Products and Mechanism of the Reactions of OH Radicals and Cl Atoms with Methyl Methacrylate (CH$_2$=C(CH$_3$)C(O)OCH$_3$) in the Presence of NOx

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ABSTRACT: The OH radical and Cl atom initiated photodegradation of methyl methacrylate has been investigated in a 1080 L quartz-glass environmental chamber at 298 ± 2 K and atmospheric pressure of synthetic air using *in situ* FTIR spectroscopy to monitor the reactants and products. The major products observed in the OH reaction were methyl pyruvate (92 ± 16%) together with formaldehyde (87 ± 12%) as a coproduct from the C$_1$−C$_2$ bond cleavage channel of the intermediate 1,2-hydroxyalkoxy radical, formed by the addition of OH to the terminal carbon of the double bond which is designated C$_1$. For the Cl atom reaction, the products identified were chloroacetone (41 ± 6%) together with its coproduct formaldehyde (35 ± 5%) and methyl pyruvate (24 ± 4%) together with its coproduct formylchloride (25 ± 4%). The results show that the fate of the intermediate 1,2-chloroalkoxy radical involves not only cleavage of the C$_1$−C$_2$ bond but also quite substantial cleavage of the C$_2$−C$_3$ bond. The present results are compared with previous studies of acrylates, showing different branching ratios for the OH and Cl addition reactions in the presence of NOx. Atmospheric implications are discussed.
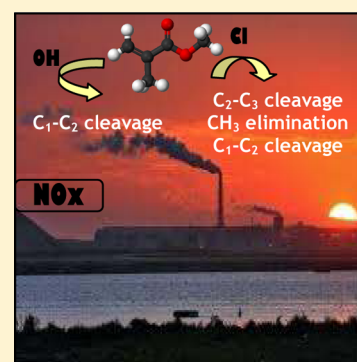
INTRODUCTION

Esters are oxygenated volatile organic compounds (OVOC) with a large number of commercial uses. They are potential replacements for traditional solvents and are used as diesel fuels or fuel components since they combine acceptable properties with low exhaust emissions and reduced combustion noise.[1]

Methacrylate esters have the structure CH$_2$=C(CH$_3$)C(O)-OCH$_2$R and are widely used in the production of polymers and resins, and as for other acrylic compounds the sources of their emissions are numerous and include the manufacturer of plastics, aircraft, and electronic components.[2] Methyl methacrylate (MMA) is listed as a high (H) production (P) volume (V) chemical in the OECD (Organisation for Economic Co-operation and Development) integrated HPV database.[3] Many different kinds of esters including methyl methacrylate have been measured in ambient air.[4]

Emissions of the unsaturated esters to the atmosphere can occur during their production, processing, storage, and disposal, and once in the atmosphere they will be subject to photo-degradation mainly by OH radicals and to a lesser extent NO$_3$ radicals and ozone and, in certain environments, also Cl atoms.[5] Oxidation by Cl atoms has been conventionally thought to have been confined largely to coastal areas and possibly some polluted industrial regions;[6−8] however, recent field work has presented evidence for Cl chemistry in continental regions remote from coastal regions,[9] suggesting that Cl-initiated photooxidation chemistry may play a more important role than previously thought in polluted continental regions.

In order to assess the contribution of the atmospheric photooxidation of methacrylate esters to the formation of photochemical oxidants and secondary organic aerosol (SOA) in urban environments, detailed kinetic and mechanistic information on their tropospheric gas-phase degradation pathways are required. There have been several kinetic studies of the OH-radical,[10−14] O$_3$-molecule,[15−20] and the Cl-atom[21−23] initiated oxidation of unsaturated esters. To date, there have only been three studies on the reactions of acrylates with NO$_3$ radicals.[24−27]

In contrast to the kinetic studies, only a few product studies on the OH[12,13] and NO$_3$[26] radicals and Cl atom[28] initiated oxidation of unsaturated esters have been reported. Blanco et al.,[12,13] reported a qualitative GC-MS product study of the reactions of OH radicals with methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, and *n*-butyl acrylate performed in a collapsible Teflon chamber in which methyl pyruvate, ethyl pyruvate, *n*-butyl pyruvate, and *n*-butyl glyoxylate were identified as unique reaction products, respectively. In a recent study from this laboratory,[28] performed in a large photoreactor using *in situ* FTIR analysis, we reported a product study of the OH and Cl

initiated oxidation of methyl acrylate (CH_2=$CHC(O)OCH_3$) in which the main product from the OH reaction was observed to be methyl glyoxylate ($HC(O)C(O)OCH_3$), and methyl 3-chloro-2-oxopropanoate ($CH_2ClC(O)C(O)OCH_3$) was tentatively assigned as a major product for the Cl reaction.

This significant difference in the major products between the reaction of OH and Cl with methyl acrylate was similar to what had been observed in a kinetic and product study of the reactions of OH radicals and Cl atoms with a fluorotelomer acrylate (CH_2=$CHC(O)OCH_2CH_2C_4F_9$) in the air using FTIR to monitor reactants and products.[29] In this study for the OH reaction, the evidence supported formation of the a fluorotelomer glyoxylate as the major product, while in the Cl reaction the experimental observations supported the addition of Cl and formation of a chain-retaining compound $CHCl$–$C(O)C(O)OCH_2CH_2C_4F_9$.

No quantitative product studies are currently available for OH-radical- and Cl-atom-initiated degradation of methacrylate esters. Since, as stated above, methacrylate esters are widely used in the production of polymers and are released to the atmosphere in substantial amounts,[3,4] this motivated us to investigate qualitatively and quantitatively the products formed in the OH-radical and Cl-atom degradation of methyl methacrylate (MMA).

$$OH + CH_2=C(CH_3)C(O)OCH_3 \rightarrow products \qquad (1)$$

$$Cl + CH_2=C(CH_3)C(O)OCH_3 \rightarrow products \qquad (2)$$
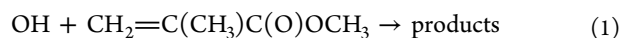
It is known that the main reaction pathway for both OH and Cl with methyl methacrylate is addition to the double bond of the alkene unit in the ester. The reactions have been investigated in the presence of NOx, thus after addition of the oxidant it is well-established that the subsequent chemistry will result in the formation of hydroxyalkoxy and chloroalkoxy radicals. The major aim of the work was to assess the relative importance of the different subsequent reaction pathways that are available to the hydroxy- and chloro-alkoxy radicals. The results will contribute to an improved representation of the degradation of methacrylate esters in the atmospheric chemical models used to assess the environmental impact of chemicals and their contribution to photooxidant and SOA formation in the atmosphere.

