OH-Initiated Photooxidations of 1-Pentene and 2-Methyl-2-propen-1-ol: Mechanism and Yields of the Primary Carbonyl Products

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The products of the gas-phase reactions of OH radicals with 1-pentene and 2-methyl-2-propen-1-ol (221MPO) at $T = 298 \pm 2$ K and atmospheric pressure were investigated by using a 4500 L atmospheric simulation chamber that was built especially for this work. The molar yield of butyraldehyde was 0.74 ± 0.12 mol for the reaction of 1-pentene. This work provides the first product molar yield determination of formaldehyde (0.82 ± 0.12 mol), 1-hydroxypropan-2-one (0.84 ± 0.13 mol), and methacrolein (0.078 ± 0.012 mol) from the reaction of 221MPO with OH radicals. The mechanism of this reaction is discussed in relation to the experimental results. Additionally, taking into consideration the complex mechanism, the rate coefficients of the reactions of OH with formaldehyde, 1-hydroxypropan-2-one, and methacrolein were derived at atmospheric pressure and $T = 298 \pm 2$ K.; the obtained values were $(8.9 \pm 1.6) \times 10^{-12}$, $(2.4 \pm 1.4) \times 10^{-12}$, and $(22.9 \pm 2.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively.

1. Introduction

Oxygenated volatile organic compounds (OVOCs) are emitted into the atmosphere as primary pollutants from a wide number of anthropogenic and biogenic sources.[1,2]

The volatile organic compounds (VOC) inventory, prepared by the U.S. Environmental Protection Agency (2005) for the year 2001, shows that 17 117 701 tons of OVOCs are emitted per year in the USA from anthropogenic sources. The major sources are the emissions from the incomplete combustion of fossil fuels: vehicular emissions (28.9 %), off-highway sources (15.3 %), and emissions from solvent use (29.2 %).[3]

Unsaturated alcohols are a class of OVOCs that are used increasingly, because they typically combine satisfactory technical performance in chemical industry applications with low costs and low health risks. Specifically, the applications of 2-methyl-2-propen-1-ol (221MPO), as cited by the manufacturers, are as an intermediate material for synthetic perfume[4] and as an additive in polycarboxylate superplasticizers and resins.[5] In China, chemical companies are producing around 500 mt per month of 221MPO.[6] To assess the impact of this chemical species on air quality, a detailed understanding of the kinetics and mechanisms of its atmospheric degradation is required.

In the troposphere, the main gas-phase removal process of unsaturated alcohols is the reaction with OH radicals. Oxidations with Cl atoms, O$_3$, and NO$_3$ radicals are other important degradation pathways.[7–13] Although the kinetics of these reactions are reasonably well-known, or can often be estimated, the corresponding reaction mechanisms and the products formed, under tropospheric conditions, are generally much less well understood.

It is known that the OH-initiated photooxidation mechanism of unsaturated alcohols leads to aldehydes, ketones, and organic nitrates as major products.[14–20] The identification and quantification of the carbonyl products of the reactions of OVOCs is of great importance, because they would be secondary pollutants that are involved in processes such as photochemical smog[21] or peroxyacyl nitrates (PANs) formation.[22]

To the best of our knowledge, no previous experimental studies on the identification of the products of the OH-initiated photooxidation of 221MPO and quantification of their yields have been reported in the literature. Thus, the main objective of this work was the identification of the primary products and the quantification of the product yields of the OH-initiated photooxidation of 221MPO.

In this paper a description of the experimental setup built for this purpose is presented, in addition to a study of the product yields of the gas-phase reaction of OH with 1-pentene, firstly with the aim of validating the reactor. Additionally, the rate coefficient values of the reactions of OH with formaldehyde, 1-hydroxypropan-2-one, and methacrolein (primary products of OH + 221MPO) were derived from fitted experimental data, considering a complex mechanism in which these are products of the OH-initiated photooxidation of 221MPO.

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Experimental Section

Experimental Setup

Experiments were carried out in an indoor photochemical reactor with a volume of 4489 L (approximated to 4500 L), which was built by lining an aluminium frame [1.34 m (L) $\times$ 1.34 m (W) $\times$ 2.5 (H)] with a 100 µm-thick fluorinated ethylene propylene (FEP)-Teflon film (DuPont). The variation of the volume was calculated as less than 2% from the dilution factor of ethanol, expanding the chamber to its maximum without changes in the internal pressure. The pressure in the chamber was measured with an MKS Baratron capacitance manometer 626A (pressure range between 0–1000 torr). The chamber was filled with ultra-pure air at a pressure of 1000 torr and no measurable leaks were observed after three days, thus ensuring that the input of impurities from the surroundings was highly unlikely. The reactor was surrounded by 12 black lamps (Philips, 36W) with $\lambda_{max} = 365$ nm and 12 germicidal lamps (Philips 36W) with $\lambda_{max} = 254$ nm. To maximize the light intensity in the chamber, reflective, stainless-steel sheeting covered the inside wall of the banks of lamps.

