Further Studies of the Temperature Dependence of the Rate Coefficients for the Reactions of OH with a Series of Ethers under Simulated Atmospheric Conditions

MARCO SEMADENI, DAVID W. STOCKER, and J. ALISTAIR KERR*
EAWAG/ETH Zürich, 8600 Dübendorf, Switzerland

(Received: 16 April 1992; in final form: 20 June 1992)

Abstract. The following temperature-dependent rate coefficients ($k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of the reactions of hydroxyl radicals with aliphatic ethers have been determined over the temperature range 247–373 K by a competitive flow technique: diethyl ether, $k_{\text{OH}} = 5.2 \times 10^{-12} \exp[(262 \pm 150)/T]$; methyl *n*-butyl ether, $k_{\text{OH}} = 5.4 \times 10^{-12} \exp[(309 \pm 150)/T]$; ethyl *n*-butyl ether, $k_{\text{OH}} = 7.3 \times 10^{-12} \exp[(335 \pm 150)/T]$; di-*n*-butyl ether, $k_{\text{OH}} = 5.5 \times 10^{-12} \exp[(502 \pm 150)/T]$ and di-*n*-pentyl ether, $k_{\text{OH}} = 8.5 \times 10^{-12} \exp[(417 \pm 150)/T]$. The data have been measured relative to the rate coefficient $k(\text{OH} + 2,3\text{-dimethylbutane}) = 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature.

Previous discrepancies in the room-temperature rate coefficients for the OH reactions with ethyl *n*-butyl ether and di-*n*-butyl ether, obtained in the flow and static experiments of Bennett and Kerr (*J. Atmos. Chem.* **8**, 87–94, 1989; **10**, 29–38, 1990) compared with those of Wallington *et al.* (*Int. J. Chem. Kinet.* **20**, 541–547, 1988; **21**, 993–1001, 1989) and of Nelson *et al.* (*Int. J. Chem. Kinet.* **22**, 1111–1126, 1990) have been resolved. The results are considered in relation to the available literature data and evaluated rate expressions are deduced where possible. The data are also discussed in terms of structure-activity relationships.

Key words. Atmospheric photo-oxidation, hydroxyl radicals, diethyl ether, methyl *n*-butyl ether, ethyl *n*-butyl ether, di-*n*-butyl ether, di-*n*-pentyl ether, relative rate coefficients, smog chamber kinetic studies.

Introduction

This study is part of a programme of research aimed at investigating the role of volatile organic compounds in the generation of photochemical oxidant in the polluted troposphere. Ethers are released to the atmosphere through evaporation during their use as solvents and as fuel additives. The major sink for ethers in the troposphere is by reaction with hydroxyl radicals and the present paper is intended to serve as a prelude to detailed studies of the photo-oxidation of ethers under laboratory conditions simulating the troposphere, which are in progress.

Previous studies of the room-temperature rate coefficients of hydroxyl radical reactions with some ethers, for example diethyl ether and methyl *t*-butyl ether, are in good agreement (Bennett and Kerr, 1989, 1990; Nelson *et al.*, 1990; Tully and

Droege, 1987; Wallington *et al.*, 1988a, 1988b, 1989), but for others, for example ethyl *n*-butyl ether and di-*n*-butyl ether, the results of Bennett and Kerr (1989, 1990) are up to 40% lower. The present work was initiated to investigate these discrepancies with the use of upgraded instrumentation and improved analytical techniques. At the same time we have expanded the data base of the temperature dependences of OH + ether reactions.

To investigate the source of possible systematic errors associated with the competitive technique and its application in our laboratories, we have performed cross-checks by using alternative reference substrates and radical sources. The major aim of these studies is to confirm that our system is capable of providing reliable and accurate determinations of the temperature-dependent rate coefficients for the reactions of hydroxyl radicals with organic substrates using the competitive technique.

2. Experimental

The experimental system has been previously used to investigate the kinetics of the reactions of hydroxyl radicals with alkanes (Harris and Kerr, 1988) and with ethers (Bennett and Kerr, 1990). The apparatus and experimental technique are described fully in these previous publications, only the modifications employed in the present experiments will be described here.

Synthetic air mixtures containing ppm concentrations of NO with either ethyl nitrite or methyl nitrite as the OH radical source, and an ether (5–14 ppm) as the test substrate together with either another ether or 2,3-dimethylbutane (5–14 ppm) as the reference substrate were prepared in a 200 dm³ Tedlar® reservoir and equilibrated for at least 2 hours in the dark. In some experiments the oxygen content of the gas mixtures was increased from 20 to 40%. Samples from the reservoir were drawn through the reactor at flow rates of 20 to 100 cm³ min⁻¹, and injected into a gas chromatograph (Carlo Erba Instruments HRGC 5300) via a 0.5 cm³ stainless steel gas sampling valve. The pressure within the reactor varied between 718 to 729 Torr, with a deviation of ± 2.9 Torr for a given series of experiments.

