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ARTICLE

Kinetics of 1- and 2-methylallyl + O₂ reaction, investigated by photoionisation using synchrotron radiation

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Domenik Schleier,^a Engelbert Reusch,^a Marius Gerlach,^a Tobias Preitschopf,^a Deb Pratim Mukhopadhyay,^a Nancy Faßheber,^b Gernot Friedrichs,^{b,*} Patrick Hemberger,^{c,*} and Ingo Fischer^{a,*}

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The reaction kinetics of the isomers of the methylallyl radical with molecular oxygen has been studied in a flow tube reactor at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source storage ring. The radicals were generated by direct photodissociation of bromides or iodides at 213 nm. Experiments were conducted at room temperature and low pressures between 1 and 3 mbar using He as the buffer gas. Oxygen was employed in excess to maintain near pseudo-first-order reaction conditions. Concentration-time profiles of the radical were monitored by photoionisation. For the oxidation of 2-methylallyl (2-MA) and with $k(2\text{-MA}+\text{O}_2) = (5.2 \pm 1.0) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, the rate constant was found to be in the high-pressure limit already at 1 mbar. In contrast, 1-methylallyl exists in two isomers, E- and Z-1-methylallyl. We selectively detected the E-conformer as well as a mixture of both isomers and observed almost identical rate constants within the uncertainty of the experiment. A small pressure dependence is observed with the rate constant increasing from $k(1\text{-MA}+\text{O}_2) = (3.5 \pm 0.7) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 1 mbar to $k(1\text{-MA}+\text{O}_2) = (4.6 \pm 0.9) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 3 mbar. While for 2-methylallyl + O₂ no previous experimental data are available, the rate constants for 1-methylallyl are in agreement with previous work. A comparison is drawn for the trends of the high-pressure limiting rate constants and pressure dependences observed for the O₂ recombination of allylic radicals with the corresponding reactions of alkyl radicals.

A Introduction

Resonance stabilized radicals (RSR) are of interest in various fields, due to their ability to delocalize the unpaired electron.¹ Their comparably low reactivity towards oxygen leads to an accumulation in combustion engines,² planetary atmospheres³ and the interstellar medium.⁴ In these environments they can contribute to the formation of benzene, polycyclic aromatic hydrocarbons (PAH) and soot.^{2,5} One of the simplest and most studied RSR is the allyl radical C₃H₅. Its properties,^{6–8} structure,⁹ and bimolecular reactions^{10–16} were assessed by a variety of spectroscopic methods. The interest in the C₄H₇ isomers 1-methylallyl (1-MA), 2-methylallyl (2-MA), both depicted in Scheme 1, and the cyclic isomer cyclobutyl, increased only recently. Similar to allyl, these radicals can also be found in interstellar media¹⁷ and flames, primarily in the combustion of isobutene¹⁸ and anti-knock additives like *tert*-butyl ethers.¹⁹ Unsaturated fatty acid esters, which are potential biofuels, preferentially loose H-atoms in the α -position to the C=C double bonds at high temperature, forming intermediates that can be described as alkylated allyl radicals.²⁰ 1- and 2-MA can thus serve as suitable models for their reactivity. The excited state dynamics²¹ as well as the details of the uni-

molecular decomposition have been explored recently.²² For the present study, the information from photoelectron spectroscopy is particularly relevant. Accurate ionisation energies (IE) were obtained for 1-MA and 2-MA.^{23,24} Information on bimolecular reactions are however still rare. The dimerization of 2-MA and its disproportionation have been investigated in shock tubes,^{25,26} and at room temperature (RT) using UV/VIS absorption spectroscopy,²⁷ but no experimental study on the reaction between 2-MA and oxygen has yet been reported. However, the rate constants have been computed using canonical transition state theory at different computational levels.²⁸

Scheme 1: The isomers of the methylallyl radicals were generated by photolysis of suitable halide precursors.

In contrast, the reaction of 1-MA with O₂ has been investigated at low pressure by Knyazev and Slagle (KS).²⁹ Crotyl bromide was photolyzed at 248 and 193 nm over a range of temperatures and pressures and the radicals were subsequently ionized with a bromine resonance lamp between 7.6–7.9 eV.

In the present work we address the kinetics of the methylallyl oxidation, to investigate the influence of methyl substitution on the bimolecular reaction rates. Previous studies on isomeric C₄H₉ radicals revealed larger rate constants with increased carbon substitution around the radical centre.^{30,31} Generally isomeric compounds can be

^a Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg; e-mail: ingo.fischer@uni-wuerzburg.de

^b Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 1, D-24118 Kiel; e-mail: friedrichs@phc.uni-kiel.de

^c Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institut (PSI), CH-5232 Villigen, Switzerland; e-mail: patrick.hemberger@psi.ch

† Footnotes relating to the title and/or authors should appear here.

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selectively generated by using different precursors when the barrier to isomerization in the radicals is high. However, the double bond in the C_4H_7 radicals leads to two diastereomeric forms in 1-MA with a low barrier to isomerization, termed E- and Z-1-MA, see Scheme 1. A detection method that can distinguish between the signals from both isomers is thus advantageous. We apply photoelectron-photoion coincidence (PEPICO) spectroscopy using tuneable synchrotron radiation. In this scheme, electrons and ions from a single ionisation event are correlated, which leads to photoion mass selected threshold photoelectron (ms-TPE) spectra,³² where isomers can be distinguished by differences in the IE and the vibrational structure of the TPE spectrum. Kinetic traces at different photon energies then yield rate constants for different isomers. PEPICO has become a state-of-the-art detection tool for reactive species in the gas-phase. It has been used to investigate molecules involved in atmospheric,³³ combustion,³⁴ interstellar,^{35, 36} and catalytic processes.³⁷ Recently we reported a kinetic study on the allyl + O_2 reaction, employing PEPICO.¹⁰ Here we extend the work to the methylallyl + O_2 system, see (1) and (2) and report a rate constant for the oxidation of 2-MA as well as a conformer-specific rate for E-1-MA.

