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FTIR Product Distribution Study of the Cl and OH Initiated Degradation of Methyl Acrylate at Atmospheric Pressure

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A product study is reported on the gas-phase reactions of OH radicals and Cl atoms with methyl acrylate. The experiments were performed in a 1080-L quartz-glass chamber in synthetic air at 298 ± 2 K and 760 ± 10 Torr using long-path in situ FTIR spectroscopy for the analysis of the reactants and products. In the absence of NO_x the major product observed in the OH reaction is methyl glyoxylate, with formaldehyde as a coproduct. For the reaction with Cl only formyl chloride (HC(O)Cl), CO, and HCl could be positively identified as products, however, the concentration−time behavior of these products show that they are secondary products and originate from the further oxidation of a major primary product. From this behavior and a comparison with simulated spectra unidentified bands in the residual product spectra are tentatively attributed to a compound of structure $CH_2ClC(O)C(O)OCH_3$, i.e., formation of methyl 3-chloro-2-oxopropanoate from the reaction of Cl with methyl acrylate. The present results are compared with previous results where available and simple atmospheric degradation mechanisms are postulated to explain the formation of the observed products.

Introduction

Volatile organic compounds (VOCs) present in the atmosphere can undergo photolysis and chemical reactions with OH radicals, NO_3 radicals, O_3 and Cl atoms, with the OH radical reactions being, in most cases, the dominant atmospheric loss process (*1*). However, a recent field study has presented evidence for Cl chemistry in continental regions (*2*), far removed from coastal and marine regions where Cl chemistry was only previously assumed to be important, suggesting that Cl chemistry is ubiquitous in the atmosphere and possibly more important than previously thought. Kinetic data and mechanistic information on the atmospheric degradation of individual compounds are, therefore, essential components in any attempts to reliably assess the possible contribution of these substances to photochemical air pollution in urban and regional areas.

Esters are oxygenated compounds commonly used as fragrances and found in essential oils and pheromones (*3*). Acrylates, unsaturated esters, are employed in the extraction of chemicals, as intermediates in the manufacture of polymers, and in the manufacture of circuit boards (*4*). This family of unsaturated esters is toxic and volatile and is a potentially major source of environmental concern in local industrial areas.

Despite their widespread industrial use and associated fugitive emissions to the atmosphere, the gas-phase atmospheric fate of esters has received relatively little attention. Recently, we have reported kinetic data for the reactions of OH radicals with unsaturated esters (*5–8*). Reactions with OH radicals constitute the important initiating oxidation step in the gas-phase degradation of these compounds in the atmosphere. The kinetic data have helped to extend the presently relatively scant database for the reactions of OH radicals with unsaturated esters and have allowed refinements to be made in the structure−reactivity relationships developed by Kwok and Atkinson (*9, 10*) to predict rate coefficients for the gas-phase reactions of OH radicals with volatile oxygenated and unsaturated organic compounds. Although kinetic data are an essential element for assessing the environmental impact of oxygentaed volatile organic compound (OVOC) emissions and give an indication of the spatial extent of the spread of emissions, a thorough assessment also requires a complete understanding of the tropospheric degradation mechanism of the OVOC and the resulting products. The atmospheric fate of esters, especially unsaturated esters, has not been studied extensively. The major uncertainty in the photodegradation mechanisms of esters is the relative importance of the competitive reaction pathways for the alkoxy radicals formed in the initial oxidation steps, i.e., decomposition, isomerization, and reaction with oxygen. A number of kinetic studies have been reported recently for the Cl-atom initiated degradation of unsaturated esters (*11–13*) and also a single study on the kinetics of the NO_3-radical initiated oxidation of a number of acrylate esters (*14*).