The walls of the reactor cell were coated with a Halocarbon wax (Chemie-mineralien). The reactor cell was illuminated by a solar simulator (Polytec XS 1000) consisting of a 1 kW Xe arc lamp, the spectral range was selected using an AM1 filter and the intensity of illumination was varied by inserting combinations of neutral density filters (Balzers). The temperature of the reactor was maintained at a preset temperature within the range -26° to +100 °C with an accuracy of ± 0.5 °C by circulating a propylene glycol/water mixture (1.1 : 1) through the outer jacket of the reactor from a thermocirculator (Lauda RKS 20).

The gas chromatograph was equipped with a capillary column and flame ionisation detector. Samples were injected onto the separating column via a split-splitless injector. The gas chromatographic conditions used for each set of experiments are listed in Table I. In all experiments H₂ was used as the carrier gas. The signals from the detector were collected and processed using a personal computer and a

Table I. Summary of the chromatographic conditions employed

Ether	Reference substrate	Gas chromatographic conditions	
		Column	Temperature/°C
diethyl ether ^{a, b}	2,3-dimethylbutane	16 m 4% PS 255 ^d	35
methyl <i>n</i> -butyl ether ^a	2,3-dimethylbutane	30 m DB-5 ^c	35–100 ^e
ethyl <i>n</i> -butyl ether ^{a, b}	2,3-dimethylbutane	30 m DB-5 ^c	35
di- <i>n</i> -butyl ether ^b	2,3-dimethylbutane	16 m 4% PS 255 ^d	35–110 ^e
di- <i>n</i> -butyl ether ^a	diethyl ether	30 m DB-5 ^c	35–100 ^e
di- <i>n</i> -butyl ether ^b	diethyl ether	16 m 4% PS 255 ^d	35–120 ^e
di- <i>n</i> -pentyl ether ^b	di- <i>n</i> -butyl ether	16 m 4% PS 255 ^d	155

^a Photolysis of methyl nitrite as radical source.^b Photolysis of ethyl nitrite as radical source.^c JWS Scientific. Carrier flow 3 cm³ min⁻¹.^d Grob and Grob (1983). Carrier flow 9 cm³ min⁻¹.^e Heating rate: 48 °C min⁻¹.

chromatographic software package (Maxima 820 Carlo Erba Instruments). Three repeat measurements were carried out for each exposure at each temperature.

The following chemicals, with stated purities of $\geq 99\%$, were used without further purification, other than bulb-to-bulb distillation: diethyl ether (Aldrich), methyl *n*-butyl ether (Fluka), ethyl *n*-butyl ether (Aldrich), di-*n*-butyl ether (Fluka), di-*n*-pentyl ether (Fluka) and 2,3-dimethylbutane (Fluka). Methyl nitrite and ethyl nitrite were prepared from the parent alcohols according to the method of Sandells *et al.* (1974), transferred to a high vacuum line and purified by bulb-to-bulb distillation.

3. Results

The formation of hydroxyl radicals by the photolysis of alkyl nitrites in air containing NO is described by the following reaction scheme (Atkinson, 1986):

If the reactant mixture contains a pair of organic substrates, these species are consumed largely by hydroxyl radical attack:

where Ref is the reference substrate, either 2,3-dimethylbutane or an ether, and ROR is the test ether under investigation. Provided that reactions (1) and (2) are the only significant removal processes for the substrates, then integration and combination of the rate expressions for reactions (1) and (2) leads to:

Table I. Summary of the chromatographic conditions employed

Ether	Reference substrate	Gas chromatographic conditions	
		Column	Temperature/°C
diethyl ether ^{a, b}	2,3-dimethylbutane	16 m 4% PS 255 ^d	35
methyl <i>n</i> -butyl ether ^a	2,3-dimethylbutane	30 m DB-5 ^c	35–100 ^e
ethyl <i>n</i> -butyl ether ^{a, b}	2,3-dimethylbutane	30 m DB-5 ^c	35
di- <i>n</i> -butyl ether ^b	2,3-dimethylbutane	16 m 4% PS 255 ^d	35–110 ^e
di- <i>n</i> -butyl ether ^a	diethyl ether	30 m DB-5 ^c	35–100 ^e
di- <i>n</i> -butyl ether ^b	diethyl ether	16 m 4% PS 255 ^d	35–120 ^e
di- <i>n</i> -pentyl ether ^b	di- <i>n</i> -butyl ether	16 m 4% PS 255 ^d	155

