Gas phase kinetics for the ozonolysis of *n*-butyl methacrylate, ethyl crotonate and vinyl propionate under atmospheric conditions

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A B S T R A C T

Rate coefficients for the reactions of ozone with *n*-butyl methacrylate, ethyl crotonate and vinyl propionate have been determined at 298 ± 1 K and atmospheric pressure. The following room temperature rate coefficients (in cm^3 molecule^{-1} s^{-1} units) were obtained: $k_1(O_3 + CH_2\text{=}C(CH_3)C(O)OC_4H_9) = (1.0 \pm 0.3) \times 10^{-17}$, $k_2(O_3 + CH_3CH\text{=}CHC(O)OCH_2CH_3) = (8.0 \pm 1.8) \times 10^{-18}$ and $k_3(O_3 + CH_3CH_2C(O)OCH\text{=}CH_2) = (5.3 \pm 1.3) \times 10^{-18}$. This is the first kinetic study for these reactions at atmospheric pressure. The effect of substituent groups on the overall rate coefficients is analyzed. Free energy relationships are presented and atmospheric lifetimes are discussed.
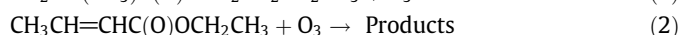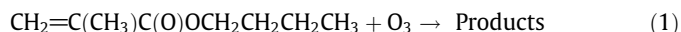
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1. Introduction

Oxygenated volatile organic compounds (OVOCs), which contain functional groups, such as the ester entity (–C(O)O–), are used in the polymer industry and their degradation can impact on the air quality and global climate. Releases of unsaturated esters to the atmosphere are expected to occur mainly during their commercial production, processing, storage, and disposal. Fugitive and stack emissions will be additional atmospheric sources. Total air releases of different unsaturated esters like methyl methacrylate, *n*-butyl acrylate and vinyl acetate for 2011 have been calculated to be around 3.561, 172, and 5.019 klbs, respectively, by the US EPA [1]. Significant atmospheric releases of the compounds are to be expected in Europe and Asia where these compounds are also produced in large quantities, production capacities for Europe can be found in Screening Information Data (SID) reports in reference [2].

The widespread industrial use of these esters on a large scale unavoidably results in fugitive emissions of the compounds to the atmosphere to be degraded by the main tropospheric oxidants (OH, NO$_3$ and O$_3$).

There have been several room temperature determinations of the rate coefficients for the gas-phase reactions of *n*-butyl methacrylate, ethyl crotonate and vinyl propionate with OH radicals [3–5] and Cl atoms [5–8]. For NO$_3$ there has only been one determination of the rate coefficient for the reaction this radical with *n*-butyl methacrylate [9]. There are currently no available kinetic data in literature for the reactions of *n*-butyl methacrylate, ethyl crotonate and vinyl propionate with O$_3$.

Although, for all three compounds, the available studies indicate that reaction with OH will probably be the dominant atmospheric loss pathway for these compounds in the troposphere reaction with O$_3$ may also be of some importance, especially in polluted areas where the O$_3$ concentrations can be high. Apart from any possible atmospheric relevance determination of the rate coefficients for the reactions of ozone with the unsaturated esters will add to the kinetic database for such compounds and will help in the improvement of the structure reactivity relationships which are used to predict rate coefficients for the reactions of O$_3$ with unsaturated VOCs. Such kinetic information is an essential element in estimations of the persistence, fate and harmful effects of these compounds in the atmosphere and also model assessments of their impact on air quality. Therefore, in order to obtain a more complete kinetic database on the rate coefficients for the reactions of unsaturated esters with important atmospheric oxidants we report in this study rate coefficient determinations for the reactions of O$_3$ molecules with *n*-butyl methacrylate (CH$_2$=C(CH$_3$)C(O)OCH$_2$CH$_2$CH$_2$CH$_3$, k_1), ethyl crotonate (CH$_3$CH=CHC(O)OCH$_2$CH$_3$, k_2) and vinyl propionate (CH$_3$CH$_2$C(O)OCH=CH$_2$, k_3) at room temperature and atmospheric pressure:

$$CH_2\text{=}C(CH_3)C(O)OCH_2CH_2CH_2CH_3 + O_3 \rightarrow \text{Products} \quad (1)$$
$$CH_3CH\text{=}CHC(O)OCH_2CH_3 + O_3 \rightarrow \text{Products} \quad (2)$$
$$CH_3CH_2C(O)OCH\text{=}CH_2 + O_3 \rightarrow \text{Products} \quad (3)$$