In general, Cl atoms and OH radicals have similar modes of attack in their reaction with organic compounds, attack by Cl atoms being faster and somewhat less selective than attack by OH radicals. Nevertheless, the subsequent chemistry is similar. Therefore, the fate of the different alkoxy radicals formed in the OH-radical initiated atmospheric degradation of the esters can also be accurately determined in studies of Cl reactions with esters, the only expected difference being a slightly different distribution in the final products. We have reported previously a qualitative product study of the reaction of OH radicals with *n*-butyl acrylate (*7*) performed in a collapsible Teflon chamber in which *n*-butyl glyoxylate was identified as a unique reaction product using the GC-MS technique. More recently, a kinetic and product study has been reported for the reactions of OH radicals and Cl atoms with a fluorotelomer acrylate ($CH_2{=}CHC(O)OCH_2CH_2C_4F_9$) in air using FTIR to monitor reactants and products (*15*). In this study the authors found that the main fate of the hydroxyalkoxy radical, formed via addition of OH to the terminal carbon of the double bond followed by subsequent addition of O_2 and reaction of the resulting peroxy radical with NO, was decomposition to give HCHO with a yield of 102 ± 7%. The expected fluorotelomer gyloxylate was found

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as coproduct. This finding is in agreement with our previous finding for the reaction of OH with *n*-butyl acrylate.

In this study, we report the first product investigation of the room-temperature gas-phase reactions of OH radicals and Cl atoms with methyl acrylate in the absence of NO_x.

$$OH + CH_2{=}CHC(O)OCH_3 \rightarrow \text{products} \quad (1)$$

$$Cl + CH_2{=}CHC(O)OCH_3 \rightarrow \text{products} \quad (2)$$

The results are used to postulate atmospheric chemical mechanisms that can be incorporated into chemistry transport models to obtain estimations of the contributions of emissions of such compounds to ozone and other photooxidant formation in the troposphere.

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 (*16*) 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^{-5} Torr. Three magnetically coupled Teflon mixing fans were mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consisted of 32 superactinic fluorescent lamps (Philips TL05 40 W: 320−480 nm, $\lambda_{max} = 360$ nm) and 32 low-pressure mercury vapor lamps (Philips TUV 40 W; $\lambda_{max} = 254$ nm), spaced evenly around the reaction vessel. The lamps were wired in parallel and could be switched individually, allowing a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber was 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 (these lamps provide UV-radiation with a λ maximum around 360 nm):

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

Hydroxyl radicals were generated by the photolysis of H_2O_2 with the mercury lamps (these lamps provide UV-radiation with a λ maximum around 254 nm):

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

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 concentrations used in the experiments for the methyl acrylate in ppm (1 ppm = 2.46×10^{13} molecules cm^{-3} at 298 K and 760 Torr of total pressure) were 0.3−0.6. The concentrations of Cl_2 and H_2O_2 were typically around 4.6 and 7 ppm, respectively.

The following infrared absorption frequency (in cm^{-1}) was used to monitor the reactant: methyl acrylate at 1211. Products were monitored at the following absorption frequencies (in cm^{-1}): formaldehyde at 2766, carbon monoxide at 2169, formyl chloride at 738.6, methyl glyoxylate at 1226, and hydrogen chloride at 2944.8.

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 acrylate (Aldrich, 99%), H_2O_2 (Interox, 85%), and Cl_2 (Messer Griesheim, >99.8%).

Results and Discussion

To investigate the mechanisms of the OH-radical and Cl-atom initiated oxidation of the methyl acrylate, mixtures of H_2O_2/ester/air or Cl_2/ester/air were irradiated for periods of 15−20 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.

To have a basis for the discussion of the experimental results the possible reaction pathways that can occur in the reactions of OH radicals and Cl atoms with the unsaturated ester will first be outlined. As has been proposed for OH/alkene reactions (*17*) the reaction of OH with an ester such as $CH_2{=}CHC(O)OCH_3$ will proceed to a large extent via addition of the OH radical to the double bond with addition at the terminal carbon of the double bond dominating. For methyl acrylate the OH addition mechanism should account for over 98% of the reaction.