^a Photolysis of methyl nitrite as radical source.^b Photolysis of ethyl nitrite as radical source.^c JWS Scientific. Carrier flow 3 cm³ min⁻¹.^d Grob and Grob (1983). Carrier flow 9 cm³ min⁻¹.^e Heating rate: 48 °C min⁻¹.

chromatographic software package (Maxima 820 Carlo Erba Instruments). Three repeat measurements were carried out for each exposure at each temperature.

The following chemicals, with stated purities of $\geq 99\%$, were used without further purification, other than bulb-to-bulb distillation: diethyl ether (Aldrich), methyl *n*-butyl ether (Fluka), ethyl *n*-butyl ether (Aldrich), di-*n*-butyl ether (Fluka), di-*n*-pentyl ether (Fluka) and 2,3-dimethylbutane (Fluka). Methyl nitrite and ethyl nitrite were prepared from the parent alcohols according to the method of Sandells *et al.* (1974), transferred to a high vacuum line and purified by bulb-to-bulb distillation.

3. Results

The formation of hydroxyl radicals by the photolysis of alkyl nitrites in air containing NO is described by the following reaction scheme (Atkinson, 1986):

If the reactant mixture contains a pair of organic substrates, these species are consumed largely by hydroxyl radical attack:

where Ref is the reference substrate, either 2,3-dimethylbutane or an ether, and ROR is the test ether under investigation. Provided that reactions (1) and (2) are the only significant removal processes for the substrates, then integration and combination of the rate expressions for reactions (1) and (2) leads to:

Fig. 2. Plot of $\ln([\text{ether}]_0/[\text{ether}]_i)$ versus $\ln([\text{reference}]_0/[\text{reference}]_i)$ for the photolysis of $\text{CH}_3\text{ONO}/\text{air}$ mixtures containing methyl *n*-butyl ether (MnBE) and 2,3-dimethylbutane (DMB) at: 250 K (○); 298 K (◆); and 353 K (*).

$$\ln \frac{k_2}{k_1} = \ln \frac{A_2}{A_1} + \frac{(E_1 - E_2)}{RT} \tag{ii}$$

Typical relative Arrhenius plots for some of the reactant mixtures are shown in Figure 3.

The rate coefficient ratios, k_2/k_1 derived from the application of Equation (i) to the reactant mixtures over the temperature range 247 to 373 K are summarised in Table II, and the corresponding relative Arrhenius parameters calculated by least-mean-squares analysis are summarised in Table III.

4. Discussion

The plots of the data shown in Figures 1 and 2 according to Equation (i) are typical of those obtained from these experiments. All data points fall on straight lines which pass through the origin, thus validating the kinetic treatment, i.e. reactions (1) and (2) adequately account for the loss of reactants under reactor illumination.

The experimental results have been placed on an absolute basis using two approaches. First, those rate coefficients measured relative to 2,3-dimethylbutane were put on an absolute basis using the value $k(\text{OH} + 2,3\text{-dimethylbutane}) =$

Fig. 3. Relative Arrhenius plot for the reactions of hydroxyl radicals with: (a) di-*n*-butyl ether (k_1) and di-*n*-pentyl ether (k_2), hydroxyl radicals were generated by the photolysis of ethyl nitrite (◆), and (b) diethyl ether (k_1) and di-*n*-butyl ether (k_2), hydroxyl radicals were generated by either the photolysis of methyl nitrite (O) or ethyl nitrite (●).

$6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the temperature range 247–498 K (Atkinson, 1989). The remaining relative rate coefficients were placed on an absolute basis using evaluated rate coefficients for the reactions of OH with diethyl ether and di-*n*-butyl ether.

Table III. Relative Arrhenius parameters for the pairs of reactants summarised in Table II

Reference substrate (k_1)	Test substrate (k_2)	$\frac{A_2^a}{A_1}$	$\frac{(E_1 - E_2)^a}{R} \text{ (K)}$
2,3-dimethylbutane ^{b,c}	diethyl ether	0.83 ± 0.17	262 ± 62
2,3-dimethylbutane ^b	methyl <i>n</i> -butyl ether	0.87 ± 0.24	309 ± 79
2,3-dimethylbutane ^{b,c}	ethyl <i>n</i> -butyl ether	1.18 ± 0.37	335 ± 86
2,3-dimethylbutane ^c	di- <i>n</i> -butyl ether	1.01 ± 0.25	478 ± 70
diethyl ether ^b	di- <i>n</i> -butyl ether	0.69 ± 0.23	360 ± 93
diethyl ether ^c	di- <i>n</i> -butyl ether	0.91 ± 0.21	298 ± 65
di- <i>n</i> -butyl ether ^c	di- <i>n</i> -pentyl ether	1.66 ± 0.18	-101 ± 32

^a Error limits are two standard deviations.