Note that for (1) $\Delta_r H$ was computed from a set of isodesmic reaction with CBS-q//MP2(full)/6-31G(d) level of theory,²⁸ whereas the average $\Delta_r H$ for E- and Z-1-MA for (2) was determined experimentally.²⁹ For comparison, $\Delta_r H^\circ = -(75.6 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ was found for the reaction of the allyl radical with O_2 .¹¹

B Methods

Experiments were performed using the double imaging CRF-PEPICO spectrometer at the VUV beamline of the Swiss Light Source (SLS). The instrument has been described in detail elsewhere, thus only a brief overview is given here.³⁸ For the experiments, a side-sampled flow reactor was utilised. Methylallyl radicals were produced by photolysis of the halide precursors 2-methylallyl iodide (2MAI) and crotylbromide, according to Scheme 1. All chemicals were purchased from Sigma Aldrich. While 2MAI is available with >97% purity, for crotylbromide only >85% purity is specified. However, the major impurity is 3-bromo-1-butene, which also yields 1-MA upon pyrolysis. The 5th harmonic of a 10 Hz Nd:YAG laser at 213 nm (about 30 mJ cm⁻² per pulse) was employed in the photolysis. Calibrated mass flow controllers were used for adjusting the partial pressures of all reactants by mixing gas flows of O_2 ($\pm 1\%$ uncertainty), precursor/He ($\pm 1.5\%$), and He buffer gas ($\pm 1\%$), resulting in about 2% uncertainty in the overall O_2 mole fraction. The precursor vapours were introduced into the flow tube by a metered flow of He through a glass container filled with the liquid halides. As their vapour pressures are not precisely known, the concentrations of the precursors were determined by UV/VIS spectroscopy in the gas phase before the mixture was introduced into the reactor. The absorption cross section of crotyl bromide at 230 nm was taken from the literature (note that the absorption of 3-bromo-1-butene at 230 nm is small),³⁹ whereas the one of 2-MAI was determined in a hexane solution. Here a value of 720 l/(mol·cm)⁻¹ was determined at 270 nm. The precursor concentra-

tions are given in Table S1 of the electronic supplementary information (ESI), the uncertainty is estimated to be less than $\pm 10\%$ for crotyl bromide, but probably higher for 2MAI. Radical concentrations were obtained from the depletion of the precursor signal upon photolysis, ignoring ionisation in the first few ms of the kinetic trace. Analysis of several data sets show that the error is negligible in comparison. Note, however, that due to the near first-order reaction conditions of the experiments (see below) the assumed precursor as well as radical concentrations have only a limited impact on the determined rate constants. Increasing or reducing the radical concentration in the fits (see below) by a factor of two lead to a difference of less than 3% in the second-order rate constants.

The quartz tube reactor was coated with halocarbon wax to suppress radical wall loss and mounted parallel to the synchrotron beam. The pressure in the reactor tube p_r was kept between $p_r = 1.0\text{--}3.0$ (± 0.05) mbar by throttling the vacuum at the flow tube exit. The total gas flow rate was set high enough to completely replace the gas mixture in the reactor tube with a fresh sample in-between two consecutive laser pulses in order to avoid accumulation of reaction products, see ESI for details. The laser beam propagated down the reactor and is assumed to create a uniform density of photolysis products, which were sampled into the ionisation region through a 300 μm pinhole at the halfway point of the tube. For 2-MA, 5% of the precursor concentration were converted upon UV photolysis, for 1-MA a slightly lower value of 4% was found. The photon energy was calibrated on the Ar 11s'-14s' autoionisation lines in the first and second order of the monochromator grating. Higher harmonic radiation was suppressed by a MgF_2 window. The effusive gas beam was crossed by the VUV radiation at a distance of 21 ± 4 mm from the flow tube and a constant extraction field of 218 V cm^{-1} accelerated the generated photoions and photoelectrons in opposite directions. The VUV photon energy was scanned between 7.3–8.0 eV for 1-MA and between 7.7–8.6 eV for 2-MA to record TPE spectra of the radicals. Threshold electrons were selected with an energy resolution of 10 meV and the contribution of hot electrons was subtracted, following the procedure given in Ref.⁴⁰. Each full scan consists of a multi-dimensional data set, which yields time-of-flight mass spectra, threshold photoelectron spectra, and reaction kinetic traces. To obtain kinetic traces, the coincidence intensity of the radical signal was plotted as function of the reaction time (difference between the coincidence and laser photolysis time stamps). For 2-MA the photon energy has been fixed to 8.5 eV and the ion signal was averaged for 120 minutes. For 1-MA the photon energies have been fixed to 7.54 eV and 7.59 eV to record kinetic traces of E-1MA and Z-1-MA, respectively at 1.0 and 2.0 mbar. For the measurement at 3.0 mbar the photon energy was fixed at 8.0 eV in order to improve the signal-to-noise ratio and data were averaged for 120–360 minutes. At the beginning and at the end of each set of experiments, the radical loss rates were recorded with no oxygen present to quantify side reactions and wall losses as a control. The detailed experimental conditions are given in Table S1 in the electronic supplementary information (ESI). In the next step, the MA decay was measured as a function of the O_2 concentration, $[O_2]$, which was at least one order of magnitude higher than the methylallyl radical concentration to maintain pseudo-first-order conditions. Kinetic traces were analysed using the CHEMKIN-II⁴¹ package and SENKIN routine.⁴² For sensitivity analysis, the sensitivity coefficient

