Kinetics and Products of Gas-Phase Reactions of Ozone with Methyl Methacrylate, Methyl Acrylate, and Ethyl Acrylate

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The kinetics and products of the gas-phase reactions of ozone with methyl methacrylate, methyl acrylate, and ethyl acrylate have been investigated at 760 Torr total pressure of air and 294 ± 2 K. The rate coefficients obtained (in cm³ molecule⁻¹ s⁻¹ units) were as follows: k(methyl methacrylate) = $(6.7 \pm 0.9) \times 10^{-18}$, k(methyl acrylate) = $(0.95 \pm 0.07) \times 10^{-18}$, and k(ethyl acrylate) = $(1.3 \pm 0.1) \times 10^{-18}$. In addition to formaldehyde being observed as a product of the three reactions, the other major reaction products were methyl pyruvate from reaction of ozone with methyl methacrylate, methyl glyoxylate from reaction of ozone with methyl acrylate. Possible reaction mechanisms leading to the observed products are presented and discussed.

1. Introduction

Acrylate esters are volatile liquids, soluble in most organic solvents but only slightly soluble in water. Containing a double bond and a functional carboxylic group, they are highly reactive chemicals and, therefore, used mainly as intermediates in the production of other materials. For example, individual molecules of acrylic acid or esters, monomers, readily combine with themselves or other monomers to form long chains of repeating units to constitute polymers which have chemical and physical properties different from the constituent monomers. They are used in formulating paints and dispersions for paints, inks, and adhesives. They are also used in making cleaning products, antioxidant agents, surfactants for making aqueous resins, and dispersions for textiles and papers. Part of these compounds may escape into the atmosphere, where they can play a role in the atmospheric chemistry and air quality at local and regional scales.

Acrylate esters contain a vinyl group, which makes them more reactive than simple esters in the gas phase toward the main atmospheric oxidants such as hydroxyl radicals (OH), nitrate radicals (NO₃), ozone (O₃), and chlorine atoms (Cl). Although numerous studies were conducted on the atmospheric degradation of saturated esters¹⁻³ and unsaturated esters initiated by reactions with OH radicals⁴⁻⁷ and Cl atoms,⁸⁻¹² fewer kinetic and mechanistic investigations have been performed on the unsaturated esters through reaction with ozone¹³⁻¹⁷ and NO₃ radicals.¹⁸⁻²⁰

In this work, we report kinetic and mechanistic studies on ozone reactions with three acrylates: methyl methacrylate (MMA, $CH_2=C(CH_3)C(O)OCH_3$), methyl acrylate (MA, $CH_2=CHC(O)OCH_3$), and ethyl acrylate (EA, $CH_2=CHC-(O)OCH_2CH_3$). Methyl methacrylate is the monomer to make polymethyl methacrylate acrylic plastics (PMMA), used as a shatterproof replacement for glass (this application consumes approximately 80% of the MMA). Methyl methacrylate is also used for production of the copolymer methyl methacrylate-butadiene-styrene (MBS), used as a modifier for PVC. In addition, MMA is a key ingredient in a number of products.

Polymers and copolymers of methyl methacrylate are also used in undissolved surface coatings, adhesives, etc. Methyl acrylate can be used as a copolymer in the process of polymerization of polyanionic cellulose (PAC) polymers to reduce the glasstransition temperature of PAC polymers. It is also used in making vitamin B1. Ethyl acrylate is used in the production of polymers including resins, plastics, etc.

In this work, the reaction rate coefficients of ozone with the three acrylates have been measured using both absolute and relative rate methods

CH₂=CH(CH₃)C(O)OCH₃ + O₃ → products
$$k_1$$

CH₂=CHC(O)OCH₃ + O₃ → products k_2
CH₂=CHC(O)OCH₂CH₃ + O₃ → products k_3

The mechanisms of these reactions have been also investigated using in situ FT-IR spectroscopy, which enabled us to determine the product formation yields. The results obtained are compared with previous studies on reactions of ozone with unsaturated esters. To date, only Grosjean and Grosjean^{15,21} reported reaction product formation yields from reaction of methyl acrylate with ozone while Grosjean et al.¹⁴ and Grosjean and Grosjean¹⁶ reported the single kinetic studies of O₃ with methyl methacrylate and methyl acrylate, respectively.

2. Experimental Section

Experiments were carried out in a 7300 L Teflon chamber in the dark at 294 ± 2 K and 760 Torr total pressure of purified air (<5% of relative humidity). Rapid mixing of reactants was ensured within 1–2 min using a set of two fans made of Teflon fitted into the chamber. After each experiment, the chamber was flushed with purified air for at least 12 h. Reactants were introduced into the chamber either via the liquid phase by streaming purified air or as a gas using a calibrated cylinder with a known volume (0.9 L) equipped with two pressure sensors (0–10 and 0–100 Torr, MKS Baratron). The temperature and relative humidity data were recorded by a combined

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sensor (T870, Series T800, Dostmann Electronic). Ozone concentrations were monitored by a Horiba (APOA-360) ultraviolet ozone analyzer. Temporal resolution of the ozone monitor enables obtaining a measurement every 5 s. The other reactants were monitored by in situ Fourier transform infrared absorption spectroscopy (Nicolet 5700 Magna FT-IR spectrometer) coupled to a white-type mirror system resulting in an optical path of about 129 m.