^b Photolysis methyl nitrite as radical source.

^c Photolysis ethyl nitrite as radical source.

Table II.

Temperature (K)	$k_{\text{DEE}}/k_{\text{DMB}}^{\text{c, d}}$	$k_{\text{MnBE}}/k_{\text{DMB}}^{\text{c}}$	$k_{\text{EnBE}}/k_{\text{DMB}}^{\text{c, d}}$	$k_{\text{DnBE}}/k_{\text{DMB}}^{\text{d}}$	$k_{\text{DnBE}}/k_{\text{DEE}}^{\text{c}}$	$k_{\text{DnBE}}/k_{\text{DEE}}^{\text{d}}$	$k_{\text{DnPE}}/k_{\text{DnBE}}^{\text{d}}$
247		3.02 ± 0.60					
248			4.29 ± 0.57		2.95 ± 0.26		
250	2.25 ± 0.28						
251			4.50 ± 1.64	6.99 ± 0.34		2.96 ± 0.24	
254					2.89 ± 0.15		
258				6.48 ± 0.10			
260					2.64 ± 0.09		
261			4.57 ± 0.69				
263	2.30 ± 0.22	2.75 ± 0.88				2.81 ± 0.35	1.13 ± 0.09
265				6.21 ± 0.65			
266					2.72 ± 0.28		
268						2.83 ± 0.24	
273	2.17 ± 0.32		4.09 ± 0.74	5.54 ± 0.42	2.70 ± 0.19	2.70 ± 0.17	
275					2.77 ± 0.24		1.17 ± 0.16
283	2.23 ± 0.06						
286					2.32 ± 0.32		
297					2.11 ± 0.08		
298	2.10 ± 0.18	2.59 ± 0.30	3.56 ± 0.27	5.04 ± 0.25		2.46 ± 0.07	18 ± 0.03
301					2.22 ± 0.09		
308	1.96 ± 0.12						
313		2.31 ± 0.20					1.18 ± 0.03
317					2.06 ± 0.19		
323	1.77 ± 0.20		3.19 ± 0.35	4.26 ± 0.07			
328					2.24 ± 0.05		
333							21 ± 0.01
338	80 ± 0.10						
343					2.01 ± 0.21		
353	1.81 ± 0.12	2.03 ± 0.14	3.12 ± 0.16	4.07 ± 0.21			
373	1.64 ± 0.17						28 ± 0.

^a Error limits are two standard deviations. ^b Key: DMB, 2,3-dimethylbutane; DEE, Diethyl ether; MnBE, methyl *n*-butyl ether; EnBE, ethyl *n*-butyl ether; DnBE, di-*n*-butyl ether; DnPE, di-*n*-pentyl ether. ^c Photolysis of methyl nitrite as radical source. ^d Photolysis of ethyl nitrite as radical source.

The evaluation of the temperature-dependent rate coefficient of the OH reaction with diethyl ether made by Bennett and Kerr (1990) was updated to include the results from the present study. The Arrhenius plot of all the available data for diethyl ether is shown in Figure 4. The level of agreement between the independent determinations of the temperature-dependent rate coefficients and the room-temperature rate coefficient for the reaction of hydroxyl radicals with diethyl ether is reasonably good, with the exception of the result of Lloyd *et al.* (1976). The results of the present study, as did those of Bennett and Kerr (1990), do not support the need for a three parameter fit as recommended by Atkinson (1989), hence the data have been fitted using a least-mean-squares analysis of the two-parameter Arrhenius equation, omitting the datum of Lloyd *et al.* (1976). The results and the data used in their derivation are listed in Table IV. For the final data presented in Table IV for each of the ethers studied, the error limits follow the procedure recommended by the NASA Panel for Data Evaluation (DeMore *et al.*, 1990). $f(298)$ is the estimated uncertainty factor in k at 298 K and $\Delta E/R$ the estimated uncertainty in E/R .