Addition of OH to the terminal carbon in the double bond of methyl acrylate followed by addition of O_2 will result in the formation of 1,2-hydroxyperoxy radicals ($CH_2OH{-}CH(O_2\bullet)C(O)OCH_3$). Under atmospheric conditions the hydroxyperoxy radicals would react with NO to form 1,2-hydroxyalkoxy radicals ($CH_2OHCH(O\bullet)C(O)OCH_3$). Under the present NO_x-free experimental conditions the peroxy radicals will undergo self- and cross-peroxy reactions which will also result to a large extent in the formation of 1,2-hydroxyalkoxy radicals; however, molecular channels are also possible which will result in the formation of multifunctional products containing hydroxy, carbonyl, and ester functionalities (*18*). The 1,2-hydroxyalkoxy radicals formed in the OH radical addition step can

(i) decompose to give the corresponding glyoxylate ($HC(O)C(O)CH_3$) and the $\bullet CH_2OH$ radical which will react with O_2 to form formaldehyde,

(ii) decompose to give glycoaldehyde ($HOCH_2C(O)H$) and $CH_3OC(\bullet)(O)$ radicals which will react further to form an aldehyde and CO_2, or

(iii) react with O_2 to form hydroxycarbonyl ester compounds, i.e., $CH_2(OH)C(O)C(O)OCH_3$.

Decomposition of the 1,2-hydroxyalkoxy radicals is expected to dominate over reaction with O_2. A simplified exemplary reaction mechanism for the reaction of OH radicals with methyl acrylate is shown in Figure 1.

As for OH the reaction of Cl atoms with methyl acrylate is predicted to proceed by more than 98% via addition of the Cl atom to the double bond. As for the OH reaction this estimate is based on the assumption that the reactivities of the groups on either side of the ester are independent and additive. Ongoing kinetic and product studies in this laboratory on the reactions of Cl atoms with alkyl acetates (*19*) indicate that this is probably not the case, at least for esters, and also show that the nondecoupling of the reactivities has consequences for the prediction of product channel routes and the determination of ester substituent factors used in structure activity relationship (SAR) estimates of rate coefficients for the reactions of Cl with esters.

The mechanism for the addition of Cl to the double bond of the acrylates is in most respects very similar to that for reaction with OH, with the exception that the C−C bond cleavage channel will result in the formation of CH_2Cl radicals which will add O_2 to give CH_2ClO_2 peroxy radicals. Under the present experimental conditions the CH_2ClO_2 radicals will

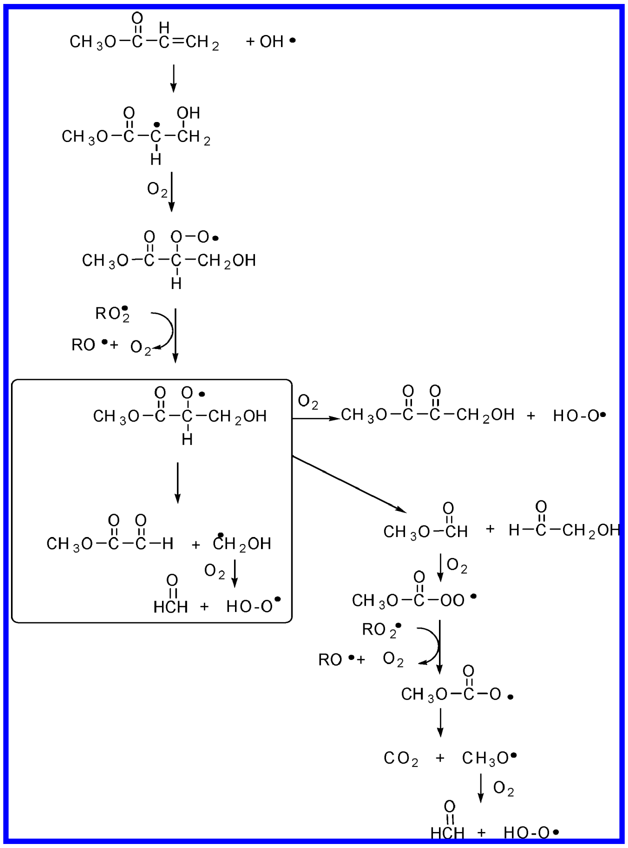

FIGURE 1. Simplified mechanism of the OH-radical initiated oxidation of $CH_2{=}CHC(O)OCH_3$ in air free of NO_x via addition of OH to the terminal carbon of the double bond.