the precursor and one at 55, due to 2-MA. The difference between the spectra with and without laser (bottom trace) shows that the radical is produced by photolysis and that contributions from dissociative ionisation are negligible. In the mass spectra (a) and (b), one small peak is identified at mass 110 and attributed to the dimerization product of the 2-MA radical. As the signal vanishes almost completely in the difference spectrum, it originates from a reaction in the precursor sample rather than in the photolysis reactor. Note that a color change of the sample was observed over the course of the experiment. An additional contribution due to 2-MA + 2-MA recombination is too small to be detected in the presence of this background. In the experiments with added oxygen, the peroxy radical reaction product of (1) was not observed. Our computations predict an IE for the 2-methylallyl peroxy radical of 8.69 eV with a triplet ground state in the cation. The cationic structure exhibits a very long C–O bond (2.64 Å) resulting in a rather flat potential energy surface (PES). The optimized structures can be found in Table S3. As already observed for allylperoxy, the detection of methylallylperoxy radicals by photolysis is impeded by the combination of the comparably low binding energies between 75 and 85 kJ·mol^{−1} and a large geometry change upon ionisation.^{10, 11}

Figure 2 shows the mass spectra for the 1-MA experiments. The precursor at m/z 134 and 136 is the dominant signal, with three minor peaks also visible at 9.50 eV. While the masses at 54 and 55 can be attributed to the beginning dissociative photoionisation, mass 100 is most likely due to an impurity, which is not ionized at 8.50 eV, as depicted in the lower trace. The precursor does not get ionized at this energy and therefore the only detected signal originates from the radical itself at mass 55. Note that different photon energies were employed to ionize the precursor, but avoid dissociative ionisation of the radical. The possible reaction products HBr (1-MA) and HI (2-MA) were not observed due to their high ionisation energy.

Fig. 2 Mass spectra of 1-MA with laser off (a) and on (b). Note that the bromine atoms generated in the photolysis cannot be detected due to their significantly higher IE.

Threshold Photoelectron spectra. ms-TPE spectra permit to monitor one isomer by selecting the signal of a specific photoionisation transition. In order to prove that the desired radicals were created, we

$\sigma(i,j,t)$ for reaction i of species j at time t was normalized with respect to the maximum concentration $c_{\max}^{\text{max}}$ of the species j over the time history, $\sigma(i,j,t) = 1/c_{\max}^{\text{max}} \times (\partial c(j,t) / \partial \ln k_j)$. The time resolution of the experiment is limited by the spread in the time it takes for the expanding gas to travel from the pinhole of the reactor to the ionisation point. It was accounted for by convoluting the concentration-time profiles with a suitable⁴³ Maxwell-Boltzmann type response function corresponding to a $\tau_{10-90} = 1.4$ ms rise time, see Figure S1. For comparison, rate constants were also obtained from pseudo-first order analysis using simple exponential decay and linear fits. The results are given in Table S2.

Next to the $\pm 2\%$ uncertainty of the O_2 content in the reaction mixtures, additional sources of error are the pressure and the temperature in the reactor. The reactor pressures are accurate to at least ± 0.05 mbar, resulting in an error of $\pm 2-3\%$. Room temperature (298 K) was assumed for all experiments. However, if the energy deposited by the laser is not fully equilibrated, the effective free radical internal temperature can deviate from room temperature. Recent work on photochemically generated methylperoxy radicals found a temperature of 330 ± 30 K, i.e. slightly higher than room temperature.⁴⁴ Deviations from room temperature of ± 20 K resulted in errors between ± 2 and $\pm 6\%$ within the kinetic model employed in the present work. Note that reaction (2) is known to have a negative temperature dependence and the same is assumed for reaction (1). Accounting for all major sources of errors, including statistical errors from fitting and pseudo-first order analysis, we assume that the rate constants determined below are accurate within $\pm 20\%$.

Heats of reaction were computed using the CBS/QB3 approach as implemented in the gaussian 09 suite of programs.⁴⁵

C Results

Fig. 1 Mass spectra of 2-MA with laser off (a) and on (b) and the difference spectrum (c). The residual precursor ion signal in the difference spectrum is due to contributions from scattered laser photons.

Mass spectra. The coincidence time-of-flight mass spectrum of the 2-MA radical recorded at a photon energy of 8.90 eV is shown in Figure 1. Two intense peaks are visible, one at mass 182 representing

recorded TPE spectra (TPES) for 1- and 2-MA and compared them to spectra previously recorded using pyrolysis for radical generation.²³ The ms-TPES of 2-MA is given in Figure S2. The IE of 7.89 eV as well as the Franck-Condon (FC) simulation of a vibrational progression of 440 cm⁻¹ fully agree with the previous data for the 2-MA radical, therefore we refer to our earlier publication for a detailed discussion of the spectrum.²³ No other species is observed up to 8.60 eV, therefore only the 2-MA isomer contributes to the kinetic traces.

The TPES of the 1-MA radical is given in Figure 3. The rather complex spectrum has also been analyzed before.²³ The low energy part of the spectrum is dominated by the E-1-MA conformer with an IE of 7.48 eV. Several vibrational fundamentals as well as two hot band transitions at 7.41 and 7.44 eV are visible. Two modes dominate the vibrational progressions, the C-C-C bending motion ν_{24}^+ (280 cm⁻¹, 35 meV) and the C-C stretching mode ν_{25}^+ (565 cm⁻¹, 70 meV), respectively.²³

Fig. 3 ms-TPE spectrum of 1-MA (black line) with a Franck-Condon simulation for comparison. The first peaks are attributed to the E-conformer with an IE of 7.48 eV. For the Z-conformer an IE of 7.59 eV has been determined. Assignment have been adopted from Ref. 23.