Fig. 4. Arrhenius plot of the rate coefficients for the reaction of the hydroxyl radicals with diethyl ether. ($\square$) Lloyd *et al.* (1976); ($\diamond$) Tully and Droegge (1987); ($\circ$) Wallington *et al.* (1988a); ($\blacktriangle$) Bennett and Kerr (1989); ($\blacktriangledown$) Bennett and Kerr (1990); ($\circ$) Nelson *et al.* (1990); ($\bullet$) This work. The line represents at least-mean-squares fit to the data, omitting the datum of Lloyd *et al.* (1976).

The uncertainty factor in k at other temperatures $f(T)$ can then be calculated from the expression

$$f(T) = f(298) \times \exp \left| \frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right|$$

where the exponent is an absolute value.

Relative rate coefficients for the hydroxyl radical reaction of di-*n*-butyl ether have been determined in three separate experiments; two employing different radical sources, namely methyl and ethyl nitrite photolysis, and a third a different reference substrate. The temperature-dependent rate coefficients obtained using the different radical sources are coincident as shown in Figure 3 and are statistically equivalent. The two sets of data from columns 6 and 7 of Table II have been combined and fitted to the Arrhenius equation using a least-mean-squares analysis, the fitted line is shown in Figure 3. The relative temperature-dependent rate coefficient obtained was placed on an absolute basis using the evaluated rate coefficient for the reaction of diethyl ether calculated above: $k(\text{OH} + \text{diethyl ether}) = 7.3 \times 10^{-12} \exp(158/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The result is shown in Table IV and is within the experimental error of that obtained from the experiment relative to 2,3-dimethylbutane. The absolute rate coefficient for the reaction of OH with di-*n*-butyl ether calculated using all the data from this study is $k = 5.5 \times 10^{-12} \exp[502 \pm 150]/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The data from the present study has been combined with the available literature data (except that of Bennett and Kerr (1989), see discussion below) and an evaluated rate coefficient determined, see Figure 5. This evaluated rate coefficient, $k = 5.2 \times 10^{-12} \exp(518/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was then used to place the relative Arrhenius parameters for the hydroxyl radical reaction of di-*n*-pentyl ether on an absolute basis.

The room-temperature rate coefficients for the reactions of methyl *n*-butyl ether and di-*n*-pentyl ether are in good agreement with previously reported values (Wallington *et al.*, 1988b, 1989; Nelson *et al.*, 1990), however, the room-temperature rate coefficients for the reactions of ethyl *n*-butyl ether and di-*n*-butyl ether are in better agreement with the results of Wallington *et al.* (1988b, 1989) and of Nelson *et al.* (1990) than with those of Bennett and Kerr (1989, 1990). In the case of ethyl *n*-butyl ether, we have also obtained different Arrhenius parameters to those of Bennett and Kerr (1990). The temperature dependencies of the rate coefficients for the reactions of methyl *n*-butyl ether, di-*n*-butyl ether and di-*n*-pentyl ether have not been determined previously.

The internal consistency of the results obtained by the use of different radical sources and by the use of different reference substrates is further indication that our experimental system should be free of error or bias. The present determinations of the absolute rate coefficients at room-temperature are in good agreement with those reported in the literature by Nelson *et al.* (1990), Tully and Droegge (1987) and Wallington *et al.* (1988a, 1988b, 1989). It is apparent that the values reported by Bennett and Kerr (1989, 1990) for ethyl *n*-butyl ether and di-*n*-butyl

Table IV. Absolute rate parameters for the reactions of hydroxyl radicals with aliphatic ethers