Rate coefficients for the studied reactions were determined using both absolute and relative methods. In the absolute method studies, the decays of ozone were measured in the presence of excess concentrations of the esters. For each reaction investigated, one run was conducted in the presence of cyclohexane to scavenge OH radicals, which could be produced during ozonolysis. The initial ester concentrations in the chamber were in the range of $(1.36-12.2) \times 10^{13}$ molecules cm⁻³ for methyl methacrylate and $(2.8-14.5) \times 10^{13}$ molecules cm⁻³ for methyl acrylate and ethyl acrylate, while the initial ozone concentrations were in the range of $(1.55-13.2) \times 10^{12}$ molecules cm⁻³. Under pseudo-first-order conditions, the rate of disappearance of O₃ followed a simple exponential rate law

$$[O_3]_t = [O_3]_0 e^{-k'_t}$$

where $k' = k_i[\text{ester}] + k'_0$ with k_i (i = 1-3) representing the rate coefficients for the reaction of O₃ with the three esters to be determined and k'_0 the first-order rate coefficient for O₃ removal in the absence of ester, which was due to dilution and loss of ozone on the wall of the chamber. Further, k_i can be obtained from the slope of the plots of $k' - k'_0$ versus [ester]₀ considering the following equation

$$k'-k'_0 = k_i [ester]_0$$

Additional measurements of the rate coefficients were conducted using the well-established relative rate method. Kinetic data were derived by monitoring the loss of unsaturated esters relative to one or more reference compounds. The loss rates of esters and reference compounds in the absence of ozone, k_d (esters) and k_d (ref), (in s⁻¹), respectively, were measured before each run, and the values obtained have been considered in the treatment of the data. Provided that the unsaturated esters and references were lost only by reaction with ozone and by dilution and neither ester nor the reference compound was formed, it can be shown that

$$\ln[[\text{esters}]_0/[\text{esters}]_t] - k_d(\text{esters})t = k_{\text{esters}}/k_{\text{ref}}(\ln([\text{ref}]_0/[\text{ref}]_t) - k_d(\text{ref})t)$$

where [esters]₀, [esters]_t, [ref]₀, and [ref]_t are the concentrations of the esters and reference at times t_0 and t and k_{esters} and k_{ref} are the rate coefficients for reactions of esters and the reference with O₃. Plots of (ln([esters]₀/[esters]_t) - $k_d(esters)t$) versus (ln([ref]₀/[ref]_t) - $k_d(ref)t$) should be linear, pass through the origin, and have a slope of k_{esters}/k_{ref} .

Ethene and propene were used as the reference compounds. Reactants and reference compounds were monitored by FT-IR spectroscopy using absorption features over the following wavenumber ranges (cm⁻¹): methyl methacrylate, 1250–1120; methyl acrylate, 1100–1049 and 1252–1156; ethyl acrylate, 1332–1246; ethene, 1055–873; propene, 968–867.

Experiments were conducted in the presence of an excess amount of cyclohexane to avoid secondary reactions with OH radicals (which could be formed during ozonolysis of unsaturated compounds). The experiments have been repeated to enable us to derive averaged ratios for k_{esters}/k_{ref} . The quoted uncertainties on the obtained rate coefficients originate from the uncertainties associated to the value of the slope (one standard deviation, 1σ).

In addition to the kinetic studies, a series of experiments was performed to investigate the mechanism of the ozonolysis of the three esters. These runs were conducted in the presence of cyclohexane (as OH scavenger) at 760 Torr of purified air and 293 ± 1 K. Initial concentrations of reactants were in the range $(1.25-5.01) \times 10^{13}$ molecules cm⁻³. Organic compounds were continuously monitored by FT-IR spectroscopy and ozone by the Horiba analyzer. FT-IR spectra were recorded every 4-5 min by coadding 110-120 scans with a resolution 1 cm⁻¹. In all experiments, esters were first introduced in the chamber in order to assess their loss rate, in the presence of cyclohexane. The temporal concentration profiles of organic compounds were monitored for 1 h before adding ozone to initiate the reaction. Unsaturated esters were monitored using absorption features over the following wavenumber ranges (cm⁻¹): methyl methacrylate, 1262-1112; methyl acrylate, 1252-1156; ethyl acrylate, 1348-1262. Gas-phase products of the investigated reactions were identified and tentatively assigned by FT-IR spectroscopy using reference spectra when possible and their formation yields obtained by plotting the concentration of formed products versus the concentration of consumed ester. Three runs were performed for each unsaturated ester-ozonecyclohexane-air mixture system. The resulting formation yields of gas-phase products arising from each experiment were then averaged, leading to the final gas-phase product yields. The quoted error on the yield values originates from one standard deviation (1σ) on the averaged yield.