■ EXPERIMENTAL SECTION

All the experiments were performed in a 1080 L quartz-glass reaction chamber at 298 ± 2 K and a total pressure of 760 ± 10 Torr of synthetic air (760 Torr = 101.325 kPa). A detailed description of the reactor can be found elsewhere,[30] and only a brief description is given here. A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10^{-3} Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40W: 320−480 nm, λ_{max} = 360 nm) and 32 low-pressure mercury vapor lamps (Philips TUV 40W; λ_{max} = 254 nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White type multiple-reflection mirror system with a base length of 5.91 ± 0.01 m for sensitive *in situ* long path infrared absorption

monitoring of reactants and products in the spectral range 4000−700 cm^{-1}. The White system was operated at 82 traverses, giving a total optical path length of 484.7 ± 0.8 m. The IR spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FT-IR spectrometer, equipped with a liquid nitrogen cooled mercury−cadmium−telluride (MCT) detector.
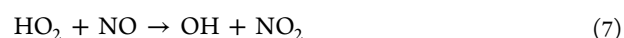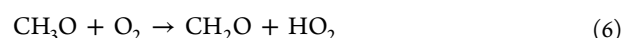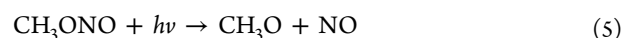
Chlorine atoms were generated by the photolysis of Cl_2 with the fluorescent lamps:

$$Cl_2 + h\nu \rightarrow 2Cl \qquad (3)$$

Hydroxyl radicals were generated by the photolysis of H_2O_2 with the mercury lamps:

$$H_2O_2 + h\nu \rightarrow 2OH \qquad (4)$$

or by the photolysis of the mixture $CH_3ONO/NO/air$ at 360 nm as follows:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (5)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (6)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (7)$$

Where possible, quantification of reactants and products was performed by comparison with calibrated reference spectra contained in the IR spectral databases of the laboratories in Wuppertal and Córdoba.

The initial concentration of methyl methacrylate used in the experiments was 0.5−1.0 ppm (1 ppm = 2.46 × 10^{13} molecules cm^{-3} at 298 K and 760 Torr of total pressure). The concentrations of Cl_2, H_2O_2, and CH_3ONO were typically around 5, 7, and 6 ppm, respectively. The concentration of added NO was typically around 4 ppm.

The infrared absorption frequency at 1169 cm^{-1} was used to monitor the concentration−time behavior of methyl methacrylate. Readily identifiable products were monitored at the following absorption frequencies (in cm^{-1}): formaldehyde at 2766, carbon monoxide at 2169, formyl chloride at 738.6, methyl pyruvate at 1040, chloroacetone at 1371, and formic acid at 1105.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), methyl methacrylate (Aldrich, 99%), H_2O_2 (Interox, 85%), and Cl_2 (Messer Griesheim, >99.8%). Methyl nitrite was synthesized by the dropwise addition of 50% H_2SO_4 to a saturated solution of sodium nitrite in methanol and was purified by vacuum distillation until a sample of 99% purity was obtained confirmed by IR spectroscopy.

■ RESULTS, DISCUSSION, AND CONCLUSIONS

To investigate the mechanisms of the OH-radical and Cl-atom initiated oxidation of methyl methacrylate, mixtures of $H_2O_2/NO/ester/air$ or $CH_3ONO/NO/ester/air$ and $Cl_2/NO/ester/air$ were irradiated for periods of around 20 min during the course of which infrared spectra were recorded with the FTIR spectrometer. Typically, 64 interferograms were coadded per spectrum over a period of approximately 1 min, and 15−20 such spectra were collected during the course of the experiment.

Dark reactions, photolysis of the methyl methacrylate in the absence of radical precursor reactions, and wall losses were negligible compared to the loss that occurred on OH radical or Cl atom photoinduced degradation.[14]

