₇	90.0		30
C ₃ H ₈	-104.5		19,54
CH ₃ COCH ₂	-23.9		30
C ₂ H ₅ CHO	-187.4		19,54
CH ₃ COCH ₃	-217.2		19,54
C ₃ H ₆ OH	-74		8
<i>n</i> -C ₃ H ₇ O	-41.4		30
<i>i</i> -C ₃ H ₇ O	-52.3		30
<i>i</i> -C ₃ H ₇ OH	-272.5		19,54
CH ₃ COCHO	-271.1		19,54
C ₃ H ₅ O ₂	87.9		36
<i>i</i> -C ₃ H ₇ O ₂	-68.9		36
<i>n</i> -C ₃ H ₇ ONO ₂	-174.1		19,54
<i>i</i> -C ₃ H ₇ ONO ₂	-190.8		19,54
CH ₃ C(O)O ₂ NO ₂	-258		12
S	277.17		20
HS	143.0		44
H ₂ S	-20.6		20
HSO	-4		37
SO	5.0	5.0	15
HSO ₂	-222		11
SO ₂	-296.81		20
HOSO ₂	-385		38
SO ₃	-395.7	-390	57
HSNO	94		10
CH ₃ S	124.6		44
CH ₃ SH	-22.9		48
CH ₃ SCH ₂	136.8		28
CH ₃ SCH ₃	-37.24		57
CS	272	268	7
CH ₃ SO	-67		14
OCS	-142	-142	57
S ₂	128.60		20
CH ₃ SS	68		7
CH ₃ SSCH ₃	-24.3		7
CS ₂	117.2	116.6	57
HOCS ₂	110.5		41
F	79.38		20
HF	-273.30		20
HOF	-98	-95	15
FO	109	109	8
FO ₂	26.1		46
FONO	67		5
FNO ₂	-108.8		47
FONO ₂	10	18	15
CH ₂ F	-31.8		30

Enthalpy Data*—Continued

Species	$\Delta_f H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_0^\circ/\text{kJ}\cdot\text{mol}^{-1}$	Reference
CH ₃ F	-232.6		32
CH ₃ CH ₂ F	-263		35
HCOF		-392.5	58
FCO	-171.5	-172.1	15
F ₂	0	0	20
CHF ₂	-238.9		30
CH ₂ F ₂	-453		35
CH ₃ CHF ₂	-501		35
CF ₂	-194.1		30
COF ₂	-634.7	-631.6	57
CHF ₃	-697.6		35
CF ₃	-467.4		30
CH ₂ CF ₃	-517.1		30
CH ₃ CF ₃	-748.7		31
CH ₂ FCHF ₂	-691		31
CF ₃ O	-655.6		6
CF ₃ OH	-893.3		6
CF ₃ OF	-785		35
CF ₃ O ₂	-614.0		36
CF ₃ CO ₂ H	-1031		48
CF ₃ O ₂ NO ₂	-686		23
CF ₄	-933	-927	51
Cl	121.30		20
HCl	-92.31		20
HOCl	-78	-75	25,39
ClO	101.6		1
ClOO	97.5		4
OCIO	95.6		26,42
<i>sym</i> -ClO ₃	232.6		18
ClNO	51.7	53.6	15
ClNO ₂	12.5	18.0	57
ClONO	56		47
ClONO ₂	22.9		3
CH ₂ Cl	121.8		55
CH ₂ ClO ₂	9.2		36
CH ₃ Cl	-82.0	-74.0	51
CHF ₂ Cl	-483.7		16
CH ₃ CHFCI	-313.4		31
CH ₃ CF ₂ Cl	-536.2		31
CICO	-21.8		43
COFCI	-427	-423	15
CFCI	-20		35
CF ₂ Cl	-279.1		30
CF ₂ ClO ₂	-406.5		36
CF ₂ ClO ₂ NO ₂	-480		33
CF ₃ Cl	-707.9	-702.9	16
Cl ₂	0	0	20
Cl ₂ O	81.4	83.2	2
Cl ₂ O ₂	127.6		42
Cl ₂ O ₃	153		13
CCl ₂	239		30
CHCl ₂	98.3		55
CHCl ₂ O ₂	1.6		36
CH ₂ Cl ₂	-95.4	-88.5	51
CHFCI ₂	-284.9		16
COCl ₂	-220.1	-218.4	25
CFCl ₂	-89.1		55
CFCl ₂ O ₂	-213.7		36
CFCl ₂ O ₂ NO ₂	-286		33
CF ₂ Cl ₂	-493.3	-489.1	16
CH ₂ ClCF ₂ Cl	-543		35
CF ₃ CHCl ₂	-740		35
CF ₂ ClCHFCl	-724		35

Enthalpy Data*—Continued

Species	$\Delta_f H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_0^\circ/\text{kJ}\cdot\text{mol}^{-1}$	Reference
CF ₂ ClCF ₂ Cl	-925.5		31
CCl ₃	71.1	69.9	27
CCl ₃ O ₂	-11.3		36
CCl ₃ O ₂ NO ₂	-83.7		33
CHCl ₃	-103.3		15
C ₂ HCl ₃	-7.8	-4.3	57
CH ₃ CCl ₃	-144.6		31
CFCl ₃	-284.9	-281.1	16
CF ₂ ClCFCl ₂	-726.8		31
CCl ₄	-95.8	-93.6	51
C ₂ Cl ₄	-12.4	-11.9	15
Br	111.87		20
HBr	-36.29		20
HOBr	-50		40
BrO	125	133	57
BrNO	82.2	91.5	57
BrONO	103		22
BrNO ₂	63		34
BrONO ₂	47		47
CH ₂ Br	169.0		55
CH ₃ Br	-38.1		9
CF ₃ Br	-650		35
CF ₂ ClBr	-438		35
BrCl	14.6	22.1	15
Br ₂ (g)	30.91		20
CHBr ₂	188		55
CF ₂ Br ₂	-379		35
CF ₂ BrCF ₂ Br	-789.9		31
CHBr ₃	23.8		9
I	106.76		20
HI	26.50		20
HOI	-90		29
IO	107		50
INO	121.3	124.3	56
INO ₂	60.2	66.5	56
CH ₂ I	230.1		30
CH ₃ I	14.2		19
CF ₃ I	-589		15
I ₂ (g)	62.42		20

*Most of the thermochemical data have been taken from evaluations or reviews. In some cases, we have selected more recent experimental data, which appear to be reliable.

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