Chemicals. Unsaturated esters (methyl methacrylate, methyl acrylate, and ethyl acrylate) and methyl pyruvate were provided by Fluka with a stated purity of $\geq 99.0\%$ and 97% (GC), respectively. Ethyl glyoxylate (50% in toluene) was provided by Alfa Aesar. Cyclohexane was obtained from Sigma Aldrich with a purity of $\geq 99.9\%$. Propene and ethene were provided by Air Liquide.

3. Results and Discussion

3.1. Rate Coefficient Measurements. Absolute Study. Figure 1 displays an example of the typical loss of ozone versus reaction time in the absence and presence of different concentrations of the ester (methyl methacrylate), and Figure 2 shows the plots of $(k' - k'_0)$ versus the ester concentrations for different esters. Values of k_i were derived from the least-squares fit of the straight lines. The measured k'_0 ozone decay rates in the absence of added reactants was $k'_{0} = (0.17 - 0.25) \times 10^{-4} \text{ s}^{-1}$. Loss rates of ozone from dilution and adsorption on Teflon film were measured before addition of the ester. The contribution of this later loss was found to represent 3-19% of the total decay of ozone for the experiments with methyl methacrylate and 9-40% for those with methyl acrylate and ethyl acrylate. The experimental conditions and measured values of the rate coefficients are listed in Table 1. As shown in Table 1 and Figure 2, the presence of an excess amount of cyclohexane led to the same rate coefficient values, which indicate that secondary reactions, involving, for example, OH radicals, were not significant in our experimental conditions. This was expected for possible OH reactions because the latter would preferentially



Figure 1. Example of plots of ozone consumption versus reaction time in the absence and presence of esters (example of methyl methacrylate).



Figure 2. Plots of absolute rate data for the ozone reaction with methyl methacrylate, methyl acrylate, and ethyl acrylate. Experiments conducted without cyclohexane are represented with filled symbols, while those conducted in the presence of an excess of cyclohexane are shown with open symbols.

react with esters (in excess) and will not have any effect on the decay rate of ozone. The rate coefficients (in cm³ molecule⁻¹ s⁻¹) obtained for reactions of O₃ with the three esters at 294 \pm 2 K and 760 Torr of air are as follows

CH₂=CH(CH₃)C(O)OCH₃ + O₃ → products
$$k_1 = (6.8 \pm 0.4) \times 10^{-18}$$

CH₂=CHC(O)OCH₃ + O₃ → products
$$k_2 = (0.95 \pm 0.06) \times 10^{-18}$$

CH₂=CHC(O)OCH₂CH₃ + O₃ → products
$$k_3 = (1.28 \pm 0.06) \times 10^{-18}$$

Relative Rate Study. The kinetics of the reactions of ozone with the three acrylates were measured relative to those of the

reactions of O₃ with ethene and propene. Prior to addition of O₃, the loss rates of reactants were measured in the presence of cyclohexane (in order to estimate the dilution and adsorption rates on the Teflon film). The initial concentrations of reactants were in the range of $(2.51-8.01) \times 10^{13}$ molecules cm⁻³, while those of ozone were in the range of $(3.26-10.0) \times 10^{13}$ molecules cm⁻³. The duration of the experiments was varied from 30 to 120 min, depending on the reactivity of the studied esters. k_d (esters) and k_d (ref) were found to be similar in our experimental conditions, ranging from 1.1×10^{-5} to 1.3×10^{-5} s^{-1} . The loss of the unsaturated esters through reaction with ozone represents about 87-92% for methyl methacrylate, 26-82% for methyl acrylate, and 40-78% for ethyl acrylate of the total loss of these species. Examples of the obtained plots of $(\ln([esters]_0/[esters]_t) - k_d(esters)t)$ versus $(\ln([ref]_0/[ref]_t) - k_d(esters)t)$ $k_{\rm d}({\rm ref})t$) are displayed in Figures 3–5. Linear squares analysis of the data gives the results shown in Table 2. The measured rate coefficient ratios were placed on an absolute scale using k(propene + O₃) = 1.0 × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹ and k(ethene $+ O_3 = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, ^{22} \text{ leading to the}^{-1}$ following rate coefficient values (in cm^3 molecule⁻¹ s⁻¹), taken as an average of all values

CH₂=CH(CH₃)C(O)OCH₃ + O₃ → products
$$k_1 = (6.5 \pm 0.7) \times 10^{-18}$$

CH₂=CHC(O)OCH₃ + O₃ → products

$$k_2 = (0.94 \pm 0.06) \times 10^{-18}$$

CH₂=CHC(O)OCH₂CH₃ + O₃ → products
$$k_3 = (1.3 \pm 0.1) \times 10^{-18}$$

As shown above, the rate coefficient values obtained using absolute and relative methods are in excellent agreement. In addition to these measurements, experiments were performed to determine the decay of ethyl acrylate (EA) against methyl acrylate (MA) and methyl methacrylate (MMA). These experiments resulted in the rate coefficients ratios of $k(EA + O_3)/k(MA + O_3) = 1.25 \pm 0.14$ and $k(MMA + O_3)/k(EA + O_3) = 5.62 \pm 0.13$, which are in good agreement with the values of 1.38 ± 0.19 and 5.0 ± 0.9 obtained from the ratios of the measured rate coefficients for these esters with ethene and propene as reference compounds.