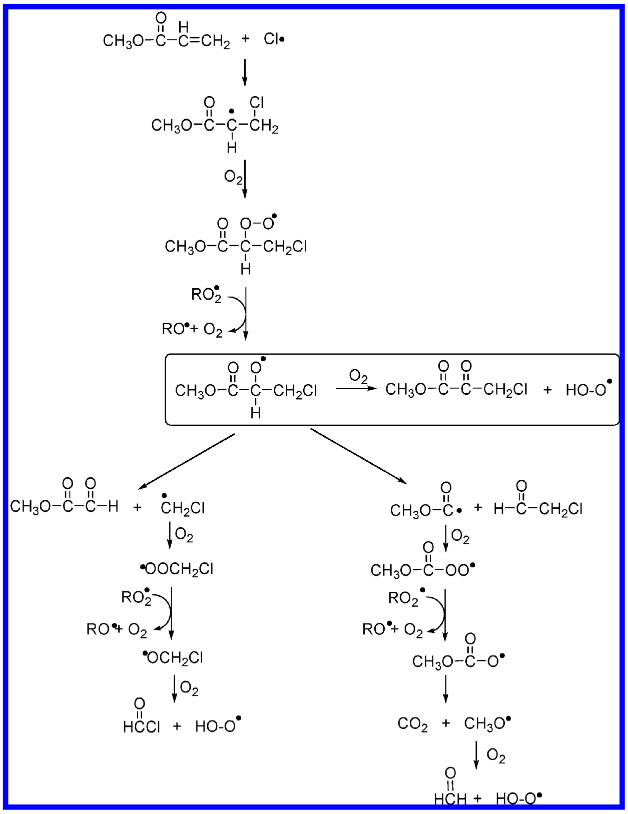

FIGURE 2. Simplified mechanism of the Cl-atom initiated oxidation of $CH_2{=}CHC(O)OCH_3$ in air free of NO_x via addition of Cl to the terminal carbon of the double bond.

undergo self- and cross-reactions with other peroxy radicals to give CH_2ClO alkoxy radicals. CH_2ClO radicals are known to undergo (i) reaction with O_2 to give formyl chloride (HC(O)Cl) and HO_2 radicals and (ii) intramolecular elimination of HCl with the formation of HCO radicals, whereby in the absence of NO the channel forming HC(O)Cl dominates (*20*). Bilde et al. (*20*) have shown that in the presence of NO, where chemically activated CH_2ClO radicals can be formed, pathways exist which lead to products other than HC(O)Cl such as HCl, HCHO, and CO. An exemplary mechanism for the Cl-atom initiated oxidation of methyl acrylate via addition of Cl to the terminal carbon of the double bond is shown in Figure 2.

Reaction with OH. Figure 3 shows an IR spectra acquired before (trace A) and after (trace B) UV irradiation of a mixture of methyl acrylate (MAC) and H_2O_2 in air where residual absorptions due to MAC have been subtracted. Figure 3 trace C shows a reference spectra of methyl glyoxylate (HC(O)-C(O)OCH$_3$) and trace D shows the residual spectrum obtained after subtraction of methyl glyoxylate from the spectrum in trace B. Methyl glyoxylate is difficult to obtain commercially, however, a semiquantitative spectrum of this glyoxylate prepared in situ in the reactor from the photolysis of $BrCH_2C(O)OCH_3$ (*21*) was available (see Supporting Information, (SI)). As indicated in Figure 3 trace B, formation of both HCHO and CO was observed in the reaction system. The similarity of many of the absorption bands in the in situ generated spectra of methyl glyoxylate with those in the product spectrum (Figure 3 trace B) strongly supports that methyl glyoxylate ($HC(O)C(O)OCH_3$) is formed in the system.

No evidence could be found for the formation of glycolaldehyde ($HOCH_2C(O)H$) in the product spectra supporting that the reaction channel involving cleavage of the C−C bond between the carbonyl and alkoxy radical entities is negligible.