The gas-supply system had two parts. The first one was the bath gas-supply system in which ultra-pure air was provided by a conventional air compressor with the following sequence of filters: post cooler and water purge, a coalescence filter, four cyclonic particulate filters of 40, 5, 1, 0.01 µm thickness, a filter of VOCs, and a water filter (the latter six were supplied by FESTO). During the experiments, the relative humidity (RH) and temperature were measured in the chamber by an E + E Electronic 31 Series humidity and temperature transducer and the values obtained were lower than 2.6% for RH (the quantification limit of this sensor) and $T = 298 \pm 2$ K. The concentrations of O_3 and NO_x were monitored with Serinus 10 and Serinus 40 analyzers supplied by Ecotech, and the values were on the order of parts per billion. The absence of VOCs was checked by gas chromatography (GC). Thus, the air quality obtained ensured adequate experimental conditions. After each experiment, the chamber was cleaned by flowing through purified air, typically for 8 h, until there were no VOCs and the required humidity conditions were reached.

The second part was the reagent injection system. The chamber was connected by Teflon tubing to a conventional greaseless vacuum system built with Pyrex glass that had three calibrated volume flasks. The pressure in this system was measured by two MKS Baratron capacitance manometers 626 A, with pressure ranges of 0–10 torr and 0–1000 torr. The gaseous reagents were carried into the center of the reactor by passing ultra-pure N_2 through 1.2 m stainless steel tubing. The liquid reagents were introduced in a 5 mL Pyrex bulb with a silicone/Teflon septum and carried into the chamber through a port in the front wall, with a stream of ultra-pure N_2. The reagents inside the chamber were mixed by a Teflon fan.

OH radicals were generated by the photolysis of ethyl nitrite (CH_3CH_2ONO) at wavelengths > 300 nm, and NO was added to the reactant mixtures to suppress the formation of O_3, and hence, NO_3 radicals.[23]

Photolysis was typically carried out in steps of $t = 15$–180 s, by switching on four black lamps, with a conversion of the reactant of between 5 and 15%. In addition, irradiation experiments were performed in the absence of the OH radical source to verify that direct photolysis of the studied VOCs did not occur. The stability and wall losses of the individual VOCs were also investigated by introducing them into the chamber and monitoring their concentra-

tion over time. The total duration of each experiment was approximately 4–5 h, and wall loss of the studied VOCs was not detected, within the limits of detection of the GC-flame ionization detector (FID), during this period of time.

The chamber had three additional stainless-steel tubes so that samples from the center, upper, and lower sections of its volume could be taken to check the homogeneity of the gas mixture. These were connected by Teflon tubing to a 5 mL evacuated loop contained in an 8 port manual valve VICI Valco Instruments Co. Inc. The detection system was a PerkinElmer Clarus 500 Gas-Chromatograph coupled to a PerkinElmer Clarus 560S Mass Spectrometer (GC–MS) and a FID. This setup will be hereafter be named GC–MS–FID. If the sampling technique was solid-phase microextraction (SPME) a port in the center of the front wall of the chamber, with a silicone/Teflon septum, was employed.

Studies of the Product Yields

The yield of a primary product of the reaction of a given unsaturated VOC with the OH radical was obtained from the slope of a plot of the absolute amount of product (P) formed, over time t, against the absolute amount of the VOC consumed ($[VOC]_0 - [VOC]_t$, in which $[VOC]_0$ and $[VOC]_t$ are the VOC concentrations at time 0 and t, respectively).

Primary products may also react with OH radicals, thus the concentration of the product at time t ($[P]_t$) was corrected to take into account its secondary reaction with the OH radical [Eq. (1)]:

$$F \times [P]_t = \alpha([VOC]_0 - [VOC]_t) \tag{1}$$

in which α is the yield of the product and F represents the correction coefficient for the product. This correction used a two-step mechanism, the formation of P through reaction of OH radicals with the VOC, followed by reaction of OH radicals with P. This approach yields Equation (2), developed by Atkinson et al. (1982):[24]

$$F = \frac{k_{VOC} - k_P}{k_{VOC}} \times \frac{1 - \frac{[VOC]_t}{[VOC]_0}}{\left(\frac{[VOC]_t}{[VOC]_0}\right)^{\frac{k_P}{k_{VOC}}} - \frac{[VOC]_t}{[VOC]_0}} \tag{2}$$

in which k_{VOC} and k_P represent the rate coefficients for the reactions of the OH radical with the unsaturated VOC and the primary product, respectively.