The relative kinetic method, using different reference compounds, has been applied to derive the rate coefficients. To the best of our knowledge this Letter provides the first kinetic study for the reactions under atmospheric conditions.

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The results are discussed in terms of the effect of the position of the methyl substituent, the ester functionality, and the double bond on the reactivity of the compounds towards O_3 molecules. This study complements ongoing work in our laboratories to understand the factors that contribute to the reactivity of unsaturated VOCs with different tropospheric oxidants $O(^3P)$ [10], OH [3–5,11] and Cl [5–7,11,12].

Additionally, the rate coefficients of the reactions of O_3 molecules have been correlated with the rate coefficients of the reaction of the same unsaturated esters with OH radicals. Tropospheric lifetimes with respect to reaction with O_3 have been calculated and compared with the lifetimes resulting from their reactions with other tropospheric oxidants (OH, Cl, NO_3).

2. Experimental

All the experiments were performed in a 480 L chamber at 298 ± 2 K in 1000 mbar of synthetic air. The chamber is composed of a cylindrical borosilicate glass vessel (3 m in length and 45 cm inner diameter) closed at both ends by aluminum end flanges. The metal flanges contain ports for the introduction of bath gasses and reactants into the chamber. A magnetically coupled Teflon mixing fan is mounted inside the chamber to ensure homogeneous mixing of the reactants. The reactor can be evacuated by a pumping system consisting of a turbomolecular pump backed by a double stage rotary forepump to 10^{-3} Torr.

A White-type mirror system mounted internally in the chamber and coupled to a FTIR spectrometer Nicolet 6700 equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector enables 'in situ' monitoring of the reactants in the infrared range 4000–700 cm^{-1}. The White mirror system was operated with the total optical absorption path length set to 48.11 m and infrared spectra were recorded with a spectral resolution of 1 cm^{-1}. Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 min and 15 such spectra were recorded per experiment. The chamber is described in greater detail elsewhere [13,14].

Ozone was added stepwise to mixtures containing the unsaturated ester, reference hydrocarbon and carbon monoxide. Carbon monoxide was present in excess to scavenge any OH radicals produced in the reaction of ozone with the unsaturated ester. An electrical discharge in a flow of pure oxygen was used to generate ozone. The initial concentrations of reactants in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K) were: n-butyl methacrylate, (8–9); vinyl propionate, (7–9); ethyl crotonate, (10–12); ozone, (1–2); carbon monoxide, (34–41); isobutene, (15–18); 1,3-butadiene (16–19) and cyclohexene (14–18). The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): n-butyl methacrylate at 1169; vinyl propionate at 1174; ethyl crotonate at 1186; isobutene at 890; 1,3-butadiene at 908 and cyclohexene at 3000 and 2840.
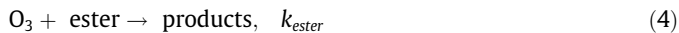
3. Materials

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%), carbon monoxide (Messer Griesheim, 99%), n-butyl methacrylate (Aldrich, 99%), ethyl crotonate (Aldrich, 99%), vinyl propionate (Aldrich, 98%), isobutene (Messer Griesheim, 99%), 1,3-butadiene (Aldrich, 99%) and cyclohexene (Aldrich, 99%).