To facilitate the discussion of the results, exemplary reaction schemes are shown for the reactions of OH and Cl with methyl
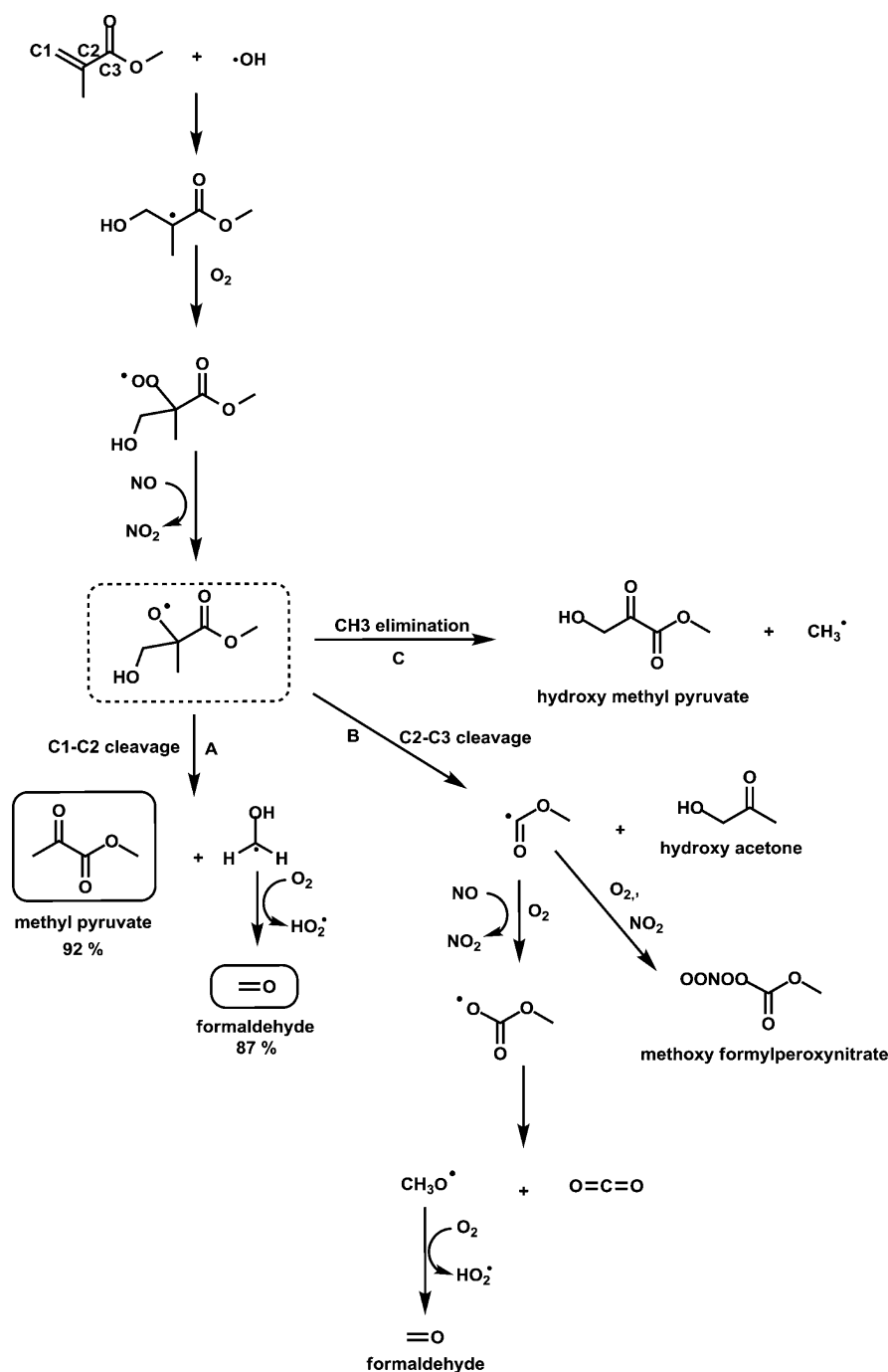
Figure 1. Simplified reaction mechanism for the addition channel in the OH-radical initiated oxidation of methyl methacrylate in the presence of NOx.

methacrylate in Figures 1 and 2, respectively. For the OH radical or Cl atom reactions, the major reaction pathway involves initial addition of the OH or Cl to the terminal carbon atom of the C= C bond, forming 1,2-hydroxyalkyl or 1,2-chloroalkyl radicals.[31−33] In the case of OH, the addition mechanism is expected to account for over 98% of the reaction.[32,33] Similarly, the reaction of Cl atoms with methyl methacrylate is estimated to proceed by more than 98% via the addition of Cl to the double bond.[34] Under the conditions of the present study, the hydroxyalkyl and 1,2-chloroalkyl radicals will react with O_2 to form the corresponding 1,2-hydroxyalkyl or 1,2-chloroxyalkyl peroxy radicals. The peroxy radicals will then react further with NO to form nearly exclusively the 1,2-hydroxyalkoxy or 1,2-

chloroalkoxy radicals, respectively.[31−33] However, under NOx-free experimental conditions, peroxy self-reactions will occur. These will also result to a large extent in the formation of the alkoxy radicals; however, molecular channels are also possible which will result in the formation of multifunctional products.[35]

The 1,2-hydroxyalkoxy or 1,2-chloroalkoxy radicals can decompose by various channels (Figures 1 and 2) which include (i) decomposing to give methyl pyruvate and CH_2OH or CH_2Cl radicals, (ii) decomposing to give hydroxyacetone or chloroacetone and $CH_3OC(O)$ radicals, or (iii) ejecting a methyl group to form methyl-3-hydroxy-2-oxopropanoate or methyl-3-chloro-2-oxopropanoate, i.e., $CH_2(OH)−C(O)−C(O)OCH_3$ or $CH_2(Cl)−C(O)−C(O)OCH_3$.
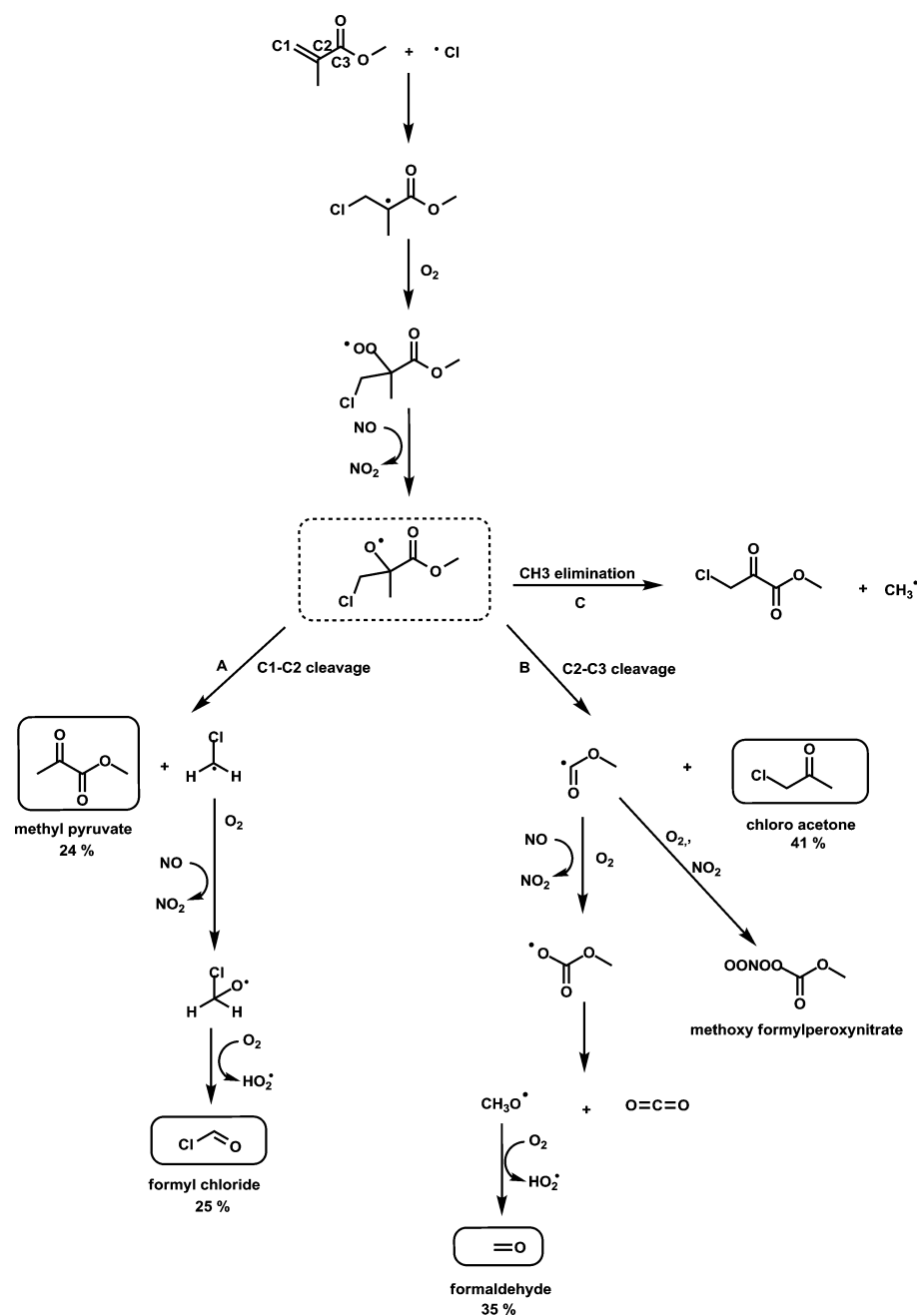
Figure 2. Simplified reaction mechanism for the addition channel in the Cl-atom-initiated oxidation of methyl methacrylate in the presence of NOx.