To verify the performance of the reactor, experiments to measure the product yields at $T = 298 \pm 2$ K and a pressure of 750 ± 20 torr, of gas-phase Reaction (1) were performed:

$$OH + 1\text{-pentene} \rightarrow primary\,products \quad (k_1) \tag{1}$$

Once the reactor was validated, product yield studies were carried out for Reaction (2):

$$OH + 221MPO \rightarrow primary\,products \quad (k_2) \tag{2}$$

The primary products of both reactions were identified and quantified by GC–MS–FID by applying three sampling methods: A) The samples were injected directly into the GC from the chamber through the evacuated 8 port valve. B) Concentration by SPME with further derivatization with o-(2, 3, 4, 5, 6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) on a 65 µm polydimethylsiloxane/divinylbenzene (PDMS–DVB) microfiber provided by Supel-

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co.[25] This involved a 2 min headspace extraction from 5 mL of aqueous solution (17 mg mL^{-1} of PFBHA) placed in a 20 mL vial. A microfiber covered with the derivatizing agent was exposed to the VOCs in the chamber for $t = 20$ s and then injected into the GC. The PFBHA carbonyl oxime formed was desorbed thermally in the injection port of the GC–MS–FID. If this technique was applied, the PFBHA oximes were identified and quantified. C) Concentration by SPME with exposure of the gas sample for 1 min to the 65 µm PDMS-DVB microfiber and subsequent injection into the GC–MS–FID.

Despite the good results obtained by combining SPME with the derivatization of analytes, whenever possible, the introduction of a derivatization step was avoided during sampling, due to the sensitivity and reproducibility problems that may arise in some cases from the derivatization reaction itself. Therefore, Method C was preferred to Method B if practical.

In each case, calibration curves of the pure compounds and mixtures of reactants and products were obtained by using commercial standards to check for possible interference.

The initial reactant concentrations in the product yield determination experiments (in molecules cm^{-3}) were: 4.5–5.4×10^{14} for 1-pentene, 6.6–6.8×10^{14} for CH$_3$CH$_2$ONO, and 0.97–1.67×10^{14} for NO in Reaction (1), 2.2–3.7×10^{14} for 221 MPO, 7.6–11.0×10^{14} for CH$_3$CH$_2$ONO, and 1.0–9.8×10^{14} for NO in Reaction (2).

Determination of Rate Coefficients

In the same reactor, HCOH, CH$_3$COCH$_2$OH, and CH$_2$=C(CH$_3$)CHO were generated in situ from the OH-radical-initiated reaction of 221MPO [Reaction 2], and the rate coefficients, at $T = 298 \pm 2$ K and a pressure of 750 ± 20 torr, of the gas-phase Reactions (3)–(5) were determined:

$$OH + HCHO \rightarrow products \quad (k_3) \quad (3)$$

$$OH + CH_3COCH_2OH \rightarrow products \quad (k_4) \quad (4)$$

$$OH + CH_2=C(CH_3)CHO \rightarrow products \quad (k_5) \quad (5)$$
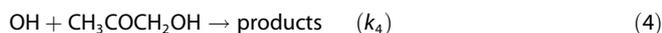
The kinetic model employed to derive k_3, k_4, and k_5 considers Reactions (3), (4), and (5) as parallel reactions, and consecutive to Reaction (2). Assuming that Reactions (2)–(5) are the only processes involving loss of 221MPO and the primary carbonyl products, the variation of the primary carbonyl product concentration with time is given by Equation (3):[24]

$$[carbonyl\ product]_t = \frac{\alpha[221MPO]_0 k_2}{(k_2 - k_y)} \left(e^{-k_2[OH]t} - e^{-k_y[OH]t} \right) \quad (3)$$

in which α is the yield of HCHO, CH$_3$COCH$_2$OH, or CH$_2$=C(CH$_3$)CHO from Reaction (2) and [carbonyl product]$_t$ is the concentration of each primary product at time t, [221MPO]$_0$ is the initial alcohol concentration, and k_2 is the rate constant for Reaction (2). k_y the rate constant for Reactions (3), (4), or (5) (i.e. k_3, k_4, or k_5) and [OH]$_t$ is the OH radical concentration at time t. In a rearranged form, and considering that ln[221MPO]$_0$/[221MPO]$_t = k_2$[OH]$_t$ and that the radical concentration is constant,[26,27] Equation (3) becomes [Eq. (4)]:

$$[carbonyl\ product]_t = A \left(e^{-x} - e^{-Bx} \right) \quad (4)$$

in which $A = \alpha[221MPO]_0 k_2/(k_y - k_2)$, $B = k_y/k_2$, $x = \ln([221MPO]_0/[221MPO]_t)$, and [221MPO]$_t$ is the 221MPO concentration at time t.

An analysis of measurements of [carbonyl product]$_t$ as a function of the extent of the reaction (x), allows k_y/k_2 to be obtained by fitting the experimental data with Equation (3); hence, allowing the rate coefficients k_y to be determined.

Initial concentrations of the reactants (in molecules cm^{-3}) were: 1.99–3.24×10^{14} for 221MPO, 0.81–1.3×10^{15} for CH$_3$CH$_2$ONO (the OH radical source), and 1.3–2.1×10^{15} for NO in Reaction (2). The photolysis was typically carried out in steps of $t = 15$–180 s, switching on six black lamps, with a conversion of 221MPO of approximately 98–99%.

The rate of loss of reactants and products, due to photolysis, dark reactions, and wall processes was found to be negligible.