4. Results and discussion

Rate coefficients for the reactions of O_3 molecules with n-butyl methacrylate, ethyl crotonate and vinyl propionate were determined by comparing their rate of decay with that of the corresponding decay of the three reference compounds: 1,3-butadiene and isobutene for the reactions (2) and (3), and cyclohexene and isobutene for reaction (1):

$$O_3 + \text{ester} \rightarrow \text{products}, \quad k_{ester} \quad (4)$$

$$O_3 + \text{reference} \rightarrow \text{products}, \quad k_{ester} \quad (5)$$

Provided that the reference compound and the reactant are lost only by reactions (4) and (5), then it can be shown that:

$$\ln \left\{ \frac{[\text{ester}]_0}{[\text{ester}]_t} \right\} = \frac{k_4}{k_5} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (I)$$

where $[\text{ester}]_0$, $[\text{reference}]_0$, $[\text{ester}]_t$ and $[\text{reference}]_t$ are the concentrations of the unsaturated ester compound under study and the reference compound at times $t = 0$ and t, respectively, and k_4 and k_5 are the rate coefficients of reactions (4) and (5), respectively.

The experiments were performed in the presence of an excess of carbon monoxide to scavenge any OH radicals produced during the reactions. The relative rate technique relies on the assumption that the unsaturated compounds and reference organics are removed solely by reaction with O_3 molecules. To verify this assumption, tests were performed to assess possible additional loss of the unsaturated esters and reference compounds through deposition on the reactor surface. The wall losses of the mixture of the studied ester, reference and carbon monoxide prior to the addition of ozone to the reactor were determined to be negligible for our experimental conditions.

Figures 1–3 show examples of the kinetic data, obtained from experiments on the reactions of O_3 molecules with the unsaturated esters measured relative to the reference hydrocarbons, plotted according to Eq. (I). In all cases each plot represents a minimum of 3–4 experiments for each reference compound. Linear relationships were obtained in all cases. The linearity of the plots with zero or near-zero intercepts supports that complications due to secondary reactions in the experimental systems were negligible.

The $k_{ester}/k_{reference}$ ratios determined from the slopes of the straight-line plots in Figures 1–3 are listed in Table 1 together with the number of experiments performed, and the absolute values of the rate coefficients, k_{ester}, calculated from the $k_{ester}/k_{reference}$ ratios. The rate coefficients for the reactions of O_3 molecules with the unsaturated esters were placed on an absolute basis using the following values for the reference reactions at 298 K:
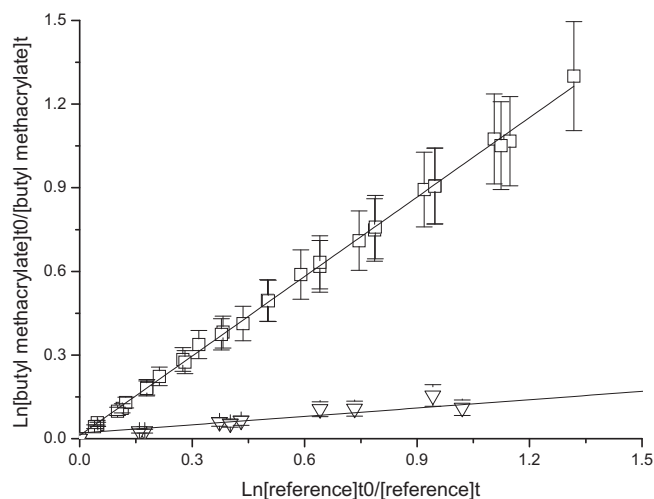