Temperature (K)	$10^{12} \times k_2^a$	$f(298)^b$	$10^{12} \times A_2^a$	$\left(\frac{E_2}{R} \pm \frac{\Delta E_2}{R} \right) \text{ (K)}$	Temperature range (K)	Technique ^c	Reference
Diethyl ether							
305	9.2					RR	Lloyd <i>et al.</i> (1976)
295	13.4		9.1 ± 0.4	-115 ± 14	295–442	LP-LIF	Tully and Droege (1987)
296	13.6		5.6 ± 1.77	-270 ± 100	240–440	FP-RF	Wallington <i>et al.</i> (1988a)
294	12.0					RR	Bennett and Kerr (1989)
298	13.3		$(k = (8.80) \times 10^{-18} T^2 e^{(844 \pm 60)/T})$		240–440	Evaluation	Atkinson (1989)
294	10.0		3.5 ± 0.6	-337 ± 48	242–325	RR	Bennett and Kerr (1990)
298	12.8					RR	Nelson <i>et al.</i> (1990)
298	11.3					PR-KS	Nelson <i>et al.</i> (1990)
298	13.0		5.2	-262 ± 150^d	250–373	RR	This work ^c
298	12.4	1.15	7.3	-158 ± 150^d	242–440	Evaluation	This work (see text)
Methyl <i>n</i> -butyl ether							
298	16.4					FP-RF	Wallington <i>et al.</i> (1988b)
295	12.9					RR	Wallington <i>et al.</i> (1989)
298	16.1	1.2	5.4	-309 ± 150^d	247–353	RR	This work ^c
298	15.0	1.2	5.3	-310 ± 150^d	247–353	Evaluation	This work (see text)
Ethyl <i>n</i> -butyl ether							
298	22.8					FP-RF	Wallington <i>et al.</i> (1988b)
294	13.4					RR	Bennett and Kerr (1989)
295	22.7					RR	Wallington <i>et al.</i> (1989)
294	14.8		8.7 ± 1.7	-156 ± 60	253–315	RR	Bennett and Kerr (1990)
298	18.7					PR-KS	Nelson <i>et al.</i> (1990)
298	22.1		7.3	-335 ± 150^d	248–353	RR	This work ^c
298	22.1	1.15	6.8	-353 ± 150^d	248–353	Evaluation	This work (see text)

Table IV (continued)

Temperature (K)	$10^{12} \times k_2^a$	$f(298)^b$	$10^{12} \times A_2^a$	$\left(\frac{E_2}{R} \pm \frac{\Delta E_2}{R}\right)$ (K)	Temperature range (K)	Technique ^c	Reference
Di-<i>n</i>-butyl ether							
296	27.8					FP-RF	Wallington <i>et al.</i> (1988a)
294	17.1					RR	Bennett and Kerr (1989)
295	27.4					RR	Wallington <i>et al.</i> (1989)
298	28.8					RR	Nelson <i>et al.</i> (1990)
298	27.2					PR-KS	Nelson <i>et al.</i> (1990)
298	26.2		6.3	-478 ± 150^d	250–353	RR	This work ^e
298	30.5		4.9	-528 ± 150^d	248–343	RR	This work ^f
298	29.6		5.2	-518 ± 150^d	248–353	Evaluation	This work (see text)
Di-<i>n</i>-pentyl ether							
296	34.7					FP-RF	Wallington <i>et al.</i> (1988a)
295	30.9					RR	Wallington <i>et al.</i> (1989)
298	34.0					RR	Nelson <i>et al.</i> (1990)
298	34.8		8.5	-417 ± 150^d	263–373	RR	This work ^g
298	34.1	1.1	8.8	-402 ± 150^d	263–373	Evaluation	This work (see text)

^a Units: $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^b $f(298)$ is the estimated uncertainty factor at 298 K (see text).^c Key: RR, relative rate; LP-LIF, laser photolysis-laser induced fluorescence; FP-RF, flash photolysis-resonance fluorescence; PR-KS, pulse radiolysis-kinetic spectroscopy.^d Errors in E/R are estimated overall error limits (see text).^e Measured relative to the value $k(\text{OH} + 2,3\text{-dimethylbutane}) = 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 246–498 K (Atkinson, 1989).^f Measured relative to the value $k(\text{OH} + \text{diethyl ether}) = 7.3 \times 10^{-12} \exp(158/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 242–440 K (evaluation, this work).^g Measured relative to the value $k(\text{OH} + \text{di-}n\text{-butyl ether}) = 5.2 \times 10^{-12} \exp(518/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 248–373 K (evaluation, this work).

Fig. 5. Arrhenius plot of the rate coefficients for the reaction of the hydroxyl radical with di-*n*-butyl ether. (▽) Wallington *et al.* (1988a); (◐) Bennett and Kerr (1989); (Δ) Wallington *et al.* (1989); (⊙) Nelson *et al.* (1990); (●) This work. The line represents a least-mean-squares fit to the data, omitting the datum of Bennett and Kerr (1989).