Materials

The chemicals used were: N$_2$ (Linde 999,999%. CAS: 7727-37-9), O$_2$ (Linde 99.999%. CAS: 7782-44-7), He (Linde; >99.9995%. CAS: 7440-59-7), ultra-pure air (synthetic air; Linde), NO (AGA; >99,0%; CAS: 10102-43-9), 1-pentene (Aldrich; ≥98,5%; CAS: 109-67-1), 1-hydroxypropan-2-one (Aldrich; 90%;CAS: 116-09-6), anhydrous butyraldehyde (Sigma Aldrich; 99%; CAS: 123-72-8), formaldehyde (Sigma Aldrich; 37 wt% in water; CAS: 50-00-0), PFBHA hydrochloride (Aldrich; ≥98%; CAS: 57981-02-9), and 221MPO (Fluka; ≥98%; CAS: 513-42-8). Ethyl nitrite was synthesized and purified in our laboratory as described in Ref. [28]. The organic compounds were degassed by repeated freeze–pump–thaw cycling and purified by vacuum distillation until gas chromatographic analysis revealed no observable impurities.

3. Results and Discussion

Prior to determining product yields and to the kinetic experiments, a series of experiments were performed to confirm that depletion rates of 1-pentene, butyraldehyde, 221MPO, 1-hydroxypropan-2-one, formaldehyde, and methacrolein (the reactants and products of the studied reactions) by photolysis, dark reactions, and wall losses were negligible compared with the rate of the reaction in all cases.

3.1 Yields of the Primary Products of 1-Pentene + OH [Reaction (1)]

The identified primary products for Reaction (1) were butyraldehyde and formaldehyde; the latter was identified from its PFBHA derivative.

Sampling Method A was used in the Reaction (1) for the sampling of 1-pentene and butyraldehyde. Sampling Method B was used for butyraldehyde and formaldehyde. Calibration curves, in air as the bath gas, were obtained by using Method A. A mixture of reactants and products was used and pure samples of each compound were used as standards; the slopes of the two curves obtained agreed within 5%. If Method B was used for butyraldehyde and formaldehyde, calibration was not possible. For butyraldehyde, the chromatographic peak of the PFBHA derivative split into two unresolved signals. For formaldehyde, the calibration curves of the standards, in

mixtures of 1-pentene, butyraldehyde, and formaldehyde, showed some scattering in a reproducible manner. This may be attributed to competition of the different carbonyl compounds for the PFBHA molecules attached to the microfiber.[29]

The molar yield (α) of butyraldehyde was obtained from the slope of the plots of the absolute amount of the product formed by Reaction (1) as a function of the absolute amount of VOC (1-pentene) consumed (Figure 1). The data were fitted
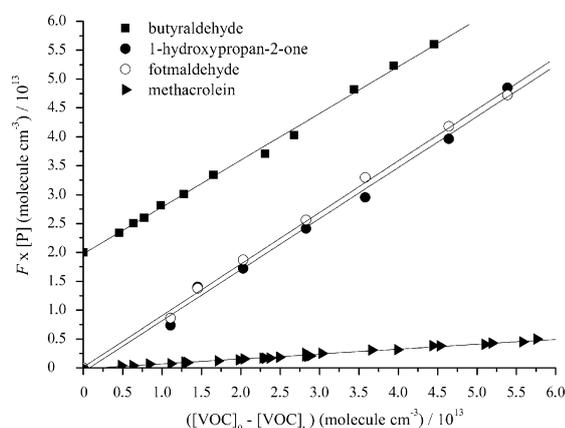
Figure 1. Plots of the amounts of products (P; these values are corrected by taking into consideration the reactions of these products with the OH radicals) against the concentration of 1-pentene [Reaction (1)] or 221MPO [Reaction (2)], denoted as VOC, for Reactions (1) and (2). The products are butyraldehyde for Reaction (1), and formaldehyde, 1-hydroxypropan-2-one, and methacrolein, for Reaction (2). The data for butyraldehyde have been displaced vertically by 2×10^{13} molecule cm^{-3}.

by using Equation (1) and linear least-squares analysis. The identified product, the number of experiments, the maximum value of the F factor, and the values of α for each experiment are summarized in Table 1. The value of α obtained for butyraldehyde was 0.74 ± 0.12 mol. To the best of our knowledge, there is only one previous study of the molar yield of butyraldehyde from Reaction (1), which was carried out by Atkinson et al.;[19] they used GC–FID and Fourier-transform infrared (FTIR) absorption spectroscopy, and their reported value was 0.73 ± 0.09 mol, under similar experimental conditions. Hence, taking into account the combined uncertainties, both values are in good agreement.

For each experiment, the experimental errors are quoted as twice the statistical deviation ($2\sigma_{n-1}$) stemming from the least-squares fit of the plots of $F \times [P]_t$ versus ($[VOC]_0 - [VOC]_t$) and the values are shown in Table 1. The uncertainties quoted for the final reported α values are twice the statistical deviation ($2\sigma_{n-1}$) arising from the average of the values obtained in each experiment. We estimate an uncertainty of 10% in our measurements, due to systematic errors, that could be added to the final reported value of the rate coefficient. With our experimental setup it is possible to reliably reproduce previous experimental results.