Figure 1. Plot of the kinetic data for the reaction of O_3 molecules with n-butyl methacrylate measured relative to isobutene (□) and cyclohexene (∇) at 298 ± 2 K and atmospheric pressure of air.
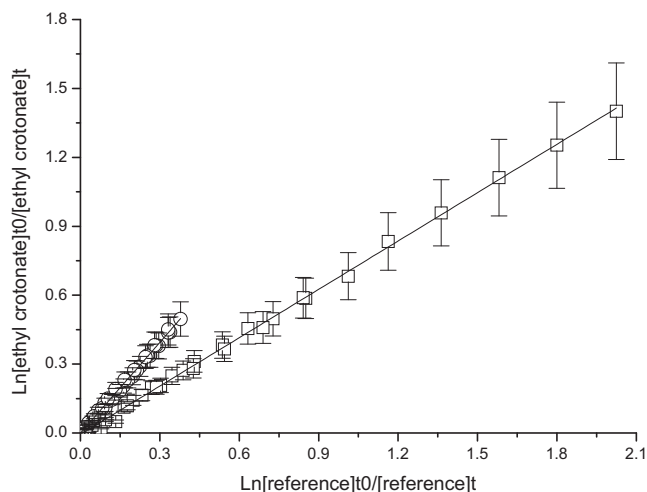
Figure 2. Plot of the kinetic data for the reaction of O_3 molecules with ethyl crotonate measured relative to isobutene (□) and 1,3-butadiene (○) at 298 ± 2 K and atmospheric pressure of air.
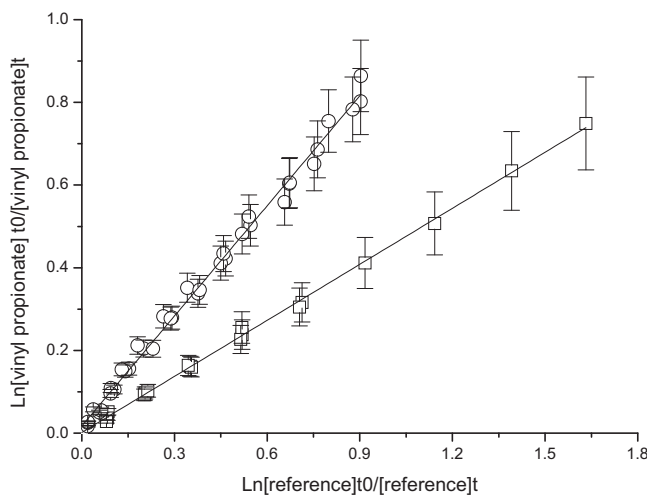

Figure 3. Plot of the kinetic data for the reaction of O_3 molecules with vinyl propionate measured relative to isobutene (□) and 1,3-butadiene (○) at 298 ± 2 K and atmospheric pressure of air.

$(1.11 \pm 0.12) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} for O_3 + isobutene [15]; $(7.4 \pm 1.5) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} for O_3 + cyclohexene [16] and $(6.2 \pm 1.3) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} for O_3 + 1,3-butadiene [17].

The errors for the $k_{ester}/k_{reference}$ ratios given in Table 1 are the 2σ statistical errors from the scatter in the plots shown in Figures 1–3. The errors quoted for k_{ester} are a combination of the 2σ statistical errors from the linear regression analysis plus an additional 20% error to cover potential uncertainties in the recommended values of the rate coefficients for the reference reactions.

Since for all the compounds investigated, there is good agreement between the values of the ozonolysis rate coefficient, k_{ester} determined using two different reference compounds in each case, we prefer to quote final values for the rate coefficients at 298 K which are averages of the individually performed values with errors which encompass the extremes of both determinations:

$$k_1 = (1.0 \pm 0.3) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (8.0 \pm 1.8) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (5.3 \pm 1.3) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To the best of our knowledge, there are no previously reported values of the rate coefficients for the ozonolysis reactions of *n*-butyl methacrylate, ethyl crotonate and vinyl propionate. Hence, the present study represents the first kinetic determination of the rate coefficient of these reactions and therefore no direct comparison with other literature values can be made.