ether are about a factor of 1.6 lower than the results obtained from the present study and those of Wallington *et al.* (1988a, 1989) and Nelson (1990). In the system where we can directly compare the present data with that of Bennett and Kerr, i.e. 2,3-dimethylbutane/diethyl ether, our data yield the relative room-temperature (298 K) rate coefficient $k(\text{diethyl ether})/k(2,3\text{-dimethylbutane}) = 2.10 \pm 0.18$ as opposed to the value of $k(\text{diethyl ether})/k(2,3\text{-dimethylbutane}) = 1.70 \pm 0.16$ at 304 K obtained by Bennett and Kerr. The results reported by Bennett and Kerr are probably influenced by a systematic error which has been eliminated in these experiments by the use of improved instrumentation and procedures. A possible cause of the discrepancy in the work of Bennett and Kerr (1989, 1990) is the low extent of reaction and the errors associated with measuring the resulting small changes in concentration on illumination. In their experiments, the initial concentrations of substrate were depleted by only up to 15% (Bennett, 1989) whereas in the present study up to 90% of the substrates were reacted. At low temperatures, the conversion is even less and the error likely to be greater. Bennett and Kerr used diethyl ether as the reference substrate in their experiments whereas here we have mainly used 2,3-dimethylbutane. Under the present gas chromatographic analytical conditions, the latter compound yielded no products which co-eluted with the substrates, leading to lower apparent conversions in one or other of the substrates. A product which co-eluted with the test ether could explain the lower results of Bennett and Kerr. The data of Bennett and Kerr for which a sys-

tematic error is apparent have not been included in the data evaluations presented in Table IV.

As a further test of the consistency of the data, the Arrhenius parameters for reactions of hydroxyl radicals with methyl *n*-butyl ether and ethyl *n*-butyl ether can be estimated using the data presented here in conjunction with the evaluated rate data from the literature for dimethyl ether ($k(\text{OH} + \text{CH}_3\text{OCH}_3) = 10.4 \times 10^{-12} \exp(-372/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1989)). Assuming that the contribution to the overall rate coefficient of the individual alkyl chains is independent and additive, then the rate coefficients for the reaction of hydroxyl radicals with methyl *n*-butyl ether and ethyl *n*-butyl ether can be calculated at any given temperature from the rate coefficients for the following pairs of ethers: dimethyl ether/di-*n*-butyl ether and diethyl ether/di-*n*-butyl ether, respectively. Arrhenius analysis of the estimated rate coefficients over the temperature range 242 to 440 K yields the rate coefficients $k(\text{OH} + \text{methyl } n\text{-butyl ether}) = 4.1 \times 10^{-12} \exp(413/T)$ and $k(\text{OH} + \text{ethyl } n\text{-butyl ether}) = 5.3 \times 10^{-12} \exp(411/T)$ in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These values are within the experimental error of the results in Table IV. This approach can be used to estimate temperature-dependent rate coefficients for ethers not yet measured.

The data presented here can be applied to extend the structure-activity relationships developed by Atkinson (1986, 1987) to estimate the rate coefficients for the reactions of hydroxyl radicals with organic compounds by estimating group rate coefficients for primary, secondary and tertiary C centres, with substituent factors to describe the influence of a functional group on the reactivity of a neighbouring alkyl group. Using the data presented in Table IV together with the available temperature-dependent rate coefficients in the literature for dimethyl ether (Atkinson, 1989), di-*n*-propyl ether and methyl *t*-butyl ether (Bennett and Kerr, 1990), a temperature-dependent substituent factor for the ether oxygen can be calculated. The rate coefficients over the temperature range 247 to 373 K were calculated and the average substituent factor fitted to an Arrhenius expression to yield $f(-\text{O}-) = (0.7 \pm 0.1) \exp[(794 \pm 23)/T]$ corresponding to $f(-\text{O}-) = 10.3$ at 298 K.

The updated substituent factor can be used to predict the room-temperature rate coefficients for the hydroxyl radical reactions of ethyl *t*-butyl ether, methyl *t*-pentyl ether and di-*iso*-butyl ether, (9.4×10^{-12}) , (3.1×10^{-12}) and $(27.8 \times 10^{-12}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively. The rate coefficients for these ethers have also been determined experimentally. The agreement between the experimental and predicted rate coefficients is excellent for ethyl *t*-butyl ether (Wallington *et al.*, 1988b, 1989) and di-*iso*-butyl ether (Bennett and Kerr, 1989), within a factor of 1.1. However, for methyl *t*-pentyl ether the agreement is somewhat less satisfactory, the procedure underestimates the rate coefficient determined experimentally (Wallington *et al.*, 1988b) by a factor of 2.5. The estimation procedure will fail if the activity influence of the functional groups extends beyond the nearest neighbouring C atom as discussed by Wallington *et al.* (1988b) and Nelson *et al.* (1990).

The present new data on the temperature dependences of the rate coefficients of

the reactions of OH with methyl *n*-butyl ether, di-*n*-butyl ether and di-*n*-pentyl ether substantiate the earlier findings of small, apparent negative activation-energies of these reactions. We concur with the view that the most likely explanation is that the reactions have zero activation-energies and what is being observed is a small temperature dependence of the A-factor (Atkinson *et al.*, 1978; Tully and Droege, 1987).