3.2 Yields of the Primary Products of 221MPO + OH [Reaction (2)]

The identified primary products of Reaction (2) were formaldehyde (HCHO), 1-hydroxypropan-2-one (CH$_3$COCH$_2$OH), and methacrolein (CH$_2$=C(CH$_3$)CHO). Sampling Method B was used for Reaction (2) for the identification and quantification of CH$_3$COCH$_2$OH and HCHO, and Method C was employed for 221MPO, CH$_3$COCH$_2$OH, and CH$_2$=C(CH$_3$)CHO.

The calibration curves for each pure compound, as the standard, in air or in a mixture of reactants and products by using Method B or C are in agreement within 5%. However, for the quantification of 221MPO, CH$_3$COCH$_2$OH, and CH$_2$=C(CH$_3$)CHO, Method C was chosen, because it has a higher sensitivity than Method B. If Method B was used for HCHO, the calibration curves showed a reproducible intercept, attributed to the formation of the HCHO–PFBHA derivative, probably due to the presence of trace amounts of HCHO in the ambient air[17] or in the water of the PFBHA solution.[30]

The α values for HCHO, CH$_3$COCH$_2$OH, and CH$_2$=C(CH$_3$)CHO were obtained and the data was treated in the same way as described for butyraldehyde. Typical plots are shown in Figure 1. The identified product, the number of experiments, the maximum value of F, and the α values for each experiment are summarized in Table 1. The α values obtained in this work were 0.84 ± 0.13, 0.82 ± 0.12, and 0.078 ± 0.012 mol for HCHO, CH$_3$COCH$_2$OH, and CH$_2$=C(CH$_3$)CHO, respectively. To the best of our knowledge this is the first report of the carbonyl-product yields for the Reaction (2). The uncertainties were determined in the same way as for Reaction (1).

As shown in Figure 2, the present results suggest that the reaction proceeds through the following pathways: the addition of OH radicals to the unsaturated alcohol and hydrogen abstraction.

Table 1. Yields of the quantified products for Reactions (1) and (2), and maximum F factor for each individual experiment along with averaged values of α.

VOC	Identified product	Expt. no.	Maximum value of F	α [mol]
1-pentene	butyraldehyde	1	1.075	0.72 ± 0.1
		2	1.018	0.69 ± 0.06
		3	1.013	0.81 ± 0.02
		average		**0.74 ± 0.12**
	formaldehyde	–	–	–
221MPO	1-hydroxypropan-2-one	1	1.019	0.79 ± 0.02
		2	1.003	0.77 ± 0.02
		3	1.005	0.72 ± 0.04
		4	1.001	0.68 ± 0.1
		average		**0.74 ± 0.11**
	formaldehyde	1	1.080	0.92 ± 0.02
		2	1.017	0.84 ± 0.04
		3	1.019	0.80 ± 0.02
		4	1.003	0.80 ± 0.06
		average		**0.84 ± 0.13**
	methacrolein	1	1.034	0.072 ± 0.002
		2	1.064	0.084 ± 0.004
		3	1.037	0.079 ± 0.002
		average		**0.078 ± 0.006**

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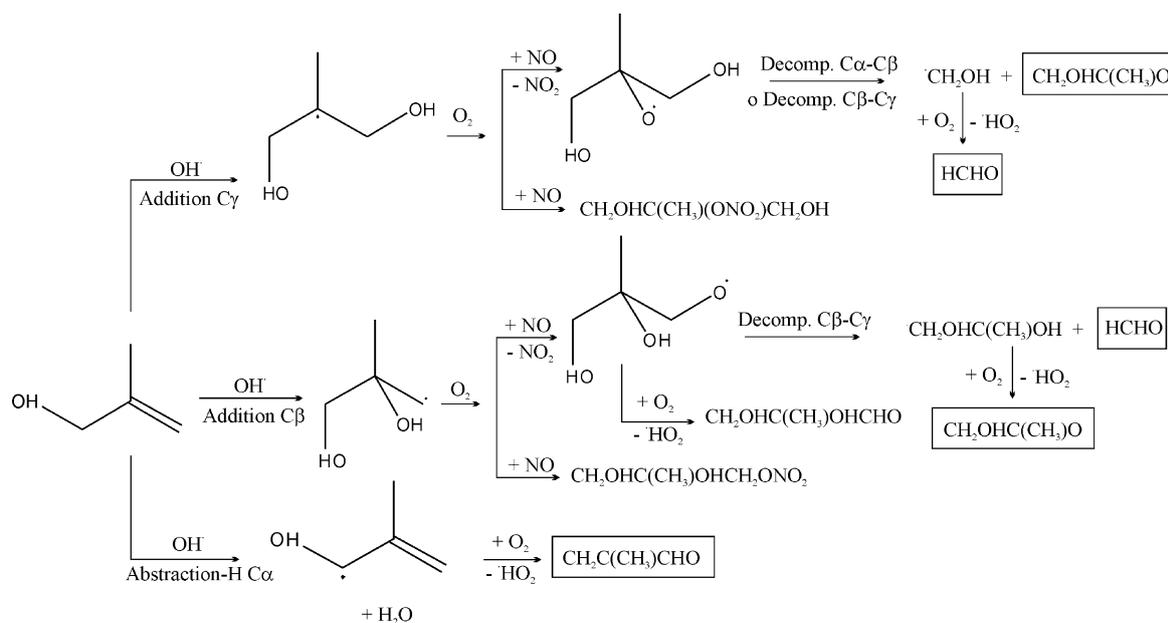
Figure 2. Proposed mechanism for Reaction (2). The identified reaction products are shown in boxes.