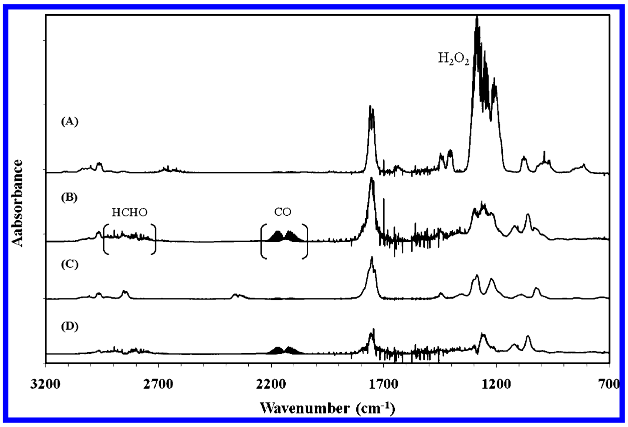

FIGURE 3. Trace A shows the infrared spectrum of $CH_2{=}CHC(O)OCH_3/H_2O_2$/air reaction mixture before irradiation and B shows the IR spectrum after irradiation and subtraction of residual methyl acrylate. Trace C shows a reference spectra of methyl glyoxylate ($CH_3OC(O)C(O)H$) and D shows the residual product spectrum obtained after subtraction of features due to $CH_3OC(O)C(O)H$ from the spectrum in trace B.

Concentration−time profiles of MAC and the identified products methyl glyoxylate, HCHO and CO, are shown in SI Figure S1. The concentration−time contours support that methyl glyoxylate and HCHO are both primary products while the source of CO is secondary in origin. A plot of the concentration of methyl glyoxylate as a function of consumed methyl acrylate is linear for most of the reaction (SI Figure S2).

Other loss processes like reaction with the oxidant are considered negligible due to the high degree of oxygenation of this saturated compound and the absence of reactive olefinic carbons. Assuming that the contribution due to wall loss of methyl glyoxylate is negligibly small, analysis of the slope in Figure S2 gives a product yield of ~90% for the formation of methyl glyoxylate from the reaction of OH with methyl acrylate.

The plot of HCHO versus consumed methyl acrylate shows curvature. The reaction of OH with HCHO has a recommended rate coefficient of 8.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (*22*), which is similar to that for OH with methyl acrylate, and HCHO will, therefore, be subjected to considerable secondary consumption. Since glycolaldehyde is not formed in the reaction system, the secondary consumption of HCHO will be mostly responsible for the formation of CO observed in the system. A plot of the combined yields of HCHO and CO as a function of consumed methyl acrylate should be linear and give a secondary loss corrected yield for HCHO. Such a plot was reasonably linear (Figure S2) and resulted in a yield of 53% for HCHO which is considerably less than the estimated yield of methyl glyoxylate. A similar value was obtained using the correction procedures for secondary loss reactions described in the literature (*23, 24*).

According to the mechanism in Figure 1 the coproduct in the reaction channel forming methyl glyoxylate is expected to be the CH_2OH radical which is known to react fast with O_2 to give HCHO (*22*). High concentrations of HO_2 radicals and other peroxy radicals will be produced in the reaction system and, apart from reaction with OH radicals, reaction with HO_2 or other peroxy radicals could also contribute to secondary removal of HCHO and explain the shortfall in the HCHO yield. For example, reaction of HO_2 radicals with HCHO is known to produce the metastable hydroperoxide $CH_2(OH)OOH$ (*25, 26*). The residual IR product spectrum from the reaction of OH with MAC (Figure 3, trace D) shows a carbonyl absorption centered around 1751 cm^{-1} and several absorptions in the fingerprint region centered around 1291, 1259, 1218, 1119, and 1060 cm^{-1}.

The semiquantitative yield for methyl glyoxylate determined in this study can be compared to a yield of 85% reported by Sidebottom et al. (*27*) from a study on the reaction of OH radicals with MAC in the presence of NO performed in the EUPHORE chamber in Valencia, Spain. Details of this study have not yet been published in the peer-reviewed literature and until this occurs it is difficult to compare the two yield values.