5. Conclusions

The results presented here demonstrate that the competitive technique, as currently employed in our laboratories, is capable of providing reliable and accurate determinations of the temperature-dependent rate coefficients for the reactions of hydroxyl radicals with organic compounds under simulated atmospheric conditions. The structure-activity relationship has been extended to provide a temperature-dependent activity coefficient for the ether group.

Acknowledgment

The authors thank Claudia Müller for carrying out some of the experiments.

References

- Atkinson, R., 1986, Kinetics and mechanisms of the gas-phase reactions of hydroxyl radicals with organic compounds under atmospheric conditions, *Chem. Rev.* **86**, 69–201.
- Atkinson, R., 1987, A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds, *Int. J. Chem. Kinet.* **19**, 779–828.
- Atkinson, R., 1989, Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds, *J. Phys. Chem. Ref. Data Monograph series 1*.
- Atkinson, R., Perry, R. A., and Pitts, Jr., J. N., 1978, Rate constants for the reactions of the OH radical with $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, and $\text{C}_2\text{H}_5\text{NH}_2$ over the temperature range 298–426 K, *J. Chem. Phys.* **68**, 1850–1853.
- Bennett, P. J., 1989, Kinetic and mechanistic studies of some reactions pertaining to the atmosphere, PhD thesis, University of Birmingham.
- Bennett, P. J., and Kerr, J. A., 1989, Kinetics of the reactions of hydroxyl radicals with aliphatic ethers studied under simulated atmospheric conditions, *J. Atmos. Chem.* **8**, 87–94.
- Bennett, P. J., and Kerr, J. A., 1990, Kinetics of the reactions of radicals with aliphatic ethers studied under simulated atmospheric conditions: temperature dependences of the rate coefficients, *J. Atmos. Chem.* **10**, 29–38.
- DeMore, W. B., Sander, S. P., Golden, D. M., Molina, M. J., Hampson, R. F., Kurylo, M. J., Howard, C. J., and Ravishankara, A. R., 1990, NASA panel for data evaluation, Chemical kinetics and photochemical data for use in stratospheric modeling, evaluation number 9, JPL publication 90-1, JPL, California Institute of Technology, Pasadena, California.
- Grob, K., and Grob, G., 1983, Capillary columns with very thick coatings, *J. High Resolution Chromat. and Chromat. Commun.* **6**, 133–139.
- Harris, S. J., and Kerr, J. A., 1988, Relative rate measurements of some reactions of hydroxyl radicals with alkanes studied under atmospheric conditions, *Int. J. Chem. Kinet.* **20**, 939–955.
- Lloyd, A. C., Darnall, K. R., Winer, A. M., and Pitts, J. N. Jr., 1976, Relative rate constants for the reactions of OH radicals with isopropyl alcohol, diethyl ether and di-*n*-propyl ether at 305 ± 2 K, *Chem. Phys. Lett.* **42**, 205–209.

- Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J., and Nielsen, O. J., 1990, Absolute and relative rate constants for the reactions of hydroxyl radicals and chlorine atoms with a series of aliphatic alcohols and ethers at 298 K, *Int. J. Chem. Kinet.* **22**, 1111–1126.
- Sandells, F. J., Penkett, S. A., and Jones, B. M. R., 1974, *Preparation of peroxyacetylnitrate (PAN) and its determination in the atmosphere*, Harwell Report, AERE-R 7087.
- Tully, F. P., and Droege, A. T., 1987, Kinetics of the reactions of the hydroxyl radical with dimethyl ether and diethyl ether, *Int. J. Chem. Kinet.* **19**, 251–259.
- Wallington, T. J., Liu, R., Dagaut, P., and Kurylo, M. J., 1988a, The gas phase reactions of hydroxyl radicals with a series of aliphatic ethers over the temperature range 240–440 K, *Int. J. Chem. Kinet.* **20**, 41–49.
- Wallington, T. J., Dagaut, P., Liu, R., and Kurylo, M. J., 1988b, Rate constants for the gas phase reactions of OH with C₅ through C₇ aliphatic alcohols and ethers: predicted and experimental values, *Int. J. Chem. Kinet.* **20**, 541–547.
- Wallington, T. J., Andino, J. M., Skewes, L. M., Siegl, W. O., and Japar, S. M., 1989, Kinetics of the reaction of OH radicals with a series of ethers under simulated atmospheric conditions at 295 K, *Int. J. Chem. Kinet.* **21**, 993–1001.