The main reaction pathway is the addition of the OH radical to the β- and γ-carbon atoms of the double bond in 221MPO, leading to the formation of two possible β-hydroxyalkyl radicals. In the presence of O_2 these react to form two possible β-hydroxyalkylperoxy radicals, which undergo reactions with NO to produce β-hydroxyalkoxy radicals. The β-hydroxyalkoxy radical resulting from OH addition to the γ-carbon atom can decompose to the form the primary products observed in this study. In contrast, the β-hydroxyalkoxy radical resulting from OH addition to the β-carbon atom can decompose to yield the products observed in this study or react with O_2 to form $CH_2OHC(CH_3)OHCHO$, which was not observed in the present experiments. This led us to the conclusion that $CH_2OHC(CH_3)OHCHO$ formation is negligible under our experimental conditions. Thus, according to the experimental results, it is not possible to distinguish which pathway, addition of the OH to the β- or γ-carbon atoms, is dominant. However, it is possible to confirm that the reaction occurs through the decomposition of β-hydroxyalkoxy radicals.

The only product observed from hydrogen abstraction is methacrolein, due to OH radical attack on the hydrogen atom attached to the α-carbon atom, as shown in Figure 2. This led to the formation of an α-hydroxyalkyl radical, which, in the presence of O_2, reacts to form a β-hydroxyperoxy radical; this radical undergoes HO_2 radical elimination to form methacrolein.

As can be inferred from the α values for each product, the main reaction pathway is OH radical addition to the double bond; hydrogen abstraction is a minor pathway. These results are consistent with the oxidation mechanism reported by Calvert et al.[3] for this alcohol.

However, the total mass balance is still incomplete, at approximately 87%, although other products may be found by using different detection techniques. It is possible to infer the formation of β-hydroxynitrates, due to reaction of NO with the two possible β-hydroxyalkylperoxy radicals. This takes into account that Aschmann et al. (1997),[16] Reisen et al. (2003),[31] Ferronato et al. (1998),[18] Chan et al. (2009),[32] and Alvarado et al. (1999)[20] observed the formation of β-hydroxynitrates as products of the reactions of unsaturated alcohols with the OH radical in the presence of NO_x and O_2. Also, Ferronato et al. (1998),[18] Chan et al. (2009),[32] and Alvarado et al. (1999)[20] estimated or measured their yields to be between 0.05 and 0.1 mol.

3.3 Determination of the Rate Coefficients

Sampling Method B was employed for the kinetic studies of Reaction (3) and Method C for Reactions (4) and (5).

k_3, k_4, and k_5 were derived from nonlinear least-squares fits of the experimental data of [carbonyl product]$_t$ versus ln-([221MPO]$_0$/[221MPO]$_t$) plots to Equation (3). The nonlinear fit gives the B parameter (k_y/k_2), and these rate coefficient ratios, given in Table 2 (along with a summary of the results and experimental details) are placed on an absolute basis by use of the rate coefficient value k_2 of $(9.3 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} provided by Cometto et al. (2008).[13] The obtained values of $(8.9 \pm 1.6) \times 10^{-12}$, $(2.4 \pm 1.4) \times 10^{-12}$, and $(22.9 \pm 2.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for k_3, k_4, and k_5, respectively, are in agreement with the IUPAC recommended values of $(8.5 \pm 1.6) \times 10^{-12}$ for k_3, $(3.0 \pm 1.0) \times 10^{-12}$ for k_4, and $(29 \pm 7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for k_5.[33] The IUPAC values are averages of the rate coefficients obtained by different experimental methods.

For each individual experiment the experimental errors of k_y/k_2 are quoted as twice the statistical deviation ($2\sigma_{n-1}$) stemming from the nonlinear least-squares fit of the plots mentioned above. k_3, k_4, and k_5 informed uncertainties for each ex-

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Table 2. Summary of the initial concentrations of 221MPO, k_y/k_2 ratios, the values of k_y for each experiment, and the average values of k_3, k_4, and k_5.