The rate coefficients recommended in this work are the averaged values obtained using both absolute and relative methods with error limits that encompass the extremes of σ error of the individual determinations

$$k(O_3 + \text{ methyl methacrylate}) =$$

(6.7 ± 0.9) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹

$$k(O_3 + \text{methyl acrylate}) =$$

(0.95 ± 0.07) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹

$$k(O_3 + \text{ethyl acrylate}) =$$

(1.3 ± 0.1) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹

The only other measurements reported in the literature so far on the title reactions are from Grosjean et al.¹⁴ and Grosjean

TABLE 1: Reaction of O₃ with Methyl Methacrylate, Methyl Acrylate, and Ethyl Acrylate: Summary of the Experimental Conditions and Results from the Absolute Study at 294 ± 2 K and 760 Torr of Air

ester	[ester] (10 ¹³ molecules cm ⁻³)	$[O_3]_0$ (10 ¹² molecules cm ⁻³)	$(k' - k'_0 \pm 1\sigma) \ (10^{-4} \text{ s}^{-1})$
methyl methacrylate,	1.36 ± 0.04	1.55	0.94 ± 0.01
$CH_2 = CH(CH_3)C(O)OCH_3^a$	3.0 ± 0.2	3.05	2.04 ± 0.01
	5.4 ± 0.2^d	2.50	3.63 ± 0.02
	7.1 ± 0.3	4.22	4.68 ± 0.02
	8.0 ± 0.4	13.2	5.30 ± 0.02
	12.2 ± 0.4	2.69	8.32 ± 0.02
		$k_1 = (6.8 \pm 0.4) \times 10^{-18}$	
methyl acrylate,	2.8 ± 0.1	2.47	0.29 ± 0.01
$CH_2 = CHC(O)OCH_3^b$	5.3 ± 0.2^d	3.12	0.51 ± 0.01
	5.8 ± 0.2	2.85	0.57 ± 0.01
	10.4 ± 0.4	3.03	1.04 ± 0.01
	13.1 ± 0.5	3.09	1.25 ± 0.01
	14.5 ± 0.6	2.93	1.40 ± 0.01
		$k_2 = (0.95 \pm 0.06) \times 10^{-18}$	
ethyl acrylate,	2.80 ± 0.07	1.65	0.27 ± 0.01
$CH_2 = CHC(O)OCH_2CH_3^c$	5.4 ± 0.2^d	1.97	0.59 ± 0.01
	7.7 ± 0.3	2.75	0.96 ± 0.01
	10.2 ± 0.2	3.86	1.19 ± 0.01
	13.2 ± 0.3	2.58	1.59 ± 0.01
	14.5 ± 0.3	2.31	1.79 ± 0.01
		$k_3 = (1.28 \pm 0.06) \times 10^{-18}$	

^{*a*} For methyl methacrylate experiments, ozone decay rate was $k'_0 = (0.23 - 0.25) \times 10^{-4} \text{ s}^{-1}$. ^{*b*} For methyl acrylate experiments, ozone decay rate was $k'_0 = (0.17 - 0.19) \times 10^{-4} \text{ s}^{-1}$. ^{*c*} For ethyl acrylate experiments, ozone decay rate was $k'_0 = (0.18 - 0.19) \times 10^{-4} \text{ s}^{-1}$. ^{*d*} Experiments conducted in the presence of cyclohexane ($\sim 7.5 \times 10^{15}$ molecules cm⁻³).



Figure 3. Plots of relative kinetic data from the ozonolysis of MMA using ethene and propene as organic references in the presence of cyclohexane (\sim (2.7–4.7) × 10¹⁵ molecules cm⁻³).

and Grosjean¹⁶ using the absolute method and Munshi et al.¹³ using the second-order kinetic condition. Grosjean et al.¹⁴ measured a rate coefficient of ozone reaction with methyl methacrylate of $k = (7.5 \pm 0.9) \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹, which differs only by 15% from the one measured in the present work. For the rate coefficient of the reaction of O₃ with methyl acrylate, Grosjean and Grosjean¹⁶ obtained $k = (1.05 \pm 0.15) \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹. This value is less than 10% higher than that obtained in this work. Munshi et al.¹³ reported much higher rate coefficient values for reactions of ozone with methyl acrylate ($k = (2.9 \pm 0.2) \times 10^{-18}$) and ethyl acrylate ($k = (5.7 \pm 0.6) \times 10^{-18}$), respectively, a factor three and five higher than our determinations. It has to be mentioned that in their work Munshi et al., using a flow tube, observed a larger



Figure 4. Plots of relative kinetic data from the ozonolysis of EA using MMA and MA as organic references in the presence of cyclohexane ($\sim 4.7 \times 10^{15}$ molecules cm⁻³).

consumption of ozone than acrylates, which may indicate the occurrence of secondary reactions in their system, explaining the larger rate coefficient values they obtained.