Pfrang et al. [18] have developed a SAR method to calculate and predict rate coefficients for the reaction of O_3 molecules with small alkenes and unsaturated and oxygenated VOCs, which is based on the available experimental rate coefficients for the reactions of O_3 with alkenes and unsaturated and oxygenated VOCs. If the SAR method of Pfrang et al. [18] is used to calculate rate coefficients for the reactions of O_3 with *n*-butyl methacrylate and ethyl crotonate values of 4.31×10^{-18} and 3.47×10^{-18} cm^3 molecule^{-1} s^{-1} are obtained, respectively. Although, the SAR method of Pfrang [18] captures the reactivity trend for the reactions determined in this Letter, *i.e.* $k_{n\text{-butyl methacrylate}}$ (10×10^{-18} cm^3 molecule^{-1} s^{-1}) > $k_{ethyl\ crotonate}$ (8.0×10^{-18} cm^3 molecule^{-1} s^{-1}), it underestimates the values of the rate coefficients measured in this study, in both cases, by approximately a factor of three.

It is interesting to compare the reactivity trends of the reactions of esters toward O_3 and with other tropospheric oxidants like OH radicals and Cl atoms. Table 2 lists the rate coefficients for the reactions of OH, Cl and O_3 with the esters studied in this Letter.

In general, for the reactions of O_3, OH and Cl with *n*-butyl methacrylate, ethyl crotonate and vinyl propionate the same reactivity tendency is observed, *i.e.* the rate coefficients for each oxidant take the order $k_{n\text{-butyl methacrylate}}$ > $k_{ethyl\ crotonate}$ > $k_{vinyl\ propionate}$. The reactions with O_3 have the lowest rate coefficients and thus the rate coefficients for the reactions are more sensitive to the presence of substituent groups than the faster reactions of Cl and OH with the same unsaturated esters.

For the reactions of O_3 with *n*-butyl methacrylate and ethyl crotonate it can be observed that the replacement of a –CH$_3$ group of the double bond by a –H atom produces a decrease of the rate coefficient in connection with a lower susceptibility of π electrons of the double bond towards the O_3 molecule electrophilic attack ($k_{n\text{-butyl methacrylate}} = 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} > $k_{n\text{-butyl acrylate}} = 7.68 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) [19] and ($k_{ethyl\ crotonate} = 8.0 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} > $k_{ethyl\ acrylate} = 1.3 \times 10^{-18}$ cm$_3$ molecule^{-1} s^{-1}) [20]. This effect was observed previously for the reactions of unsaturated esters with OH radicals [3,5].

The rate coefficient for the reaction of O_3 molecules (Table 2) with *n*-butyl methacrylate is higher than the rate coefficient for the reaction of O_3 with ethyl crotonate, indicating that the positive inductive effect of the –CH$_3$ group, which increase the charge density on the double-bonded carbon atoms, is higher when –CH$_3$ is attached to a α-carbon (CH$_2$=C(CH$_3$)C(O)O(CH$_2$)$_3$CH$_3$) than when it is attached to a β-carbon (CH$_3$CH=CHC(O)OCH$_2$CH$_3$). The same behavior is observed when we compare the rate coefficients for the reactions of O_3 with methyl methacrylate (CH$_2$=C(CH$_3$)-C(O)OCH$_3$) and methyl crotonate (CH$_3$CH=CHC(O)OCH$_3$); $k_{methyl\ methacrylate}$ (6.7×10^{-18} cm^3 $^{-1}$ s^{-1}, [20]) > $k_{methyl\ crotonate}$ (4.38×10^{-18} cm^3 molecule^{-1} s^{-1} [21]).

It is interesting to analyze the reactivity of these three esters toward O_3 molecules in comparison with the corresponding alkenes, since these compounds react via similar addition mechanisms, mainly addition of the O_3 on the >C=C< followed by unimolecular decomposition of the 1,2,3-trioxolane adduct formed into two carbonyls and two Criegee biradicals [22–23],

Table 3 lists the room temperature rate coefficients for the reactions of O_3 molecules with the unsaturated esters studied in this Letter together with rate coefficients obtained from the literature for the reactions of the alkene analogs with O_3. It can be seen that

Table 1
Rate coefficient ratios $k_{Reactant}/k_{Reference}$ and rate coefficients for the reactions of ozone with n-butyl methacrylate, ethyl crotonate and vinyl propionate at 298 ± 2 K in 760 ± 10 Torr of air.