It is interesting to compare the products formed from the addition of OH to the double bond in methyl acrylate with those formed from the OH radical addition route in the reaction of OH with acrolein ($CH_2{=}CHC(O)H$). In the OH + acrolein reaction the major product from the addition channel is glycoaldehyde ($HOCH_2C(O)H$) (*28*) which is formed from scission of the C−C bond in the 1,2-hydroxyalkoxy radical, $HOCH_2CH(O\cdot)CHO$, binding the alkoxy and −CHO entities. This is in stark contrast to the OH + methyl acrylate reaction where the major addition pathway product is methyl glyoxylate formed by the scission of the C−C bond binding the alkoxy and hydroxyl entities of the 1,2-hydroxyalkoxy radical, $HOCH_2CH(O\cdot)C(O)OCH_3$. This indicates that the −CHO and $-C(O)OCH_3$ entities are having different effects on the stability of the C−C bonds formed by the alkoxy group. Replacing one H atom by a $-OCH_3$ group from acrolein to methyl acrylate, the lone pair electrons in the case of the ester will increase the electron density between the adjacent carbons, making the bond stronger, leading to a reduction of the importance of the scission in this part of the alkoxy radical. A scission pattern similar to that of methyl acrylate will be expected for the reaction of $CH_2{=}CHC(O)CH_3$ + OH where the $-CH_3$ substituent has a positive inductive effect compared with the H atom in acrolein. Theoretical calculations on the intermediates may help to reveal the reason for the difference in the reaction pathways.

Based on the observed reaction products, it has been concluded that the main fate of the $CH_2OHCO(\cdot)HC(O)OCH_3$ radical formed in the addition of OH to MAC is decomposition to give methyl glyoxylate, and CH_2OH radicals as a coproduct. This is in agreement with a previous GC-MS product study on the reaction of OH with *n*-butyl acrylate by Blanco and Teruel (*7*) in which evidence was found for formation of *n*-butyl glyoxylate in significant yield and also the recent FTIR study of the reaction of OH radicals with 4:2 fluorotelomer acrylate ($C_4F_9CH_2CH_2OC(O)CH{=}CH_2$) by Butt et al. (*15*) in a photoreactor in the presence of NO_x in which they conclude that 4:2 fluorotelomer glyoxylate ($C_4F_9CH_2CH_2O$-$C(O)C(O)H$) is the sole product based upon a 102 ± 7% formation yield for the coproduct HCHO. Reaction of the CH_2OH radical coproduced with the glyoxylate is expected to give HCHO. Although HCHO production has been observed in the OH-radical initiated oxidation of MAC the quantity is much lower than that of the glyoxylate. We attribute the deficiency in HCHO to its possible efficient removal via reaction with peroxy radicals in the NO_x free system used for the investigations.

We looked for but could find no evidence for the formation of hydroxydicarbonyl compounds or $HOCH_2CHO$ that could be produced via the reaction with O_2 or a C_2−C_3 bond cleavage of the 1,2-hydroxyalkoxy radical $CH_2OHCO(\cdot)HC(O)OCH_3$ which by way of reaction channel elimination further supports that the main reaction channel in the reactions of OH with MAC is addition to the double bond with subsequent decomposition of the intermediate 1,2-hydroxyalkoxy radical to form methyl glyoxylate.

Cl Reaction. Figure S3, panel A, shows a spectrum of a MAC/Cl_2/air reaction mixture and panel B shows a spectrum after irradiation and subtraction of absorptions due to MAC. Panels C and D show reference spectra of formyl chloride (HC(O)Cl) and HCl, respectively. Panel E shows the residual product spectrum obtained after subtraction of features attributable to HC(O)Cl. The only products that could be positively identified in the reaction were HC(O)Cl, HCl, and CO. The concentration−time profiles of the products (Figure S4) show that they are all of secondary origin, i.e., they are being formed from the oxidation of a primary product. It was difficult to determine whether or not methyl glyoxylate was being formed in the reaction, however, the delay in formation of HC(O)Cl supports that the C−C cleavage channel resulting in formation of methyl glyoxylate is negligible (Figure 2). No evidence could be found for the formation of chloroacetaldehyde ($CH_2ClC(O)H$) supporting that the alternative C−C cleavage reaction channel is also negligible. Since attack of the Cl atom at the CH_3 group in MAC will be very minor and the C−C cleavage reactions channels appear to be negligible, the experimental evidence supports that the overwhelming pathway in the reaction of Cl with MAC must be addition at the terminal carbon of the double bond to form methyl 3-chloro-2-oxopropanoate ($ClCH_2C(O)C(O)OCH_3$).