As expected, the rate coefficient value for reaction of O₃ with methyl methacrylate is higher than those with methyl acrylate and ethyl acrylate (by a factor of ~7 and ~5, respectively). This might be due to the presence of the electron-donating methyl group on the carbon–carbon double bond, which increases the electronic density and therefore the reactivity toward ozone. Table 3 summarizes the rate coefficients values available for reactions of O₃ with unsaturated esters. Examination of the data presented in this table shows that $k(O_3 + CH_2=CHC(O)OCH_3) < k(O_3 + CH_2=CHC(O)OCH_2CH_3) <$



Figure 5. Plots of relative kinetic data from the ozonolysis of EA and MA using ethene as organic reference in the presence of cyclohexane ($\sim 5.5 \times 10^{15}$ molecules cm⁻³).

 $k(O_3 + CH_2 = CHC(O)O(CH_2)_3CH_3)$, which could indicate that the length of the R' group in RC(O)OR' may have an effect on the reactivity even though O₃ is expected to add mainly to the >C=C<. According to the limited existing data, $k(O_3 + CH_2 = CHC(O)OCH_3)$ is a factor 1.3 lower than $k(O_3 + CH_2 = CHC(O)O(CH_2)CH_3)$ and a factor 2.4 lower than $k(O_3 + CH_2 = CHC(O)O(CH_2)CH_3)$. However, this trend in the reactivity needs to be confirmed. On the other hand, the presence of the methyl group on >C=C< enhances the reactivity ($k(O_3 + CH_2 = CHC(O)OCH_3) < k(O_3 + CH_2 = CHC(O)OCH_3)).$

3.2. Gas-Phase Reaction Products. A set of three experiments has been conducted for each unsaturated ester in the presence of an excess amount of cyclohexane and one experiment in its absence. Reaction mixtures consisted of (1.25-4.99) \times 10¹³ molecules cm⁻³ of the esters and (1.0–2.5) \times 10¹³ molecules cm⁻³ of ozone. The concentration of cyclohexane, when present, was typically 7.5×10^{15} molecules cm⁻³. The gas-phase reaction products were monitored and tentatively assigned by FT-IR spectroscopy using reference spectra when available. Cyclohexanone, a product of the OH-initiated oxidation of cyclohexane, was not observed in our experimental conditions, which indicates that its formation was below the detection limit of our instrumentation or/and the OH formation vield was negligible. While formic acid (HCOOH) and carbon monoxide (CO) were observed as reaction products with minor yields (<5%), formaldehyde (HCHO) was one of the main reaction products in the three reactions investigated. Methyl

TABLE 3: Rate Constants of Unsaturated Esters byReaction with Ozone in the Gas Phase

unsaturated esters	$k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	ref
methyl methacrylate, CH ₂ =C(CH ₃)C(O)OCH ₃	$\begin{array}{c} (7.5\pm0.9)\times10^{-18} \\ (6.7\pm0.9)\times10^{-18} \end{array}$	14 this work
methyl acrylate, CH ₂ =CHC(O)OCH ₃	$\begin{array}{c} (1.05\pm0.15)\times10^{-18} \\ (2.9\pm0.2)\times10^{-18} \\ (0.95\pm0.07)\times10^{-18} \end{array}$	16 13 this work
ethyl acrylate, CH ₂ =CHC(O)OCH ₂ CH ₃	$(5.7 \pm 0.6) \times 10^{-18}$ $(1.3 \pm 0.1) \times 10^{-18}$	13 this work
methyl crotonate, CH ₃ CH=CHC(O)OCH ₃	$(4.4 \pm 0.3) \times 10^{-18}$	14
ethyl methacrylate, CH ₂ =C(CH ₃)C(O)OCH ₂ CH ₃	$(7.68 \pm 0.88) \times 10^{-18}$	17
<i>n</i> -butyl acrylate, CH ₂ =CHC(O)O(CH ₂) ₃ CH ₃	$(2.40 \pm 0.29) \times 10^{-18}$	17

pyruvate (CH₃C(O)C(O)OCH₃) was observed as a product from O_3 + methyl methacrylate, methyl glyoxylate (HC(O)-C(O)OCH₃) was observed as a product from O_3 + methyl acrylate, and ethyl glyoxylate (HC(O)C(O)OCH₂CH₃) was observed as a product from O_3 + ethyl acrylate.