Reaction	Reference	$k_{Reactant}/k_{Reference}$	$k_{Reactant}$ (cm^3 molecule^{-1} s^{-1})
CH$_2$=C(CH$_3$)C(O)OC$_4$H$_9$ + O$_3$ n-butyl methacrylate	Isobutene	0.94 ± 0.01	$(1.0 \pm 0.1) \times 10^{-17}$
	Isobutene	0.97 ± 0.01	$(1.1 \pm 0.1) \times 10^{-17}$
	Isobutene	0.94 ± 0.01	$(1.0 \pm 0.1) \times 10^{-17}$
	Cyclohexene	0.15 ± 0.01	$(1.1 \pm 0.2) \times 10^{-17}$
	Cyclohexene	0.16 ± 0.01	$(1.2 \pm 0.3) \times 10^{-17}$
	Cyclohexene	0.10 ± 0.01	$(0.7 \pm 0.2) \times 10^{-17}$
	Average		$(1.0 \pm 0.3) \times 10^{-17}$
CH$_3$CH=CHC(O)OCH$_2$CH$_3$ + O$_3$ ethyl crotonate	Isobutene	0.72 ± 0.02	$(8.0 \pm 1.1) \times 10^{-18}$
	isobutene	0.69 ± 0.01	$(7.7 \pm 0.9) \times 10^{-18}$
	Isobutene	0.70 ± 0.01	$(7.8 \pm 0.9) \times 10^{-18}$
	1,3-butadiene	1.28 ± 0.01	$(8.0 \pm 1.7) \times 10^{-18}$
	1,3-butadiene	1.33 ± 0.02	$(8.2 \pm 1.8) \times 10^{-18}$
	1,3-butadiene	1.36 ± 0.02	$(8.4 \pm 1.8) \times 10^{-18}$
	Average		$(8.0 \pm 1.8) \times 10^{-18}$
CH$_3$CH$_2$C(O)OCH=CH$_2$ + O$_3$ vinyl propionate	Isobutene	0.45 ± 0.01	$(5.0 \pm 0.6) \times 10^{-18}$
	Isobutene	0.43 ± 0.01	$(4.8 \pm 0.6) \times 10^{-18}$
	Isobutene	0.50 ± 0.01	$(5.6 \pm 0.7) \times 10^{-18}$
	1,3-butadiene	0.89 ± 0.01	$(5.5 \pm 1.2) \times 10^{-18}$
	1,3-butadiene	0.86 ± 0.02	$(5.3 \pm 1.2) \times 10^{-18}$
	1,3-butadiene	0.93 ± 0.01	$(5.8 \pm 1.3) \times 10^{-18}$
	Average		$(5.3 \pm 1.3) \times 10^{-18}$

Table 2
Rate coefficients (cm^3 molecule^{-1} s^{-1}) for the gas phase reactions of O$_3$ with the unsaturated compounds studied in this Letter and the corresponding values their reactions with the oxidants OH and Cl.

Unsaturated ester	k_{O_3}	k_{OH}	k_{Cl}
n-Butyl methacrylate	1.0×10^{-17a}	6.63×10^{-11b}	3.60×10^{-10e}
Ethyl crotonate	8.0×10^{-18a}	4.96×10^{-11c}	2.52×10^{-10c}
Vinyl propionate	5.3×10^{-18a}	2.46×10^{-11d}	2.06×10^{-10f}

[a] This Letter.
[b] Ref. [3].
[c] Ref. [5].
[d] Ref. [4].
[e] Ref. [6].
[f] Ref. [7].

replacing a –CH$_2$– group by –C(O)O– leads to a decrease in the O$_3$ rate coefficients by a factor of $\sim$2 for vinyl propionate and a factor of $\sim$13 for ethyl crotonate, since the introduction of the ester entity produces an electron withdrawing effect that reduces the reactivity in both esters, whereby the effect is largest when the double bond is attached to the carbonyl in the ester entity than when it is attached to the alkyl oxygen.