OH Reaction. Figure 3a shows IR spectra acquired before (panel A) and after (panel B) UV irradiation of a mixture of methyl methacrylate and H_2O_2 in air, in the presence of NOx. Panel C in Figure 3a, shows a reference spectrum of methyl pyruvate $(CH_3C(O)C(O)OCH_3)$ and panel D, the residual product spectrum obtained after subtraction of reactants and identified products from the spectrum in panel B. Methyl pyruvate, HCHO, and CO were readily identifiable as reaction products. In the residual product spectra, unidentified absorption bands were observed at 939, 1066, 1164, 1201, 1446, 1753, and 2970 cm^{-1}. The concentration−time profiles of methyl pyruvate and HCHO (Figure 3b) show that they are both primary products, whereas the delayed formation in the profile of CO shows that formation is secondary in nature.

Least-squares analyses of plots of the concentrations of methyl pyruvate and HCHO as a function of the amount of reacted

methyl methacrylate (Figure 3c) give molar yields of 92 ± 16% and 83 ± 12%, respectively, for these compounds (see Table 1). Formaldehyde will be subject to secondary oxidation with OH, whereas methyl pyruvate reacts only very slowly with OH, and loss via secondary reaction with OH should be negligible. Correction of the HCHO yield for secondary reaction with OH using the method outlined in Tuazon et al.[36] gives a final corrected yield of 87 ± 12% for formaldehyde. The mechanism presented in Figure 1 (channel A) predicts equal yields of HCHO and methyl pyruvate, and within the experimental error limits, this is the case.

The absorption band observed at 1753 cm^{-1} in the residual product spectrum indicates the presence of other carbonyl-containing products; however, based on the measured yields of methyl pyruvate and HCHO, the yields of these carbonyl products will be small. Other possible carbonyl-containing
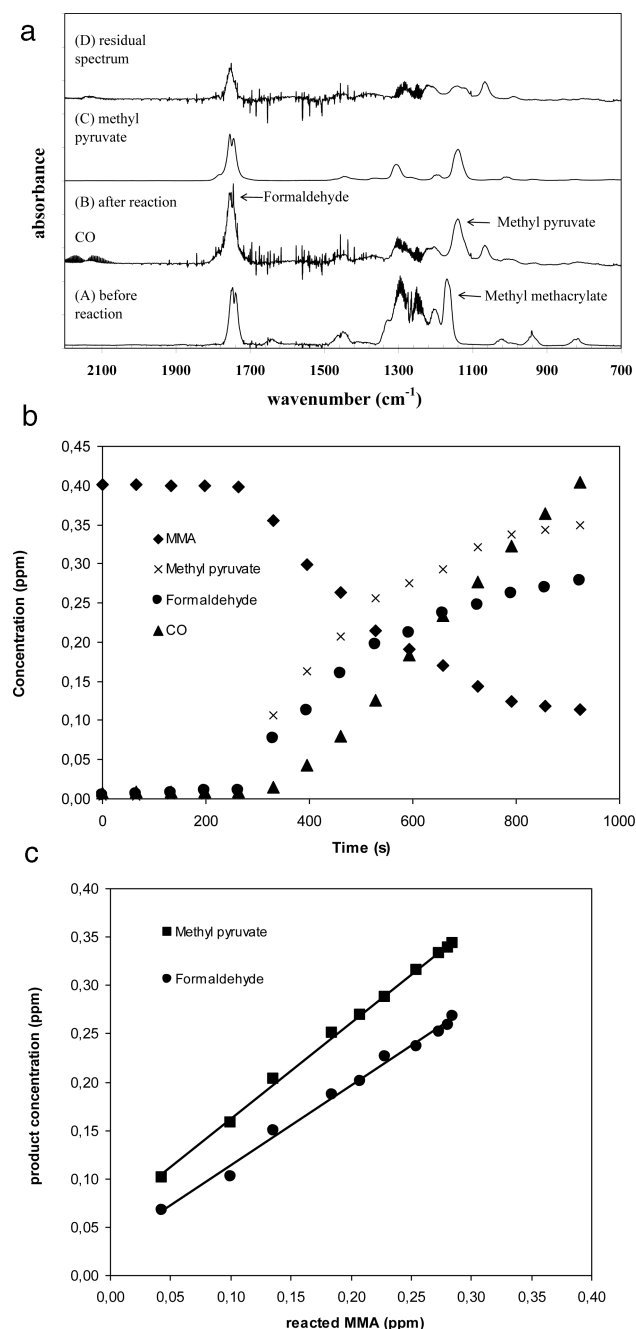
Table 1. Formation Yields of the Oxidation Products Identified from the OH Radical and Cl Atom Oxidation of Methyl Methacrylate in the Presence of NOx