A second intense peak appears at 7.59 eV and is assigned to the IE of the Z-conformer. It is also accompanied by a vibrational progression in the CCCC bending mode ν_{23}^+ (565 cm⁻¹, 70 meV) and the ν_{21}^+ symmetric stretching mode of the carbon atoms (800 cm⁻¹, 100 meV). The peaks assigned to ν_{24}^+ for E-1MA and ν_{21}^+ for Z-1MA represent further bands that have not been resolved in the pyrolysis experiments, due to the higher temperatures of the source.²³ The TPES shows that both E- and Z-conformer are formed, although the precursor is predominantly in E-conformation. Photodissociation studies by Lau *et al.* showed that radicals from the photolysis of crotylbromide at 234 nm carry internal energies between 29 and 126 kJ/mol.³⁹ This is not enough to surmount the barrier to isomers like 3-buten-1-yl (>201 kJ/mol), but sufficient to overcome the rotational barrier between E- and Z-1MA. It is calculated to lie between 60 and 67 kJ/mol,⁴⁶ hence a quick equilibration can be safely assumed. Since we use 213 nm for photolysis, an even higher amount of internal energy is available for rapid isomerization before the radical is thermalized

by the bath gas within 100 ns - 1 μ s, as can be estimated from the RRKM data given in Ref. 46.

The TPES shows that below 7.55 eV contributions of the Z-conformer to the spectrum are negligible and the E-conformer can be monitored exclusively. It is more difficult to probe the Z-conformer, because above 7.59 eV contributions of E-1-MA to the TPE-signal cannot be neglected. Furthermore, it was shown that predictions of the ratio between Z- and E-isomer ($R_{Z/E}$) at equilibrium are critically dependent on the computational method as well as pressure, temperature and available average internal energy of the radical. At 300 K and 10 mbar, $R_{Z/E}$ lies somewhere between 1 and 2.⁴⁶ Based on this we have assumed that equal amounts of E- and Z-isomer are formed after photolysis.

Fig. 4 a) Typical decay trace of 2-MA with (black) and without oxygen (red). Symbols refer to experimental data points and lines to the optimized simulation. b) Sensitivity analysis of the 2-MA concentration-time profile to various reactions with 0.5% oxygen present. The reaction between 2-MA and O₂ dominates the decay.

Kinetics of 2-Methylallyl

In the next section we will discuss the results obtained for the kinetics of the 2-methylallyl radicals. As the peroxy radical products were not observed, the kinetics of the 2-MA + O₂ reaction was monitored by following the decay of the reactant signal. Background and side reactions, in particular radical self-recombination and wall loss, may contribute to the observed decay of the C₄H₇ radical signal over time. To account for these side reactions, kinetic traces without oxygen were initially recorded under the same conditions and the reaction profiles were analyzed based on a small reaction mechanism accounting for the most important radical loss processes, see Table 1.

Reactions without O₂. A typical decay of the 2-MA signal is given by the red curve in Figure 4 a). Without oxygen, dimerization of 2-MA (3), recombination of 2-MA and I atoms (4) as well as formation of I₂ (8) are the most important side reactions. In addition, a first-order wall loss reaction for 2-MA was included and its rate constant has been adjusted to reproduce the observed 2-MA decay. In this way, the wall loss reaction also accounts for possible minor contributions from additional, non-considered side reactions. In particular, possible reactions of the 2-MA radical with the precursor can be treated in this way. As the precursor is in excess, such reactions are of

pseudo-first order. This background mechanism was then used without changes to analyze the experiments with oxygen.

Table 1: Background reactions included in the analysis of the decay of the methylallyl radicals.

No.	Reaction	Rate constant k	Ref.
(3)	$2 \text{ C}_4\text{H}_7 \rightarrow \text{C}_8\text{H}_{14}$	$2.6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Bayrakceken et al. ²⁷
(4)	$2\text{-MA} + \text{I} \rightarrow 2\text{-MAI}$	$1.0 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	estimated, ^a from Jenkin et al. ¹²
(5)	$2\text{-MA} \rightarrow \text{wall}$	32 s^{-1}	This work
(6)	$1\text{-MA} + \text{Br} \rightarrow 1\text{-MABr}$	$8.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	estimated, ^a Jenkin et al. ¹²
(7)	$1\text{-MA} \rightarrow \text{wall}$	15 s^{-1}	This work
(8)	$\text{I} + \text{I} + \text{M} \rightarrow \text{I}_2 + \text{M}$	$2.96 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	Baulch et al. ⁴⁷
(9)	$\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2$	$1.02 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	Clyne et al. ⁴⁸

^a estimated based on corresponding allyl radical reaction, see text.

Note, that rate constants for many of the reactions are not accurately known at the pressures and temperatures of the experiments, the dimerization of iodine (8) and bromine atoms (9) being an exception. The dimerization of 2-MA was studied behind shock waves, hence at much higher temperatures and pressures.^{25, 26} Therefore, we adopted the rate constant of the only study performed at RT, which was also measured at a relatively high pressure of 133 mbar,²⁷ but is comparable to the rate constant of allyl radical recombination at pressures of 1.3–8.0 mbar.⁴⁹ Along the same line, for the recombination of 2-MA + I $\rightarrow$ 2-MAI (4) we employed the values determined for allyl.¹² The sensitivity analysis in the lower trace of Figure 4 (red curve) shows that reaction (4) has a negligible influence on the results of the fit. Changing its rate constant by a factor of three lead to a 3% change in the rate constant of (1).