Carbonyl product	Expt. no.	[221MPO]$_0$	k_y/k_2	$k_y/10^{12}$ [molecules cm^{-3} s^{-1}]
formaldehyde	1	3.24×10^{14}	0.10 ± 0.01	9.3 ± 1.1
	2	2.07×10^{14}	0.09 ± 0.01	8.4 ± 1.1
	average			8.9 ± 1.6
1-hydroxypro-pan-2-one	1	3.24×10^{14}	0.023 ± 0.01	2.1 ± 0.9
	2	2.07×10^{14}	0.024 ± 0.009	2.2 ± 0.8
	3	3.12×10^{14}	0.031 ± 0.01	2.9 ± 0.9
	average			2.4 ± 1.4
methacrolein	1	1.99×10^{14}	0.261 ± 0.001	24.3 ± 0.6
	2	2.39×10^{14}	0.232 ± 0.006	21.6 ± 1.0
	average			22.9 ± 2.3

periment include the error in the B parameter and in k_2. The informed values of the second-order rate coefficients k_3, k_4, and k_5, are the average of the independent experiments, and we choose to quote for them error values that encompass the extremes of the individual determinations. As noted by Baker et al.[26] with the method used, the sensitivity decreases as the ratio k_y/k_2 decreases, and derivation of k_y becomes difficult for values of $k_y/k_2 < 0.2$. Although, the values of R^2 of the nonlinear fits are > 0.98, especially for k_4, we could consider an error factor of up to 2, given the indirect and relative nature of the method.

Typical plots are shown in Figure 3 for Reactions (3)–(5). For each product, CH$_3$COCH$_2$OH, HCHO, and CH$_2$=C(CH$_3$)CHO, two simulated curves are provided, changing the k_y/k_2 value by a factor of two. It can be observed that the scattering is lower than the proposed limits. Thus, in spite of the limitations of this method, it can be assumed that the experimental measurements obtained with the present setup are reliable. Therefore, this method should be a useful tool to determine the rate constants of reactions of compounds that are not commercially available.
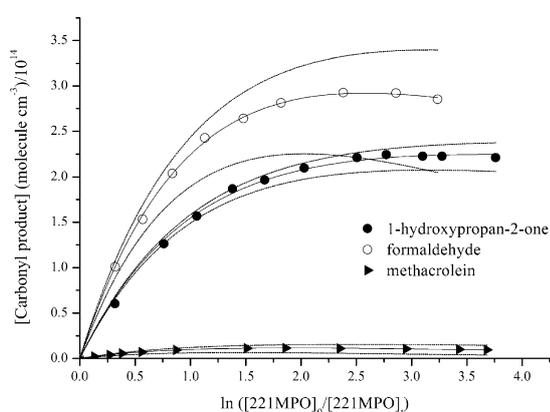
Figure 3. Plots of [carbonyl product]$_t$ versus ln([221MPO]$_0$/[221MPO]$_t$) for the formation of formaldehyde, 1-hydroxypropan-2-one, and methacrolein from Reaction (2), together with curves calculated (dotted lines) by using Equation (3) for different values of k_y/k_2.

4. Conclusions

A 4500 L atmospheric simulation chamber was built to study the OH-initiated photooxidations of 1-pentene [Reaction (1)] and 221MPO [Reaction (2)]. By using this experimental setup we identified that the products of Reaction (1) were butyraldehyde and formaldehyde and showed that Reaction (2) resulted in the formation of formaldehyde, 1-hydroxypropan-2-one, and methacrolein; the molar yields of which were determined to be 0.82 ± 0.12, 0.84 ± 0.13, and 0.078 ± 0.012 mol, respectively. This is the first example of the determination of the product molar yield of formaldehyde, 1-hydroxypropan-2-one, and methacrolein from Reaction (2). The rate coefficients of the reactions of OH with formaldehyde, 1-hydroxypropan-2-one, and methacrolein were derived at atmospheric pressure and $T = 298 \pm 2$ K; the obtained values were $(8.9 \pm 1.6) \times 10^{-12}$, $(2.4 \pm 1.4) \times 10^{-12}$, and $(22.9 \pm 2.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, respectively. From our experimental results, we were able to infer that the main reaction pathway for Reaction (2) is the OH radical addition to the double bond.

This work shows that our atmospheric simulation chamber should be a useful tool to determine the rate constants of reactions of compounds that are not commercially available.