No comparison can be made for n-butyl methacrylate since a rate coefficient for reaction of O$_3$ with the analogous alkene, CH$_2$=C(CH$_3$)CH$_2$C$_4$H$_9$, is not available, although a similar tendency is expected as observed for the reactions of O$_3$ with vinyl propionate and ethyl crotonate.

Several authors have proposed linear correlations between the rate coefficients of OH addition reactions and those of other tropospheric oxidants like NO$_3$ radicals [25], Cl atoms with alkenes,

Table 3
Rate coefficients (cm^3 molecule^{-1} s^{-1}) for the gas phase reactions of O$_3$ with the unsaturated compounds studied in this Letter and their analogous alkene.

Unsaturated ester	k_{O3}	Alkene	k_{O3}
CH$_2$=C(CH$_3$)C(O)OC$_4$H$_9$	1.0×10^{-17a}	CH$_2$=C(CH$_3$)CH$_2$C$_4$H$_9$	–
CH$_3$CH=CHC(O)OCH$_2$CH$_3$	8.0×10^{-18a}	CH$_3$CH=CHCH$_2$CH$_2$CH$_3$	1.06×10^{-16b}
CH$_3$CH$_2$C(O)OCH=CH$_2$	5.3×10^{-18a}	CH$_3$CH$_2$CH$_2$CH=CH$_2$	9.97×10^{-18b}

[a] This Letter.
[b] Ref. [24].

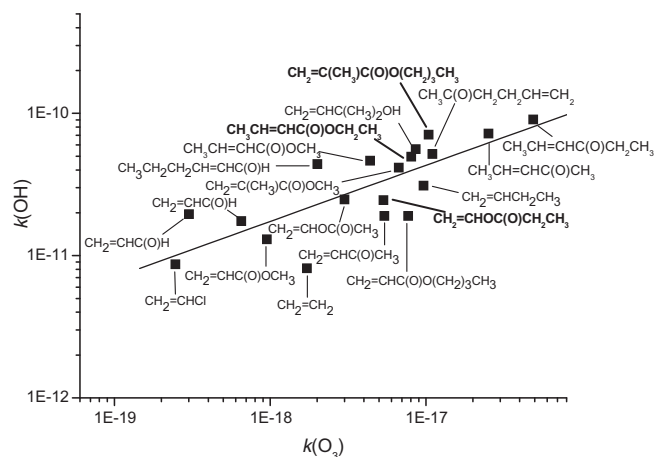**Figure 4.** Linear free energy plot of log k_{OH} versus log k_{O3} at room temperature for a series of unsaturated volatile organic compounds (VOCs) including the room temperature rate coefficients for the reactions of O$_3$ molecules with n-butyl methacrylate, ethyl crotonate and vinyl propionate obtained in this Letter. Rate coefficients are in units of cm^3 molecule^{-1} s^{-1}.

unsaturated and oxygenated VOCs [6] and O$_3$ molecules with alkenes and methyl vinyl ketone [26] which also proceed primarily via an addition mechanism.

In this Letter we present, for the first time, a correlation between k_{OH} and k_{O3} for a wide range of different alkenes and unsaturated VOCs which contain alcohol, carbonyl, ether and ester functionalities. Figure 4 shows the correlation obtained between the rate coefficients for the reactions of O$_3$ molecules with a given alkene or unsaturated VOC and those for the corresponding reactions with OH radicals. As seen in Figure 4 a reasonable correlation is obtained and a least-squares treatment of the data points yields the following expression (with the rate coefficients in units of cm^3 molecule^{-1} s^{-1}):

$$\log k_{OH} = (0.39 \pm 0.08) \log k_{O_3} - (3.7 \pm 1.3) \qquad (II)$$

The good correlation supports that the main mechanism of the reactions of O$_3$ molecules with the unsaturated VOCs is similar to that observed for the reactions of OH with unsaturated VOCs, $i.e.$

Table 4
Estimated tropospheric lifetimes for the unsaturated esters studied in this Letter with respect to their reactions with O_3, OH, Cl and NO_3.