Reactions with O₂. In the next set of experiments, different amounts of oxygen (0.25% - 2%) were added to the gas flow. The trace for $x(\text{O}_2) = 1\%$ at 2 mbar is given in figure 4 a) as black triangles. As visible the signal decays much faster upon addition of oxygen, showing immediately that (1) becomes the dominant reaction.

It should be noted that all methylallyl radicals have inequivalent sites for O₂ attack, which lead to different peroxy products, in the case of 2-MA two terminal and one central site. As only the decay of the reactant is observed, we cannot distinguish between these sites in our analysis. The heats of reaction for the recombination products, computed by us using the CBS/QB3 method, are given in Scheme 2. As visible, in 2-MA the central site is energetically unfavorable, because the peroxy product is not resonantly stabilized anymore, and its formation is endothermic. The values for the two terminal sites are comparable. Note that the computed heat of reaction for 2-MA + O₂ is lower than the previous MP2 value mentioned above by almost 10 kJ·mol⁻¹, due to the different methods employed,²⁸ while the computed heat of reaction of -75.6 kJ·mol⁻¹ for allyl (bottom trace of

Scheme 2) is in excellent agreement with the previous experimental value of -76.2 kJ·mol⁻¹.⁵

Scheme 2: CBS/QB3 heats of reaction for the allyl/methylallyl + O₂ recombination reactions, computed in this work.

In principle, reverse reaction (-1), i.e. the decomposition of the peroxy radical product, can also influence the 2-MA transient.

However, no indication for a possible equilibration is seen in the signals that directly decay to the background level. Reaction (-1) is assumed to become important only at higher temperatures. Actually, Chen and Bozzelli²⁸ calculated the rate constant for the dissociation of C₄H₇OO at 300 K to be $1.6 \times 10^{-4} \text{ s}^{-1}$ (CBS/MP2) or $1.5 \times 10^{-3} \text{ s}^{-1}$ (DFT/B3LYP), depending on the computational method. Even the higher value is still way to low to be of any importance for our experiment taking place on the millisecond time scale. A further common side reaction in the kinetics of radicals, loss of HO₂ does not lead to a stable product for 2-MA.

The concentration-time profiles were analyzed by fitting the rate constant of reaction (1) in the numerical simulation. All other fit parameters, like response function, initial radical concentration and background rate constants, were kept constant. After adding oxygen, the accuracy of the fit depends predominately on the assumed rate constant for reaction (1). This is further illustrated by the sensitivity plot in figure 4 b) that shows the influence of the diverse reactions for simulating the 2-MA concentration-time profile. Next to reaction (1), only the wall loss reaction exhibits significant sensitivity, in line with near pseudo-first order experimental conditions.

Figure 5 summarizes the extracted first-order rate constants k^{1st} as function of [O₂] where the slope of the linear fit to the data corresponds to the second-order rate constant of reaction (1) according to $k^{1st} = k^{2nd} \times [\text{O}_2]$. All data were also analyzed by a standard pseudo-first order treatment by fitting single-exponential functions to the

observed 2-MA decay, not accounting for the convolution of the instrument response function. The resulting pseudo-first order plots are included in the ESI (Fig. S5a). As expected, in particular due to the non-zero influence of the wall loss reaction, the plots yield y-axis intercepts. Moreover, up to 27% lower k^{2nd} values have been obtained. This relatively large deviation is actually due to the neglect of the convolution of the radical decay with the instrument response function. With observed decay profiles on the ms time scale, at high O_2 content the simple analysis yields systematically too low decay constants. An alternative pseudo-first order analysis taking into account the convolution of a single-exponential with the instrument's response function (Fig. S5c) is in agreement with the full kinetic simulation within 9% on average. Clearly, the numerical simulation of the signal ensures a more accurate rate constant result. However, the different analyses reveal the importance of the assumed response function and therefore we included a related uncertainty of $\pm 5\%$ into the error estimate of the total rate constant (*vide supra*). The obtained values of k^{2nd} for reaction (1) at reactor pressures $p_r = 1 - 3$ mbar are displayed in Table 2. As visible, no dependence on p_r is observed within error limits, indicating that reaction (1) takes place essentially in its high pressure limit and therefore the average rate constant of $5.1 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ can be taken to be equivalent with the high pressure limit k_∞ .

Table 2: Rate constants for second-order recombination reaction 2-MA + O_2 at 298 K.

Pressure / mbar	$k^{2nd} / 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1.0	5.2 ± 1.0
2.0	5.1 ± 1.0
3.0	5.1 ± 1.0

Fig. 5 Pseudo-first-order rate constants determined for the 2-MA + O_2 reaction (1) for buffer gas pressures between 1 and 3 mbar, determined by numerical simulation of the 2-MA profiles. Within the experimental error bars, no pressure dependence is found.

1-MA:

The kinetics of the two 1-MA isomers were investigated at two different photon energies. On the one hand, for E-1-MA, $h\nu = 7.54$ eV was chosen, because no other isomer contributes to the signal and

hence the kinetics of the E-1-MA isomer can be selectively monitored. To follow the kinetics of Z-1-MA, on the other hand $h\nu = 7.59$ eV was used. Initially only threshold electrons were recorded to minimize the contributions from the E-conformer. Due to the low signal-to-noise ratio, we switched to ion detection, which yields the signal from both isomers and thus yields the rate constants for an about 1:1 mixture of E- and Z-isomer. Note, however, that kinetic traces based on the analysis of threshold electrons at 7.59 eV yielded approximately the same rate, but with considerably larger error bars, see Figure S3 and S4.