Unfortunately, $ClCH_2C(O)C(O)OCH_3$ is not commercially available and thus a direct comparison with the product spectrum (Figure S3, panel E) cannot be made. However, an infrared spectrum has been simulated for $ClCH_2C(O)$-$C(O)OCH_3$ using the using Gaussian 03 ab initio quantum chemistry package (*29*). The spectrum was calculated using the B3LYP/6 31+G level of theory (*30–32*). The simulated infrared spectrum is compared in Figure 4, panel B, with the residual product spectrum, panel A, from the Cl + $CH_2{=}CHC(O)OCH_3$ reaction. The computed IR spectrum is in many respects, in both the carbonyl and fingerprint spectral regions, very similar to the residual product spectrum, the only major difference being a shift of a few cm^{-1} of the computed absorption bands compared to those obtained experimentally. The resonably good similarity between computed and experimental absorption bands adds additional support to the conclusion reached on the basis of

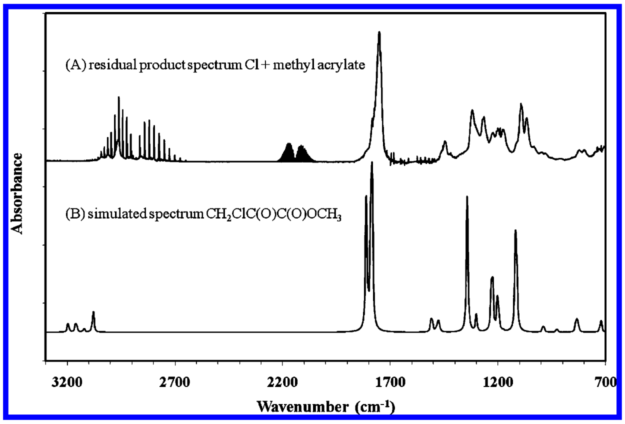

FIGURE 4. Comparison of the residual product IR spectrum obtained for the reaction of Cl with $CH_2{=}CHC(O)OCH_3$ with the simulated IR spectrum for the expected major product $ClCH_2C(O)C(O)OCH_3$.

the product identification that the residual product spectrum is very probably mainly due to $ClCH_2C(O)C(O)OCH_3$.

It is interesting to compare the products formed from the addition of Cl to the double bond in methyl acrylate with those formed from the Cl radical addition route for other unsaturated aldehydes and ketones. In the reaction of Cl with acrolein reaction Canosa-Mas et al. (*33*) have observed that chloroacetaldehyde ($ClCH_2CHO$), formed from the scission of the C−C bond binding the alkoxy and carbonyl entities of the 1,2-chloroalkoxy radical, $ClCH_2CH(O\bullet)CHO$, is the major product from the addition channel. Similarly, Orlando et al. (*34*) and Canosa-Mas et al. (*33*) have observed that addition of Cl to the double bond in methacrolein produces chloroacetone as the main product via scission of the C−C bond binding the alkoxy and carbonyl entities of the 1,2-chloroalkoxy radical formed in the oxidation process. Finally, Orlando et al. (*34*) have observed chloroacetaldehyde as a main product from the addition of Cl to the double bond in methyl vinyl ketone ($CH_2{=}CHC(O)CH_3$) which is again formed from severance of the C−C bond binding the alkoxy and carbonyl entities of the 1,2-chloroalkoxy radical formed in the oxidation process.