reaction	product	yield (%)[a]
methyl methacrylate + OH	methyl pyruvate	92 ± 16
	formaldehyde	87 ± 12[b]
methyl methacrylate + Cl	formylchloride	25 ± 4
	chloroacetone	41 ± 6
	methyl pyruvate	24 ± 4
	formaldehyde	35 ± 5[c]

[a]The errors quoted are 2σ statistical errors from the linear regression analysis. [b]Yield corrected for secondary reaction with OH radicals. [c]Yield corrected for secondary reaction with Cl atoms.

Figure 1, and (ii) $CH_3OC(O)C(CH_3)(OH)CHO$ produced from reaction of O_2 with the 2,1-hydroxyalkoxy radical formed from OH addition to the carbon of the double bond adjacent to the carbonyl entity of the ester group. No indication could be found in the product spectra for the formation of hydroxy acetone. The compound giving rise to the residual carbonyl absorption in the product spectrum is, therefore, most probably $CH_3OC(O)C(CH_3)(OH)CHO$. On the basis of the yields of methyl pyruvate and HCHO, the molar yield of $CH_3OC(O)C(CH_3)(OH)CHO$ is estimated to be <8%.

Cl Reaction. Figure 4a, panel A, shows a spectrum of a $MMA/NO/Cl_2$/air reaction mixture before irradiation, panel B the product spectra after 10 min irradiation and subtraction of spectral features due to MMA, and panel C the residual product spectrum after the subtraction of features attributable to the major identified MMA oxidation products from the spectrum in panel B. Chloroacetone $(CH_3C(O)CH_2Cl)$, formaldehyde, methyl pyruvate, formyl chloride $(HC(O)Cl)$, and carbon monoxide were positively identified as reaction products. In the residual product spectra (Figure 4a, panel C), absorption bands can be seen in the regions 782−849 cm^{-1}, 1191−1308 cm^{-1}, and 1670−1840 cm^{-1}.

Concentration−time profiles of MMA, $CH_3C(O)CH_2Cl$, $HC(O)Cl$, HCHO, $CH_3C(O)C(O)OCH_3$, and CO are shown in Figure 4b. The concentration−time profiles of HCHO, $HC(O)Cl$, and $CH_3C(O)C(O)OCH_3$ show that all are primary in origin, and the upward curve of the CO profile shows that its formation is secondary in nature. Secondary rapid reactions of Cl with HCHO will result in the formation of CO. The amounts of $CH_3C(O)CH_2Cl$, $HC(O)Cl$, HCHO, and $CH_3C(O)C(O)OCH_3$ formed plotted as a function of the amount of reacted MMA are shown in Figure 4c. The plots are linear and give molar yields for formyl chloride, chloroacetone, methyl pyruvate, and formaldehyde of 25 ± 4%, 41 ± 6%, 24 ± 4%, and 23 ± 3%, respectively. The corrected yield of formaldehyde was 35 ± 5%.

The formation of chloroacetone shows that a major fate of the $CH_2(Cl)C(CH_3)(O^\bullet)C(O)OCH_3$ 1,2-chloroalkoxy radicals formed in the reaction of Cl with MMA in the presence of NOx is cleavage of the $C_2−C_3$ bond to form chloroacetone $(CH_3C(O)CH_2Cl)$ and $CH_3OC(O)$ radicals with a yield of ~41% (Figure 2, channel B). The formation of $HC(O)Cl$ and methyl pyruvate shows that cleavage of the $C_1−C_2$ bond to form these products (Figure 2, channel A) is also operative and accounts for around 25% of the reaction.

The identified products, however, account for only around 65% of the reacted MMA. Since all possible C−C bond cleavage products have been detected and quantified, the missing product(s) must be in a form retaining all or most of the

Figure 3. (a) Panel A: A spectrum of methyl methacrylate (MMA) in the spectral range 2200−700 cm^{-1} before irradiation in a $MMA/H_2O_2/NO$/air reaction mixture. Panel B: The product spectrum obtained after irradiation and subtraction of absorptions due to MMA. Absorptions due to the products CO and HCHO highlighted. Panel C: A reference spectrum of methyl pyruvate. Panel D: The residual spectrum obtained after subtraction of all identified products. (b) Concentration−time profiles of methyl methacrylate (MMA) and the reaction products methyl pyruvate, HCHO, and CO obtained from the irradiation of a $MMA/H_2O_2/NO$/air reaction mixture. (c) Plots of the concentrations of the reaction products methyl pyruvate and HCHO as a function of reacted methyl methacrylate (MMA) obtained from the irradiation of a $MMA/H_2O_2/NO$/air reaction mixture.