Reactions without O_2 : When only E-1MA is detected, the bromine concentration will be twice the concentration of E-1MA, because E- and Z-isomer will be generated in about equal amounts. This was considered in the analysis of the kinetics.

A typical concentration-time profile for E-1MA with and without oxygen addition is given in Figure 6 a). Again, the initial rise of the signal reflects the time resolution of the experimental setup (*vide supra*). For the simulation without oxygen, the rate constants from Table 1 were used and the wall loss rate constant was optimized to account for the difference between experiment and simulation. Furthermore, the rate constant for the 1-MA + Br recombination, which was derived from the corresponding reaction of allyl radicals with iodine,¹² has been slightly scaled by a factor of 0.8, yielding a slightly better fit of the data at longer reaction times. Since there is also no kinetic data available on the dimerization of 1-MA, we assumed that the dimerization rates of the different isomers (E/E, E/Z, Z/Z) are all equivalent and approximately equal to the 2-MA dimerization rate (3). Probably due to these necessary rate constant estimates and remaining uncertainties in the background mechanism, the wall loss of 1-MA was found to differ by about a factor of 2 from the 2-MA experiments.

Fig. 6 a) Typical decay of the E-1-MA radical over time with and without oxygen present. b) Sensitivity of each reaction towards the E-1-MA radical concentration-time profile over time.

Reactions with O_2 : Having set the background mechanism, 0.25 – 1.5% of oxygen were added to the reaction mixtures and the profiles were fitted by optimizing the rate constant of the reaction 1-MA + O_2 . The red trace in Figure 6 a) shows a typical decay with 0.5% oxygen added to the mixture and Figure 6 b) corresponds to the sensitivity analysis of 1-MA for the same experiment. It can be seen that the addition of oxygen is by far the most important reaction, confirming

near pseudo-first order reaction conditions. For the sake of completeness, the consistent results of a standard pseudo-first order analysis (with and without convolution of the instrument's response function) have been included in the ESI (Figs. S5c, S5d and Table S1). However, it is notable that the recombination with the bromine atom becomes more important than the wall loss, which is simply due to the fact that the bromine concentration was twice as high as in the 2-MA experiments. Again, the reverse reaction $\text{C}_4\text{H}_7\text{OO} \rightarrow 1\text{-MA} + \text{O}_2$ (-2) was not considered in the mechanism, because it will only become important at higher temperatures (*vide supra*).¹⁰

1-MA even has three inequivalent reaction sites for oxygen attack, two of them prochiral. Computed CBS/QB3 enthalpies of reaction in Scheme 2 are only included for the two resonantly stabilized products for both the E- and Z-isomer. As shown above for 2-MA, oxygen addition to the central carbon atom leads to products that are much higher in energy and therefore assumed to be unimportant. Following the arguments given in the literature, due to similar spin densities at the terminal and non-terminal C atoms as well as insignificant sterical effects of analogue alkyl radical reactions,²⁹ similar rate constants are expected for both sites. The optimized structures and energies of the recombination products of both isomers are shown in Table S3 in the ESI. Stable neutral and cationic species were found for all three of them. The neutral species have recently been detected by cavity ringdown IR spectroscopy,⁵⁰ but detection by photoionisation is not possible, as discussed above. Their IEs were all computed to be around 8.30 eV with an almost planar CCCC framework in the cation.

Table 3: Rate constants for the oxidation of E- and a mixture of E- and Z-1MA. At 3 mbar the radicals were non-selectively ionized, the value thus represents an average over both isomers.

p_r /mbar	$k^{2\text{nd}}$ (E-1MA) / $10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k^{2\text{nd}}$ (Z-/E-1MA) / $10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Ref. ²⁹ / $10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1	3.6 ± 0.7	3.4 ± 0.7	-
1.25	-	-	3.87 ± 0.35
2	3.9 ± 0.8	3.7 ± 0.8	-
2.5	-	-	5.17 ± 0.47
3	4.6 ± 0.9		-
4.95	-	-	7.91 ± 0.98
9.95	-	-	8.06 ± 1.31

The $k^{1\text{st}}$ rate constant values obtained from numerical fitting of the concentration-time profiles are summarized in Figure 7. All experiments, which have been performed at three different total pressures of 1, 2, and 3 mbar, exhibit a linear $[\text{O}_2]$ dependence, with the slope of the linear fit corresponding to $k^{2\text{nd}}$. Clearly, a comparison of the two data sets based on either E-isomer or E/Z-isomer detection reveals no significant isomer-dependence of the rate constant. Both at 1 and 2 mbar the two data sets nearly overlap. As already described in more detail for 2-MA, all data were also analyzed by a standard pseudo-first order analysis, again yielding consistent rate constant values (see ESI).

Fig. 7 Pseudo-first-order rate constants for the 1-MA + O_2 reaction, determined by numerical simulation of the 1-MA profiles. A weak pressure dependence is observed. Data for E- and E-/Z-1MA yield the same rate constants.

We also evaluated the experimental data for both radicals by fitting single-exponential functions to the observed decays. The linear fits shown in the pseudo-first order plots in Figures S5a and b do not intersect the y-axis at zero, which illustrates that the background chemistry has to be taken into account. In contrast, the pseudo-first-order plots in Figures 5 and 7 are based on rate constants $k^{1\text{st}}$ obtained from the ChemKin analysis. The negligible intercept shows that the relevant side reactions have been properly included.

Fig. 8 Pressure dependent second-order rate constants of the 1-MA + O_2 reaction (2), measured in He buffer gas. (Inner) error bars corresponds to the 2σ statistical uncertainty of the rate constant fits in Fig. 7 and reported in Ref. 25, outer error bars to the total estimated error of the data from this work. The data from Ref. 29 indicate that around 5 mbar the rate constant are already close to their high pressure limit.