Figure 6 shows IR spectra of the gas mixture in the chamber at different stages of the reaction. Figure 6 A shows the IR spectrum of methyl methacrylate. Figure 6B is a mixture of methyl methacrylate and O₃ at the start of the experiment. Figure 6C shows the IR spectrum after 4 h of the reaction. Figure 6D and Figure 6E display, respectively, IR spectra of methyl pyruvate and formaldehyde (main reaction products). Figure 6F shows the residual spectrum obtained after subtraction of the identified products. Figure 7 shows a plot of the observed formaldehyde and methyl pyruvate formation versus methyl methacrylate loss (in the presence of cyclohexane). As seen from Figure 7, formation of formaldehyde and methyl pyruvate scales linearly with the loss of methyl methacrylate (up to 63% consumption of methyl methacrylate). This was also the case for product formation for reactions of ozone with the other esters. The linearity of the formation of HCHO and the other carbonyl compounds (methyl pyruvate (CH₃C(O)C(O)OCH₃), methyl glyoxylate (HC(O)C(O)OCH₃), and ethyl glyoxylate $(HC(O)C(O)OCH_2CH_3))$ versus consumption of the acrylates suggests the absence of a significant loss or formation of the products observed via secondary reactions in the chamber. Tables 4, 5, and 6 summarize the measured formation yields of the oxidation products detected in the ozonolysis of methyl methacrylate, methyl acrylate, and ethyl acrylate in the presence and absence of OH scavenger. Formic acid and carbon monoxide are formed in the three systems with low yields (less than 5%).

TABLE 2: Reaction of O3 with Methyl Methacrylate, Methyl Acrylate, and Ethyl Acrylate: Summary of the ExperimentalConditions and Results from the Relative Rate Study at 294 \pm 2 K and 760 Torr of Air

esters	references	N° of runs	$(k/k_{\rm ref} \pm 1\sigma)$	$(k \pm 1\sigma),$ (cm ³ molecule ⁻¹ s ⁻¹)
methyl methacrylate,	propene	2	$\begin{array}{c} 0.65 \pm 0.07 \\ 5.62 \pm 0.13 \end{array}$	$(6.5 \pm 0.7) \times 10^{-18}$
CH ₂ =CH(CH ₃)C(O)OCH ₃	ethyl acrylate	1		$(7.2 \pm 0.2) \times 10^{-18}$
methyl acrylate, CH2=CHC(O)OCH ₃	ethene	3	0.59 ± 0.04	$(0.94\pm0.06)\times10^{-18}$
ethyl acrylate,	ethene	5	$0.83 \pm 0.06 \\ 1.25 \pm 0.14$	$(1.3 \pm 0.1) \times 10^{-18}$
CH ₂ =CHC(O)OCH ₂ CH ₃	methyl acrylate	2		$(1.2 \pm 0.1) \times 10^{-18}$



Figure 6. Methyl methacrylate $+ O_3$ (in the presence of cyclohexane). Reference IR spectra of methyl methacrylate (A). IR spectra of a mixture of methacrylate and O_3 at the start of the experiment (B). IR spectra of a mixture of methacrylate and O_3 after 4 h of reaction (C). Reference IR spectra of methyl pyruvate (D) and formaldehyde (E). IR residual spectra after subtraction of reactants (methyl methacrylate and ozone) and identified products (major products, methyl pyruvate and formaldehyde; minor products, carbon monoxide and formic acid) (F).



Figure 7. Formation of formaldehyde and methyl pyruvate versus loss of methyl methacrylate in the presence of ozone and an excess of cyclohexane ($\sim 7.5 \times 10^{15}$ molecules cm⁻³).

The main products of the reaction of ozone with methyl methacrylate are formaldehyde (\sim 55%) and methyl pyruvate (\sim 69%). Calibrated reference spectra of methyl pyruvate were obtained in our experimental conditions from which calibration curves were derived. The observed yields obtained were similar

TABLE 4: Reaction of Methyl Methacrylate with O3:Gas-Phase Product Yields in the Absence and Presence ofScavenger (cyclohexane)

scavenger (molecules cm ⁻³)	cyclohexane (7.5×10^{15})	_
number of runs methyl pyruvate formaldehyde carbon monoxide formic acid carbon balance	$\begin{array}{c} 3\\ 0.55\pm 0.02\\ 0.69\pm 0.01\\ 0.05\pm 0.02\\ 0.02\pm 0.02\\ 0.59\pm 0.02 \end{array}$	$\begin{array}{c} 1\\ 0.552\pm 0.003\\ 0.69\pm 0.02\\ 0.02\pm 0.01\\ 0.030\pm 0.009\\ 0.58\pm 0.01\end{array}$

 TABLE 5: Reaction of Methyl Acrylate with O₃: Gas-Phase

 Product Yields in the Absence and Presence of Scavenger

 (cyclohexane)