products include (i) hydroxyl methyl pyruvate $(CH_3OC(O)C(O)CH_2(OH))$ and hydroxy acetone $(CH_3C(O)CH_2OH)$ produced by CH_3 elimination from the 1,2-hydroxyalkoxy radical or a $C_2−C_3$ bond cleavage, channels C and B, respectively
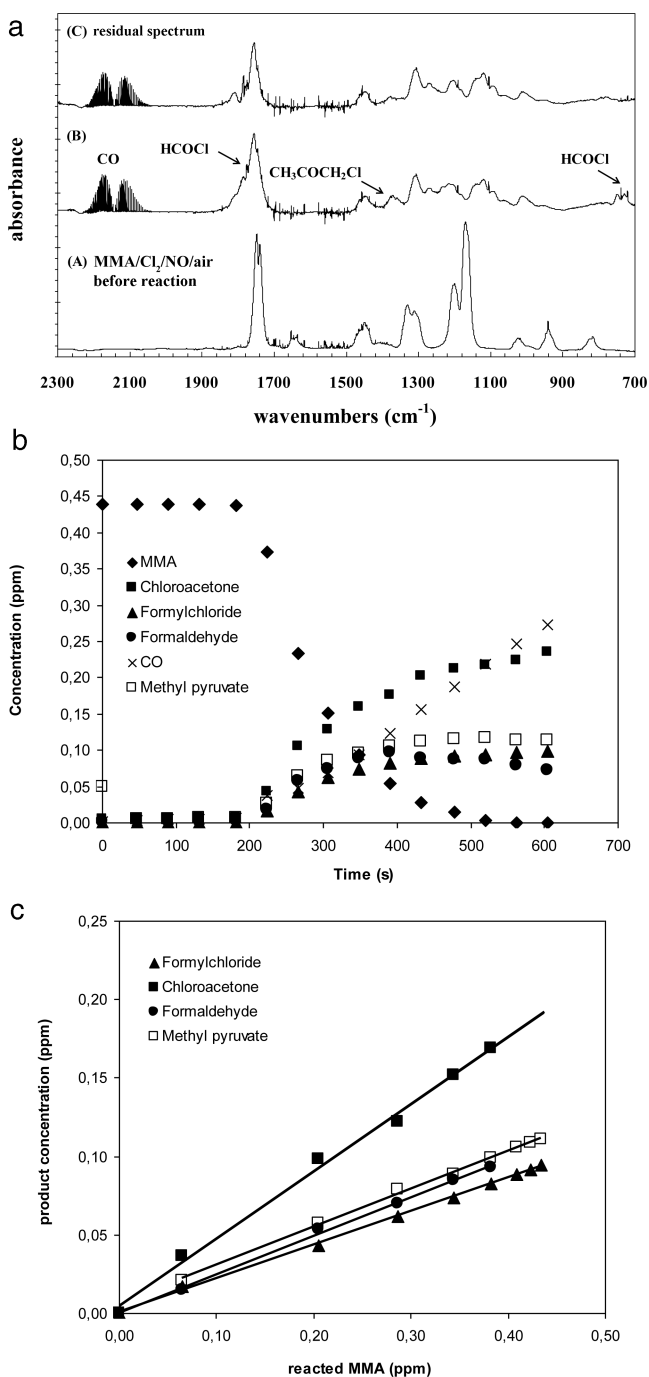
Figure 4. (a) Panel A: A spectrum of methyl methacrylate (MMA) in the spectral range 2300−700 cm^{-1} before irradiation in a MMA/Cl$_2$/NO/air reaction mixture. Panel B: The product spectrum after irradiation and subtraction of features due to MMA. Absorptions due to the products CO, HC(O)Cl, and CH$_3$C(O)CH$_2$Cl are highlighted. Panel C shows the residual product spectrum after subtraction of HC(O)Cl, CH$_3$C(O)CH$_2$Cl from the spectrum in panel B. (b) Concentration−time profiles of methyl methacrylate (MMA) and the reaction products CH$_3$C(O)CH$_2$Cl, HC(O)Cl, CO, HCHO, and methyl pyruvate obtained from the irradiation of a MMA/Cl$_2$/NO/air reaction mixture. (C): Plots of the concentrations of the reaction products CH$_3$C(O)CH$_2$Cl, HC(O)Cl, CH$_3$C(O)C(O)OCH$_3$ and CH$_2$O as a function of reacted methyl methacrylate (MMA) obtained from the irradiation of a MMA/Cl$_2$/NO/air reaction mixture.

MMA carbon skeleton. Close inspection of the residual product spectrum (Figure 4a, panel C) shows that it contains absorptions

from nitrosyl chloride (ClNO) and nitryl chloride (ClNO$_2$) formed from reactions of Cl with NOx in the system. Absorptions from nitric acid (HNO$_3$) are also visible. Although the residual product spectrum that is obtained after subtraction of these compounds is quite noisy, there is positive evidence for the presence of methoxy formylperoxynitrate (CH$_3$OC(O)-O$_2$NO$_2$). This compound can be formed from consecutive reactions of the CH$_3$OC(O) radical with O$_2$ and NO$_2$ and is reasonably thermally stable at room temperature.[37−39] Other remaining absorptions strongly resemble those of the product observed in the reaction of Cl with methyl acrylate,[28] which was assigned to methyl-3-chloro-2-oxopropanoate (CH$_2$(Cl)C(O)-C(O)OCH$_3$). The compound can be formed in the reaction of Cl with MMA via elimination of the CH$_3$ group from the intermediate 1,2-chloroalkoxy radical, CH$_2$(Cl)C(CH$_3$)(O$^{\bullet}$)C-(O)OCH$_3$, i.e., pathway C in Figure 2, and could potentially account for ≤35% of the overall reaction. However, a contribution from the C-skeleton retaining product methyl 2-chloro-2-methyl-3-oxo-propanoate (OCHC(Cl)(CH$_3$)C(O)-OCH$_3$), formed from reaction of 2,1-chloroalkoxy radicals, OCH$_2$CCl(CH$_3$)C(O)OCH$_3$, with O$_2$ cannot be completely excluded.

The measured yield for HCHO is lower than that expected from the occurrence of pathway B in Figure 2; however, the observation of the formation of methoxy formylperoxynitrate supports that quite a substantial fraction of the CH$_3$OC(O) radicals, formed in pathway B, are retained in the form of this fairly stable peroxy nitrate.[37−39]

The finding that OH addition to the double bond in MMA results in close to unity cleavage of the C$_1$−C$_2$ bond to form methyl pyruvate and CH$_2$OH radicals, which react further to form HCHO, is in agreement with the findings of a previous GC-MS product determination study on the reactions of OH with methyl methacrylate, ethyl methacrylate, and *n*-butyl methacrylate.[12]

The results contrast sharply with those obtained for the reaction of Cl with MMA, where although cleavage of the C$_1$−C$_2$ bond to form methyl pyruvate and formyl chloride was observed, it only accounted for around 25% of the degradation mechanism. Cleavage of the C$_2$−C$_3$ bond to form chloroacetone and CH$_3$OC(O) radicals was found to be a more important channel with a yield of around 41%. Further, the gap in the carbon balance and the lack of other C−C bond cleavage products in the residual product spectrum supports that a C-chain retaining channel is also operative, leading most probably to the formation of CH$_2$ClC(O)C(O)OCH$_3$.