The determined second-order rate constants, together with the 2σ uncertainty of the linear regression in Figure 7 (inner error bars), are shown in Figure 8 in comparison with literature data. The rate constants values are summarized in Table 3, including systematic errors

(vide supra) the total uncertainty is estimated to be $\pm 20\%$, also shown as outer error bars in Figure 8. The data reveal a positive pressure dependence over the measured range. Overall, our data are in good agreement with the earlier values by Knyazev and Slagle (blue squares) who also used He as the buffer gas.²⁹ They observed almost identical rates at 5 and 10 mbar and it can be concluded that the corresponding rate of $8 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is very close to the high pressure limit.

D Discussion

The most relevant aspect of the work is a comparison of the two MA isomers with the allyl radical, C_3H_5 . The allyl + O_2 reaction has been thoroughly investigated by both theory and experiment and the mechanism, which proceeds via an association pathway, is well understood. Rate constants of $k_\infty = 3.5 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ¹² and $k_0 = 2.2 \times 10^{18} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ (in Ar)¹⁰ were determined. In contrast, less information is available for MA. While reaction (2), 1-MA + O_2 , has been investigated experimentally, only computational work is available for (1), 2-MA + O_2 . Chen and Bozzelli predicted the rate constants of reaction (1) based on canonical transition state theory and also investigated secondary reactions from the 2-methylallyl peroxy radical.²⁸ For reactions (1) and (2), an association mechanism following (10) has been assumed, where the excited association complex has to be collisionally stabilised.

As visible in Table 3 and Figure 8, the rates determined for (2) agree with the earlier experimental data within the error bars, although the pressure dependence is somewhat less pronounced in the present work. Note, however, that the abrupt change of the pressure dependence observed at 5 mbar in Ref. 29 is very unusual for typical falloff behaviour and may hint to a systematic overestimation of this data point. For sure, in the pressure range of this work and with a 30% increase of the rate constant from 1 mbar to 3 mbar, reaction (2) is still in the falloff region.

Although we can distinguish between the isomers of 1-MA by choosing different photon energies, no significant difference between the E- and Z-1-MA is observed in our work. This may be taken as an indication that sterical effects play a minor role.

While a pressure dependence is found for 1-MA, our study reveals no pressure dependence for 2-MA between 1 and 3 mbar, i.e. the reaction is already very close to the high pressure limit. At room temperature we find a value of $k_{2\text{nd}} = (5.1 \pm 1.0) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \approx k_\infty$. Chen and Bozzelli theoretically predicted the high-pressure rate constant and provide the Arrhenius expression:

$$k_\infty / (\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 4.65 \cdot 10^8 \cdot T^n \cdot \exp(-E_a/RT)$$

With the reported DFT values $n = 1.18$ and $E_a = 2218 \text{ J/mol}$, a rate of $k_\infty = 1.60 \cdot 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K is obtained, in reasonable agreement with our experimental value. However, their CBS/MP2 values would yield a rate constant that is almost two orders of magnitude lower. In their computations, the reverse reaction (-1) was found to be irrelevant at room temperature. Moreover, potential isomerization channels of the association complex have barriers well above the reverse barrier for (-1) and therefore can be excluded to

play a role for the overall reaction as well. The only exception is an intramolecular H-shift over a six-membered transition state forming a hydroperoxide structure exhibiting an MP2-barrier of 86.6 kJ mol^{-1} , but further product channels are inaccessible ($\geq 117.9 \text{ kJ mol}^{-1}$).

Similarly, theoretical calculations of Dibble et al.⁴⁶ on CBS/QB3 level of theory performed for 1-methylallyl peroxy radical show that the 1,6 H-shift with a tight activation barrier of 87.4 kJ mol^{-1} , which is available for the Z-conformer, cannot compete with the loose activation barrier of the reverse reaction (-2) at 74.1 kJ/mol . However, at elevated temperatures this reaction channel may give access to a number of consecutive products. The activation barrier of the 1,5 H-shift reaction of the E-isomer with 104.6 kJ/mol is even higher, hence this reaction channel does not play a role at room temperature as well. The reaction of 1-methylallyl peroxy radical to $\text{C}_4\text{H}_6 + \text{O}_2\text{H}$ was also found to be endothermic.

Table 4: High-pressure limiting rate constants for the recombination of allyl radicals with molecular oxygen.

	Allyl + O_2	1-MA + O_2	2-MA + O_2
$k_\infty / \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$3.5 \cdot 10^{11}$ [Ref. 12]	$\approx 8.1 \cdot 10^{11}$ [Ref. 29]	$5.1 \cdot 10^{11}$

Compared to the allyl + O_2 reaction, (1) and (2) are faster by about a factor of two to three in the investigated pressure range and show either a small (1-MA) or no (2-MA) pressure dependence. Thus both reactions are very close to the high-pressure limit already at ≤ 10 mbar, whereas for allyl + O_2 rate constants at 10 mbar still deviate from k_∞ by a factor of about two.^{10, 11} The deduced values for k_∞ are summarised in Table 4, they increase in the order allyl < 2-MA < 1-MA. Obviously, the increase of k_∞ (instead of a decrease) upon methylation rules out simple steric effects to be responsible for the different reactivities.