-		
scavenger (molecules cm ⁻³)	cyclohexane (7.5×10^{15})	_
number of runs methyl glyoxylate formaldehyde carbon monoxide formic acid 1113 cm ^{-1 a} 1214 cm ^{-1 a} acrbon balance	$30.30 \pm 0.060.43 \pm 0.01<0.011.00 \pm 0.131.00 \pm 0.020.33 \pm 0.05$	$1 \\ 0.32 \pm 0.01 \\ 0.565 \pm 0.005 \\ < 0.01 \\ < 0.01 \\ 1.04 \pm 0.01 \\ 0.99 \pm 0.01 \\ 0.38 \pm 0.01 \\ \end{bmatrix}$
	5122 ± 0100	

 $^{\it a}$ Yield of unidentified FT-IR bands have been normalized to unity.

 TABLE 6: Reaction of Ethyl Acrylate with O₃: Gas-Phase

 Product Yields in the Absence and Presence of Scavenger

 (cyclohexane and water)

scavenger (molecules cm ⁻³)	cyclohexane (7.5×10^{15})	_	cyclohexane (7.5 × 10 ¹⁵), water (2.0 × 10 ¹⁴)
number of runs	3	1	1
ethyl glyoxylate	0.53 ± 0.08	0.56 ± 0.01	0.71 ± 0.02
formaldehyde	0.45 ± 0.07	0.23 ± 0.01	0.60 ± 0.04
carbon monoxide	0.03 ± 0.01	0.02 ± 0.01	0.23 ± 0.01
formic acid	0.015	0.022 ± 0.003	
$1113 \text{ cm}^{-1 a}$	1.00 ± 0.16	0.94 ± 0.01	0.19 ± 0.01
$1211 \text{ cm}^{-1 a}$	1.00 ± 0.12	0.75 ± 0.02	
carbon balance	0.52 ± 0.08	0.492 ± 0.009	0.73 ± 0.03

 $^{\it a}$ Yield of unidentified FT-IR bands have been normalized to unity.

in the presence and absence of cyclohexane. For the reaction of ozone with methyl acrylate, formaldehyde and methyl glyoxylate were the main reaction products with formation yields of ~43% and ~30%, respectively. The run conducted in the absence of cyclohexane led to the same formation yield of methyl glyoxylate but a slightly higher yield for formaldehyde. Methyl glyoxylate was quantified using a reference spectrum obtained from the Euphore facilities. Ethyl glyoxylate (~53%) and formaldehyde (~45%) were observed to be the main products of the ozonolysis of ethyl acrylate.

To the best of our knowledge, among the studied esters, only the gas-phase products from the ozonolysis of methyl acrylate have been reported so far.¹⁵ Grosjean and Grosjean¹⁵ reported the following formation yields: 0.54 ± 0.04 for formaldehyde and 0.43 ± 0.01 for methyl glyoxylate. Nevertheless, methyl glyoxylate was quantified in their study using ethyl glyoxylate as a surrogate based on DnPH derivatization. Moreover, in the studies of Grosjean and Grosjean,¹⁵ experiments were conducted in a system with a relative humidity equivalent to 50%, which could impact the fate of Criegee biradical intermediate and potentially the formation yields of oxygenated products such as formaldehyde, formic acid, and carbonyl compounds.



Figure 8. Comparison of residual spectra after subtraction of all known products: methyl methacrylate $+ O_3$ (A), methyl acrylate $+ O_3$ (B), ethyl acrylate $+ O_3$ (C), and ethyl acrylate $+ O_3$ in the presence of an excess amount of water (D).

As shown in Figure 8, after subtraction of the identified reaction products, the residual spectrum obtained from ozonolysis of methyl acrylate and ethyl acrylate showed unidentified IR features at 1113 cm⁻¹ for both esters and 1214 and 1211 cm⁻¹ for methyl acrylate and ethyl acrylate, respectively. Assessments of IR bands have been carried out by subtraction of all known oxidation products. The residual spectrum was then used to integrate unknown FT-IR bands from the global spectra. Absorbance time profiles of unknown IR bands near 1113, 1211, and 1214 cm⁻¹ were derived, and their yields were normalized to unity for the experiments conducted in the presence of cyclohexane and compared to those without cyclohexane and in the presence of water vapor (Tables 5 and 6).