[1] J. Kesselmeier, M. Staudt, *J. Atmos. Chem.* **1999**, *33*, 23.
[2] G. König, M. Brunda, H. Puxbaum, C. N. Hewitt, S. C. Duckman, J. Rudolph, *Atmos. Environ.* **1995**, *29*, 861.
[3] J. G. Calvert, A. Melluoki, J. J. Orlando, M. J. Pilling, T. J. Wallington, *Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York **2011**; ISBN 978-0-19-536581-8.
[4] http://www.unikem.com.cn.
[5] http://www.gzqschem.com.
[6] http://www.made-in-china.com/products-search/hot-china-products/Methallyl_Alcohol.html.
[7] P. Liang, Y. J. Mu, V. Daële, A. Mellouki, *Chem. Phys. Lett.* **2011**, *502*, 154.
[8] Y. Rudich, R. Talukdar, J. B. Burkholder, A. R. Ravishankara, *J. Phys. Chem.* **1995**, *99*, 12188.
[9] M. Hallquist, S. Langer, E. Ljungström, I. Wängberg, *Int. J. Chem. Kinet.* **1996**, *28*, 467.
[10] E. Grosjean, D. Grosjean, *Int. J. Chem. Kinet.* **1994**, *26*, 1185.
[11] D. Grosjean, E. Grosjean, E. L. Williams II, *Int. J. Chem. Kinet.* **1993**, *25*, 783.
[12] J. J. Orlando, G. S. Tyndall, N. Ceazan, *J. Phys. Chem. A* **2001**, *105*, 3564.
[13] P. M. Cometto, P. R. Dalmasso, R. A. Taccone, S. I. Lane, F. Oussar, V. Daële, A. Mellouki, G. Le Bras, *J. Phys. Chem. A* **2008**, *112*, 4444.

These are not the final page numbers! ⬀⬀

[14] D. Grosjean, E. Grosjean, E. L. Williams II, *Environ. Sci. Technol.* **1993**, *27*, 2478.

[15] G. Fantechi, N. R. Jensen, J. Hjorth, J. Peeters, *Atmos. Environ.* **1998**, *32*, 3547.

[16] S. M. Aschmann, Y. Shu, J. Arey, R. Atkinson, *Atmos. Environ.* **1997**, *31*, 3551.

[17] S. S. H. Ho, J. Z. Yu, *Anal. Chem.* **2002**, *74*, 1232.

[18] C. Ferronato, J. J. Orlando, G. S. Tyndall, *J. Geophys. Res.* **1998**, *103*, 25579.

[19] R. Atkinson, E. C. Tuazon, S. M. Aschmann, *Environ. Sci. Technol.* **1995**, *29*, 1674.

[20] A. Alvarado, E. C. Tuazon, S. M. Aschmann, J. Arey, R. Atkinson, *Atmos. Environ.* **1999**, *33*, 2893.

[21] Committee on Aldehydes, National Research Council, Formaldehyde and other aldehydes. *National Academy Press*, **1981**, Washington DC.

[22] R. P. Wayne, *Chemistry of atmospheres*, Oxford University Press, New York, **2000**.

[23] R. Atkinson, W. P. L. Carter, A. M. Winer, J. N. Pitts, Jr., *Air Pollut. Control Assoc.* **1981**, *31*, 1090.

[24] R. Atkinson, S. M. Aschmann, W. P. L. Carter, A. M. Winer, J. N. Pitts, Jr., *J. Phys. Chem.* **1982**, *86*, 4563.

[25] E. G. Alvarez, *Talanta* **2007**, *72*, 1757.

[26] J. Baker, J. Arey, R. Atkinson, *J. Phys. Chem. A* **2004**, *108*, 7032.

[27] J. Baker, J. Arey, R. Atkinson, *Environ. Sci. Technol.* **2005**, *39*, 4091.

[28] W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, G. A. Takacs, *Int. J. Chem. Kinet.* **1980**, *12*, 231.

[29] J. Koziel, M. Jia, J. Pawliszyn, *Anal. Chem.* **2000**, *72*, 5178.

[30] Q. Wang, J. O'Reilly, J. Pawliszyn, *J. Chromatogr. A* **2005**, *1071*, 147.

[31] F. Reisen, S. Aschmann, R. Atkinson, J. Arey, *Environ. Sci. and Technol.* **2003**, *37*, 4664.

[32] A. W. H. Chan, M. M. Galloway, A. J. Kwan, P. S. Chhabra, F. N. Keutsch, P. O. Wennberg, R. C. Flagan, J. H. Seinfeld. *Environ. Sci. and Technol.* **1995**, *29*, 1674.

[33] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crwoley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, and IUPAC Subcommittee *Atmos. Chem. Phys.* **2006**, *6*, 3625.

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ARTICLES

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■■ – ■■

OH-Initiated Photooxidations of 1-Pentene and 2-Methyl-2-propen-1-ol: Mechanism and Yields of the Primary Carbonyl Products
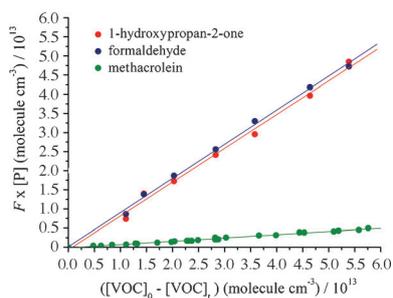
Following a radical start: OH-initiated atmospheric oxidation of 2-methyl-2-propen-1-ol can proceed by two reaction pathways: OH addition, which leads to the formation of 1-hydroxypropan-2-one and formaldehyde (major products), and H abstraction, from which methacrolein is formed (see picture). Taking into consideration the complex mechanism, the rate coefficients of the reactions of OH with these products were derived.