It is well-known that the effect of pressure (and temperature) on the overall rate constant of recombination reactions can be treated in terms of Rice-Ramsperger-Kassel-Marcus / Master-Equation (RRKM/ME) type of calculations and is governed by a complex interplay of collisional activation/deactivation steps and microcanonical rate constants corresponding to the possible reaction steps of the association complex.^{51, 52} Although such a full RRKM/ME analysis of the methylallyl radical + O_2 system would be beyond the scope of this paper, it is tempting to draw a direct comparison with the corresponding, prototypical alkyl radical + O_2 system. Recently, Miyoshi⁵³ theoretically analysed systematic trends in the high-pressure and low-pressure limiting rate constants of several alkyl radical + O_2 reactions and derived molecular size dependent falloff rate constant rules. In his RRKM/ME analysis, subsequent dissociation/isomerization reaction channels, which are actually known to be important for the alkyl + O_2 system but are not relevant in our case,^{54, 55} have been ignored intentionally to derive "hypothetical" fall-off curves for the isolated recombination step. In this sense, the identified trends should be well transferable to the allylic radical + O_2 system. Note in this context, however, that the well depth, i.e. the binding energy of the association complex is much lower for resonance-stabilized radicals compared to simple alkyl radicals.

The high-pressure limiting rate constants k_{∞} , in agreement with experimental data, decrease in the order tertiary > secondary > primary but were found to be nearly the same within the groups of primary, secondary, or tertiary alkyl radicals of different size.^{53, 55} This trend goes along with more attractive potential energy curves at short internuclear distances resulting from the higher well-depth, i.e. bond dissociation energies (BDE) of the alkylperoxy radicals, which decrease in the same order.⁵³ We assume that a very similar mechanism is operative in allyl and methylated allyl radicals and speculate that the overall reactivity of the radical may be understood as a superposition of the reactivities of the different radical sites. Allyl and 2-MA have two primary (terminal) sites for recombination with O₂ (note that the central site does not lead to a resonantly stabilized peroxy radical), while 1-MA has a secondary (non-terminal) and a primary site, hence consistent with the highest k_{∞} for 1-MA. Also note that in 1-MA the BDE is larger for the secondary peroxide compared to the primary one (see Scheme 2) and it is largest for the Z-1-MA isomer. Moreover, for allylperoxy the computed BDE is lower than for 2-MA, hence consistent with the smallest observed k_{∞} value for the allyl radical reaction. Altogether, it can be concluded that the deduced trend of k_{∞} for the allylic radicals is consistent with the corresponding alkyl radical trend.

Myoshi also analyzed the low-pressure limiting rate constants k_0 that are in turn directly related to the observed pressure dependence of the reaction. Mostly reflecting the density of state of the association complex around the dissociation threshold, k_0 was found to increase with the molecular size of the alkyl radical, but was the same for same-sized C₄ radicals irrespective of the radical structure.⁵³ Transferred to the allylic radicals studied in our work, this would correspond to $k_0(1\text{-Me}) \approx k_0(2\text{-Me}) > k_0(\text{Allyl})$. As the falloff of the recombination reaction is determined by the interplay of collisional deactivation and reverse dissociation, a lower k_0 leads to a falloff of the high-pressure limiting rate constant at higher bath gas pressures. In other words, as it is typically found for the falloff behavior of unimolecular dissociation and recombination reactions at low temperatures,⁵⁶ larger molecules already reach the high pressure limit at overall lower pressures. Moreover, assuming a similar broadening of the falloff curve, the same k_0 (as deduced for 1-MA and 2-MA) will cause the falloff to take place at higher pressures when k_{∞} increases (as it is the case going from 2-MA to 1-MA). Consequently, at pressures in the vicinity of the falloff range, the pressure dependence can be expected to increase in the order 2-MA < 1-MA < allyl – again in qualitative agreement with the finding of this and previous work.^{10, 11, 29} In case of 2-MA, however, the already mentioned, minor isomerization channel of the RO₂ adduct to a R'OOH radical structure via a six-membered, low-lying H-transfer pathway,²⁸ followed by collisional stabilization of that product may contribute to the observed pressure dependence as well.

Summary and Conclusions

The radicals 1-methylallyl (1-MA) and 2-methylallyl (2-MA) were generated in a flow reactor by photolysis of their halides at 213 nm. Rate constants were determined at 298 K and at reactor pressures p_r between 1 and 3 mbar. Radicals were ionized by synchrotron radiation and electrons and ions were detected by

a photoelectron/photoion coincidence spectrometer. The identity of the detected species was confirmed by photoion mass selected threshold photoelectron spectroscopy (ms-TPES). In all experiments, rate constants were extracted from the decay of the reactant signal, because the peroxy radical products could not be detected. Due to the low binding energies (74 – 83 kJ·(mol)⁻¹) and the large geometry change upon ionisation they ionize dissociatively. The recombination of 2-MA with molecular oxygen exhibits no pressure dependence and yields a high-pressure rate constant of $k_{\infty} = (5.2 \pm 1.0) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For 1-MA, a conformer-selective kinetic trace for the E-conformer was recorded, as well as traces for a mixture of E- and Z-isomer. However, the rate constants are almost identical within the error bars. A small positive pressure dependence is observed, in agreement with previous work.²⁹ Rate constants between $(3.5 \pm 0.7) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(4.6 \pm 0.9) \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were determined for pressures between 1 and 3 mbar. As expected for the recombination of larger molecules at low temperatures, compared to allyl the high-pressure limit for 1- and 2-MA is already reached at a lower pressure. The high-pressure rate constant k_{∞} increases upon methylation in the order $k_{\text{allyl}} < k_{2\text{-MA}} < k_{1\text{-MA}}$. The trend is reflected in a slight increase in the bond dissociation energies of the corresponding peroxy radicals presumably going along with more attractive bonding potentials. It confirms the relationship between high pressure limiting rate constant on the one hand and size of the radical, reaction site and bond dissociation energy on the other hand, derived previously for the alkyl + O₂ reaction system.

Conflicts of interest

There are no conflicts to declare.

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