This product channel branching behavior observed for the reaction of Cl with MMA not only contrasts sharply with that of the analogous OH reaction as stated above but also with that observed for the reaction of Cl with methyl acrylate (MA) where no C−C bond cleavage was observed,[28] and the only product channel was assumed to be a C-chain retaining product, i.e., CH$_2$ClC(O)C(O)OCH$_3$, the same product that is thought to be formed in the Cl/MMA/NO reaction through elimination of a CH$_3$ group from the MMA C-skeleton. This dramatic difference in the contributions of the various reaction channels to the fate of the 1,2-hydroxyalkoxy and 1,2-chloroalkoxy formed in the reactions of OH and Cl with MA and MMA can probably be attributed to the differences in the distribution of the excess energy in the hydroalkoxy and chloroalkoxy radicals arising from the exothermic reactions of the corresponding peroxy radicals with NO. It would be interesting to study any changes in the product distributions when the 1,2-hydroxyalkoxy and 1,2-

chloroalkoxy are formed via nearly thermo-neutral peroxy—peroxy reactions. Such information is necessary for modeling the oxidation of the VOCs in low NOx regimes.

Reactions of Cl atoms with VOCs are often used as a surrogate for the corresponding OH reactions since the Cl reactions are approximately 1 order of magnitude faster, are generally easier to study, and are assumed to proceed by similar reaction mechanisms. These studies show that, although these assumptions are probably true for mechanisms involving only H-atom abstraction, care should be taken into account when addition to alkene entities is involved in the mechanism since branching ratios for the possible product channels can be completely different and would lead to completely wrong reaction schemes and prediction of environmental impacts if transferred to the OH radical.

The persistence of methacrylates in the atmosphere is short, on the order of a few hours (dominated by OH radical chemistry).[14,22] These short lifetimes indicate that the methacrylates will be degraded close to their emission sources. Since the degradation products can contribute to ozone and photooxidants formation in the troposphere to different degrees, it is important to know the product branching for different atmospheric conditions. This study and ongoing work in our laboratories supports that the product branching ratios for the reactions of OH radicals and Cl atoms with acrylate esters are particularly NOx sensitive and need further investigation to correctly represent the oxidation mechanisms of this class of compounds in atmosphere CT models.

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Notes

The authors declare no competing financial interest.

■ **ACKNOWLEDGMENTS**

■ **REFERENCES**

(1) BASF Golobal − BASF − The Chemical Company − Corporate Website. http://www.basf.com.

(2) Graedel, T. E. *Chemical Compounds in the Atmosphere*; Academic Press: New York, 1978.

(3) Organization for Economic Co-operation and Development. http://cs3-hq.oecd.org/scripts/hpv/index.asp.

(4) Pankow, J. F.; Luo, W.; Bender, D. A.; Isabelle, L. M.; Hollingsworth, J. S.; Chen, C.; Asher, W. E.; Zogorski, J. S. Concentrations and co-occurrence correlations of 88 volatile organic compound (VOCs) in the ambient air of 13 semi-rural to urban locations in the United Sates. *Atmos. Environ.* **2003**, *37*, 5023−5046.

(5) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press, New York, 2000.

(6) Wingenter, O. W.; Kubo, M. K.; Blake, N. J.; Smith, T. W.; Blake, D. R.; Rowland, F. S. Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine and vertical mixing obtained during Langrangian flights. *J. Geophys. Res.* **1996**, *101*, 4331−4340.

(7) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastidge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. Observations of molecular chlorine in coastal air. *Nature* **1998**, *394*, 353−356.

(8) Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. Kinetics of reactions of chlorine atoms with a series of alkenes at 1 atm and 298 K: structure and reactivity. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5813−5820.

(9) Thornton, J. A.; Kercher, J. P.; Riedel, T. P.; Wagner, N. L.; Cozic, J.; Holloway, J. S.; Dubé, W. P.; Wolfe, G. M.; Quinn, P. K.; Middlebrook, A. M.; Alexander, B.; Brown, S. S. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* **2010**, *464*, 271−274.

(10) Saunders, S. M.; Baulch, D. L.; Cooke, K. M.; Pilling, M. J.; Smurthwaite, P. I. Kinetics and mechanisms of the reactions of OH with some oxygenated compounds of importance in tropospheric chemistry. *Int. J. Chem. Kinet.* **1994**, *26*, 113−130.

(11) Teruel, M. A.; Lane, S. I.; Mellouki, A.; Solignac, G.; Le Bras, G. OH reaction rate constants and UV absorption cross-sections of unsaturated esters. *Atmos. Environ.* **2006**, *40*, 3764−3772.

(12) Blanco, M. B.; Taccone, R. A.; Lane, S. I.; Teruel, M. A. On the OH-initiated degradation of methacrylates in the troposphere: gas-phase kinetics and formation of pyruvates. *Chem. Phys. Lett.* **2006**, *429*, 389−394.

(13) Blanco, M. B.; Teruel, M. A. Photodegradation of butyl acrylate in the troposphere by OH radicals: kinetics and fate of 1,2-hydroxyalcoxy radicals. *J. Org. Chem.* **2008**, *21*, 397−401.

(14) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. OH-Initiated Degradation of Unsaturated Esters in the Atmosphere: Kinetics in the Temperature Range of 287−313 K. *J. Phys. Chem. A* **2009**, *113*, 5958−5965.

(15) Munshi, H. B.; Rao, K. V. S. R.; Iyer, R. M. Rate constants of the reactions of ozone with nitriles, acrylates and terpenes in gas phase. *Atmos. Environ.* **1989**, *23*, 1971−1976.