The reaction of ozone with unsaturated compounds proceeds by electrophilic addition on the carbon–carbon double bond. This leads to the formation of a primary ozonide, which decomposes in energy-rich Criegee biradical and a corresponding carbonyl as follows for the studied unsaturated esters

$$H_2C = CR_1C(O)OR_2 + O_3$$

$$\rightarrow [CH_2OO]^* + R_1C(O)C(O)OR_2 \quad (A)$$

$$\rightarrow \text{HCHO} + [\text{R}_1 \text{COOC}(\text{O})\text{OR}_2]^* \qquad (\text{B})$$

with $R_1 = R_2 = -CH_3$ corresponding to methyl methacrylate, $R_1 = H$ and $R_2 = -CH_3$ to methyl acrylate, and $R_1 = H$ and $R_2 = -CH_2CH_3$ to ethyl acrylate. As shown by the experimental data, formaldehyde is a primary product formed in the ozonolysis of the three studied esters at similar formation yield for methyl and ethyl acrylate, ~43% and ~45%, respectively, and at higher yield for methyl methacrylate (~9%). This indicates that the two decomposition pathways of the primary ozonide formed in the reactions of ozone with methyl acrylate and ethyl acrylate are of the same importance while channel B will dominate decomposition of the biradical from ozonolysis of methyl methacrylate. To date, the fate of the Criegee intermediate [CH₃COOC(O)OCH₃]* has not been elucidated. Grosjean et al.²¹ speculated that [CH₃OC(O)CHOO]* may lead to the carboxylic acid (CH₃C(O)C(O)OH). This was checked in our work using an IR spectrum of pyruvic acid taken in our laboratory, which was compared to the residual spectra after subtraction of the known compounds during ozonolysis of MMA. This enabled us to conclude that the unidentified FT-IR band near 1775 cm^{-1} observed in this work does not correspond to pyruvic acid (Figure 6F).

Regarding the energy-rich Criegee intermediate $[CH_2OO]^*$, which is formed in the three reactions studied here, it can be either stabilized or decompose to form HCOOH, CO, CO₂, H₂O, H₂, and OH radical.

It should be noted that the experiments conducted in the presence and absence of cyclohexane led essentially to the same product yield formation. On the other hand, the ratio Δ [esters]/ Δ [O₃] was close to unity. These two observations indicate that OH radicals were not significantly formed through ozonolysis of methyl methacrylate. Grosjean and Grosjean¹⁵ reported that ozonolysis of methyl acrylate leads to less than 1% of the OH radicals formation yield.

In order to assess the role of the Criegee intermediates in formation of the unidentified products, one run was conducted on the ozonolysis of ethyl acrylate in the presence of water vapor, which is known to scavenge the Criegee intermediate biradicals. The run was performed in the presence of cyclohexane. In these conditions, the biradical [CH₂OO]* reacts with H₂O to form hydroxymethyl hydroperoxide (HMHP), which decomposes, leading to formic acid²³

$$[CH_2OO]^* + H_2O \rightarrow HOCH_2OOH \rightarrow HCOOH + H_2O$$

Figure 6 compares the residual IR spectra of MMA + O_3 reaction (Figure 6A), the residual IR spectra of MA + O₃ reaction (Figure 6B), the residual IR spectra of $EA + O_3$ reaction (Figure 6C), and the residual IR spectra $EA + O_3$ in presence of water (Figure 6D). From ethyl acrylate experiments, the IR bands near 1113 and 1211 cm⁻¹ observed in the absence of H₂O disappear in its presence (Figure 6D). In the presence of an excess of H_2O , the 1113 cm⁻¹ IR band decreased 80% compared to dry conditions. The same trend is observed for the 1211 cm⁻¹ IR band, where it disappeared completely under humid conditions. In the same experiment, the yields of ethyl glyoxylate increased from 53% to 71% and from 45% to 60% for formaldehyde compared to dry experiments. These observations indicate that the Criegee intermediates may have contributed to formation of the unidentified products corresponding to the observed bands. However, we are not able to draw definite conclusions from this single experiment. Further investigations are required in order to understand the fate of the Criegee intermediates formed through the ozonolyzis of such unsaturated oxygenated VOCs (e.g., in the presence of scavengers such as HCOOH and HCHO).

4. Atmospheric Implications

In the troposphere, unsaturated esters react with the major atmospheric oxidants O_3 , OH, and NO_3 radicals and Cl atoms. Using a typical concentration of ozone of 50 ppb and the reaction rate coefficients measured in this work, the tropospheric lifetimes of the three unsaturated esters with respect to reaction with ozone are estimated to be ~10 days for methyl acrylate, ~7 days for ethyl acrylate, and around 33 h for methyl methacrylate. These lifetimes can be compared with those obtained against reactions with the other major atmospheric oxidants. The available kinetic data shows that the reaction with OH radicals is the dominant degradation process of unsaturated Kinetics and Products of Gas-Phase Reactions of Ozone

esters in the atmosphere with lifetimes of a few hours.²⁴ However, the reaction with ozone can constitute an important sink for these compounds in some areas (such as the highly polluted urban areas where these esters might be present) where the average concentration of ozone could be much higher than 50 ppb used to estimate the lifetimes here). The short atmospheric lifetimes indicate that these compounds will be oxidized near their emission sources. The reaction of ozone with unsaturated esters leads to formaldehyde and other highly oxygen-containing compounds such as methyl pyruvate, methyl glyoxylate, and ethyl glyoxylate, which are expected to be removed from the atmosphere through partitioning in the aqueous phase.²⁵

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