Unsaturated ester	τ_{OH} (h)	τ_{Cl} (h)	τ_{NO_3} (h)	τ_{O3} (h)
$CH_2=C(CH_3)C(O)OC_4H_9$ n-butyl methacrylate	2	77	71	40
$CH_3CH=CHC(O)OCH_2CH_3$ ethyl crotonate	3	110	–	50
$CH_3CH_2C(O)OCH=CH_2$ vinyl propionate	6	135	–	75

In these calculations the rate constant value of n-butyl methacrylate + NO_3 used was: 7.87×10^{-15} cm^3 molecule^{-1} s^{-1} [9]. The rate coefficients for the reactions of the unsaturated esters studied with O_3, OH and Cl are listed in Table 2.

addition to the double bond of the unsaturated VOC occurs in a primary reversible step forming an adduct which can form products in subsequent fast reactions [15,23,27,28].

Using the correlation obtained in Eq. (II), estimations can be made of rate coefficients for reactions of O_3 with unsaturated compounds which have not been determined experimentally.

With respect to the atmospheric implications of the reactions studied, the rate coefficients summarized in Table 1 can be used to calculate atmospheric lifetimes for the unsaturated esters due to reaction with O_3 which can be compared with lifetimes calculated for the other major atmospheric oxidants (OH, Cl, and NO_3). Lifetimes have been calculated using the expression: $\tau_x = 1/k_x[X]$ with X=O_3, OH, Cl or NO_3, where k_x is the rate coefficient for the reaction of the oxidant X with the ester and [X] is the typical atmospheric concentration of the oxidant. For the calculations, the following oxidant concentrations have been used: $[O_3] = 7 \times 10^{11}$ molecule cm^{-3} [29]; $[OH] = 2 \times 10^6$ radical cm^{-3} [30]; $[Cl] = 1 \times 10^4$ atom cm^{-3} [31] and $[NO_3] = 5 \times 10^8$ radical cm^{-3} [32]. The estimated tropospheric lifetimes at room temperature of the esters with respect to reactions with the tropospheric oxidants (where data are available) are presented in Table 4. Photolytic loss of the esters will be negligible since they are photolytically stable in the actinic region of the electromagnetic spectrum. The lifetimes indicate that the esters will be removed rapidly in the gas phase, the reaction with OH being the major loss process for n-butyl methacrylate, ethyl crotonate and vinyl propionate. Unfortunately, no data are available on the reactions of NO_3 radicals with vinyl propionate and ethyl crotonate, although, on the basis of structural similarities, it is probable that they will show a similar reactivity toward NO_3 radicals as n-butyl methacrylate and thus have a similar lifetime with respect to reaction with this oxidant.

The short lifetimes for the esters, in the range of a few hours, imply that the unsaturated VOCs are likely to be removed rapidly in the gas phase close to their source of emission with removal by OH radicals dominating. Nevertheless, in polluted areas, where peak concentrations of O_3 molecules will increase and in some episodes as during long dark winters at high latitudes, and during the night when the sun goes down, OH concentration could be decreased and under these conditions O_3-initiated degradation of n-butyl methacrylate, ethyl crotonate and vinyl propionate can then be a significant and primary sink of these compounds if not dominant homogeneous loss process.

Consequently, O_3-initiated degradation in these scenarios will be the main fate of these unsaturated esters in the troposphere.

The O_3 molecule initiated atmospheric degradation of the studied unsaturated esters in polluted areas is expected to result in the formation of mainly acids, aldehydes, anhydrides and other dicarbonyls compounds which will be subject to further reaction with oxidants like OH radicals and also photolysis. Thus, the high reactivity of these unsaturated compounds and also their primary products implies they will be contributors to the photochemical smog formation and secondary organic aerosol formation (SOA) in the atmosphere, if emitted in large quantities.

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