(16) Grosjean, D.; Grosjean, E.; Williams, E. L., II. Rate constants for the gas-phase reactions of ozone with unsaturated alcohols, esters, and carbonyls. *Int. J. Chem. Kinet.* **1993**, *25*, 783−794.

(17) Grosjean, E.; Grosjean, D. Rate constants for the gas-phase reaction of ozone with unsaturated oxygenates. *Int. J. Chem. Kinet.* **1998**, *30*, 21−29.

(18) Gai, Y. B.; Ge, M. F.; Wang, W. G. Rate constants for the gas phase reaction of ozone with n-butyl acrylate and ethyl methacrylate. *Chem. Phys. Lett.* **2009**, *473*, 57−60.

(19) Al Mulla, I.; Viera, L.; Morris, R.; Sidebottom, H.; Treacy, J.; Mellouki, A. Kinetics and Mechanisms for the reactions of ozone with unsaturated oxygenated compounds. *Chem. Phys. Chem.* **2010**, *11*, 4069−4078.

(20) Bernard, F.; Eyglunent, G.; Daele, V.; Mellouki, A. Kinetics and Products of Gas-Phase Reactions of Ozone with Methyl Methacrylate, Methyl Acrylate, and Ethyl Acrylate. *J. Phys. Chem. A* **2010**, *114*, 8376−8383.

(21) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. The Cl-initiated oxidation of $CH_3C(O)OCH=CH_2$, $CH_3C(O)OCH_2CH=CH_2$, and $CH_2=CHC(O)O(CH_2)_3CH_3$ in the troposphere. *Env. Sci. Pollut. Res.* **2009**, *16*, 641−648.

(22) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. Temperature-dependent rate coefficients for the reactions of Cl atoms with methyl methacrylate, methyl acrylate and butyl methacrylate at atmospheric pressure. *Atmos. Environ.* **2009**, *43*, 5996−6002.

(23) Martín, M. P.; Gallego-Iniesta, M. P.; Espinosa, J. L.; Tapia, A.; Cabaňas, B.; Salgado, M. S. Gas phase reactions of unsaturated esters with Cl atoms. *Env. Sci. Pollut. Res.* **2010**, *17*, 539−546.

(24) Canosa-Mas, C. E.; Carr, S.; King, M. D.; Shallcross, D. E.; Thompson, K. C.; Wayne, R. P. A kinetic study of the reaction of NO3 with methyl vinyl ketone, methacrolein, acrolein, methyl acrylate and methyl methacrylate. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4195−4202.

(25) Wang, K.; Ge, M.; Wang, W. Kinetics of the gas-phase reactions of NO3 radicals with ethyl acrylate, *n*-butyl acrylate, methyl methacrylate and ethyl acrylate. *Atmos. Environ.* **2010**, *44*, 1847−1850.

(26) Salgado, M. S.; Gallego-Iniesta, M. P.; Martín, M. P.; Tapia, A.; Cabañas, B. Night-time atmospheric chemistry of methacrylates. *Env. Sci. Pollut. Res.* **2011**, *18*, 940−948.

(27) Canosa-Mas, C. E.; Flugge, M. L.; King, M. D.; Wayne, R. P. An experimental study of the gas-phase reaction of the NO₃ radical with α,β-unsaturated carbonyl compounds. *Phys. Chem. Chem. Phys.* **2005**, *7*, 643−650.

(28) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. FTIR Product Distribution Study of the Cl and OH Initiated Degradation of Methyl Acrylate at Atmospheric Pressure. *Environ. Sci. Technol.* **2010**, *44*, 7031−7036.

(29) Butt, C. M.; Young, C. J.; Mabury, S. A.; Hurley, M. D.; Wallington, T. J. Atmospheric Chemistry of 4:2 Fluorotelomer acrylate [C₄F₉CH₂CH₂OC(O)CH=CH₂]: kinetics, mechanisms, an products of chlorine-atom-and OH-radical-initiated oxidation. *J. Phys. Chem. A* **2009**, *113*, 3155−3161.

(30) Barnes, I.; Becker, K. H. An FTIR Product Study of the Photooxidation of Dimethyl Disulfide. *J. Atmos. Chem.* **1994**, *18*, 267−289.

(31) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *The Mechanisms of Atmospheric Oxidation of Alkenes*; Oxford University Press: New York; ISBN: 0195131770, 2000.

(32) Atkinson, R.; Arey, J. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* **2003**, *103*, 4605−4638.

(33) Atkinson, R. Gas Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215−290.

(34) Aschmann, S. M.; Atkinson, R. Rate constants for the gas-phase reactions of alkanes with Cl atoms at 296 ± 2 K. *Int. J. Chem. Kinet.* **1995**, *27*, 613−622.

(35) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. Organic peroxy radicals: kinetics, spectroscopy and tropospheric chemistry. *Atmos. Environ.* **1992**, *26A*, 1805−1964.

(36) Tuazón, E. C.; MacLeod, H.; Atkinson, R.; Carter, W. P. L. α-Dicarbonyl yields from NOₓ-air photooxidations of a series of aromatic hydrocarbons in air. *Environ. Sci. Technol.* **1986**, *20*, 383−387.

(37) Cavalli, F.; Barnes, I.; Becker, K. H.; Wallington, T. J. Atmospheric oxidation mechanism of methyl propionate. *J. Phys. Chem. A* **2000**, *104*, 11310−11317.

(38) Orlando, J. J.; Tyndall, G. S. The atmospheric oxidation of ethyl formate and ethyl acetate over a range of temperatures and oxygen partial pressures. *Int. J. Chem. Kinet.* **2010**, *42*, 397−413.

(39) Pimentel, A. S.; Tyndall, G. S.; Orlando, J. J.; Hurley, M. D.; Wallington, T. J.; Sulbaek Andersen, M. P.; Marshall, P.; Dibble, T. S. Atmospheric chemistry of isopropyl formate and *tert*-butyl formate. *Int. J. Chem. Kinet.* **2010**, *42*, 479−498.

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