The dominance of the C−C cleavage channel observed for the addition reactions of Cl with the unsaturated aldehydes and ketones contrasts starkly with the results obtained here for the addition of Cl to methyl acrylate where the experimental evidence supports that the major fate of the 1,2-hydroxyalkoxy radical $ClCH_2CH(O\bullet)C(O)OCH_3$ formed in the oxidation process is reaction with O_2 to form the chain-retaining product $ClCH_2C(O)C(O)OCH_3$ and HO_2 radicals. This behavior also contrasts very sharply with the analogous OH reaction discussed above where scission of the C−C bond binding the alkoxy and hydroxyl entities of the 1,2-hydroxyalkoxy radical ($HOCH_2{-}CH(O\bullet)C(O)OCH_3$) is the dominating reaction pathway.

In contrast, the experimental evidence supports that the main fate of the $CH_2ClCO(\bullet)HC(O)OCH_3$ radical formed in the addition of Cl to MAC is reaction with O_2, via H-atom abstraction, to give $ClCH_2C(O)C(O)OCH_3$.

The conclusion that $ClCH_2C(O)C(O)OCH_3$ is the main product of the reaction of Cl with MAC is in agreement with the observations of Butt et al. (*15*) who came to the conclusion in their FTIR product study of the Cl + $C_4F_9CH_2CH_2OC(O)CH{=}CH_2$ reaction that the main fate of the intermediate 1,2-chloroalkoxy $C_4F_9CH_2CH_2OC(O)CH(O\bullet)CH_2Cl$ radical was reaction with O_2 to give the chain-retaining compound $C_4F_9CH_2CH_2OC(O)C(O)CH_2Cl$.

Atmospheric Implications. Unsaturated esters are removed from the troposphere mainly by their rapid reactions with OH radicals (*5–8*) which results in atmospheric lifetimes of a few hours. However, in some marine regions, peak values of 1×10^5 atoms cm^{-3} for Cl atoms have been observed (*35, 36*). Under such circumstances the reaction of Cl with the esters can be a significant if not dominant loss process. Photolysis is not an important atmospheric loss process for these unsaturated esters as they do not absorb radiation at actinic wavelengths (*6*). Losses by uptake in surface and rainwater or cloud droplets are also not important sinks for these compounds as they are highly volatile and sparingly soluble in water.

The relatively short atmospheric lifetimes of the unsaturated esters due to reaction with OH indicates that the compounds will be oxidized near their anthropogenic source origins where they can contribute to the formation of O_3 and other photooxidants. The product investigations presented in this study show that the major products of the OH-radical initiated oxidation of methyl acrylate ($CH_2{=}CHC(O)OCH_3$) under NO_x-free conditions will be methyl glyoxylate ($HC(O)C(O)OCH_3$) and it is expected that this will also be the case in the atmosphere in the presence of NO_x. The alkyl glyoxylate will be further oxidized fairly rapidly by reaction with OH radicals and may also photolyze because they probably absorb quite strongly in the atmospheric actinic region due to the presence of the −C(O)H chromophore. The glyoxylates have the potential to contribute to secondary aerosol formation (SOA), i.e., depending on their reactive uptake coefficients the glyoxylates may partition into cloud droplets where they can undergo various types of chemical reactions which result in the formation of oligomers as has been discussed intensively in the recent literature for glyoxal and methylglyoxal (*37*). Further studies on the product distributions from the OH-radical initiated oxidation of unsaturated esters need to be performed over the range of temperatures, NO_x, and pressures of oxygen typically prevailing in the troposphere to gain a better quantitative understanding of their contribution to photooxidant and SOA formation in the atmosphere.

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Supporting Information Available

Concentration−time profile and yields plots for the reaction of OH radicals with methyl acrylate (Figures S1 and S2); product identification plots and concentration−time profiles for the reactions of Cl atoms with methyl acrylate (Figures S3 and S4); and details of the semiquantitative spectrum of methyl glyoxalate prepared in situ in the 6-m reactor of Wuppertal from the photolysis of $BrCH_2C(O)OCH_3$/air/NO mixture. This information is available free of charge via the Internet at http://pubs.acs.org.

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