OH-Initiated Degradation of Unsaturated Esters in the Atmosphere: Kinetics in the Temperature Range of 287−313 K

María B. Blanco,[†] Iustinian Bejan,[‡,§] Ian Barnes,[‡] Peter Wiesen,[‡] and Mariano A. Teruel*[,†]

Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina and FB C−Physical Chemistry Department, University of Wuppertal, Wuppertal, Germany

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The kinetics of the gas-phase reactions of hydroxyl radicals (OH) with methyl methacrylate (k_1), butyl methacrylate (k_2), butyl acrylate (k_3), and vinyl acetate (k_4) have been investigated for the first time as a function of temperature using the relative technique. The experiments were performed in a 1080 L quartz glass photoreactor over the temperature range ($T = 287-313$ K) at a total pressure of 760 ± 10 Torr synthetic air using in situ FTIR absorption spectroscopy to monitor the concentration−time behaviors of reactants. OH radicals were produced by the 254 nm photolysis of hydrogen peroxide (H_2O_2). The following Arrhenius expressions (in units of cm^3 $molecule^{-1}$ s^{-1}) adequately describe the measured rate coefficients as a function of temperature: $k_1 = (1.97 \pm 0.95) \times 10^{-12} \exp[(921 \pm 52)/T]$, $k_2 = (1.65 \pm 1.05) \times 10^{-11} \exp[(413 \pm 34)/T]$, $k_3 = (4.4 \pm 2.5) \times 10^{-13} \exp[(1117 \pm 105)/T]$, and $k_4 = (4.06 \pm 2.02) \times 10^{-12} \exp[(540 \pm 49)/T]$. All of the rate coefficients display a negative temperature dependence and low pre-exponential factor, which supports an addition mechanism for the reactions involving reversible OH-adduct formation. The rate coefficients (in units of cm^3 $molecule^{-1}$ s^{-1}) determined at room temperature (298 K) were as follows: $k_1 = (4.30 \pm 0.98) \times 10^{-11}$, $k_2 = (6.63 \pm 1.42) \times 10^{-11}$, $k_3 = (2.17 \pm 0.48) \times 10^{-11}$, and $k_4 = (2.48 \pm 0.61) \times 10^{-11}$. The results are compared with previous values of the rate coefficients reported in the literature, which were mainly measured at room temperature. The reactivity of the various unsaturated esters toward the OH radical is discussed in terms of structure activity relationships and parallels are drawn with the OH-radical activities of structurally similar compounds. Using the kinetic parameters determined in this work, residence times of the esters in the atmosphere with respect to their reaction with OH have been determined and are compared with other possible degradation pathways. Possible atmospheric implications of the various degradation pathways studied are discussed.

Introduction

Oxygenated volatile organic compounds (OVOCs) are widely emitted into the troposphere by both anthropogenic (use as solvents, paints, adhesives, etc.) and biogenic sources.[1,2] However, OVOCs can be produced in the troposphere by the oxidation of other VOCs like alkanes, alkenes, and aromatic hydrocarbons.[3−5]

Depending on the oxygenated functionalities in the compound, many unsaturated OVOCs will be as reactive and sometimes more reactive than their analogous alkenes since the double bonds in the molecule are very receptive to addition of the tropospheric oxidants OH and NO_3 radicals and O_3 which initiate their photodegradation.

Acrylates and methacrylates are unsaturated esters, which are employed as intermediates in the manufacture of polymers and plastics. The most important polymer types are cast acrylic sheets and molding/extrusion compounds, in addition to emulsions, dispersions, and solvent-based polymers. The unsaturated esters under investigation in this study methyl methacrylate ($CH_2{=}C(CH_3)C(O)OCH_3$), butyl methacrylate ($CH_2{=}C(CH_3)$-$C(O)O(CH_2)_3CH_3$), butyl acrylate ($CH_2{=}CHC(O)O(CH_2)_3CH_3$), and vinyl acetate ($CH_3C(O)OCH{=}CH_2$), hereafter referred to as MMA, BMA, BA, and VA, respectively, are all listed as high (H) production (P) volume (V) chemicals in the OECD integrated HPV database.[6]

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 MMA, BA, and VA for 2006 have been calculated to be around 2.506, 132, and 2.419 klbs, respectively, by the US EPA.[7] No production figures are available for BMA. 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.[6]

The unsaturated esters are used in a host of applications, for example, the polymers which they are initially used to manufacture are used to make, among many other things, automotive coatings, lacquers and enamels, toners, printing inks, furniture and floor polishes, adhesives, etc.[7] Industrial organic chemicals, plastic materials and resins, paints and allied products, and commercial printing industries have been identified as potential sources of atmospheric releases of vinyl acetate.[6] Despite large potential releases of the unsaturated esters to the atmosphere,

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* To whom correspondence should be addressed. Fax: (+54) 351-4334188, E-mail: mteruel@fcq.unc.edu.ar.

[†] Instituto de Investigaciones en Fisicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria.

[‡] FB C−Physical Chemistry Department, University of Wuppertal.

[§] Present address: Department of Chemistry, University College Cork, College Road, Cork, Ireland.

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there have been surprisingly few measurements of their ambient concentration levels and most of the measurements are relatively old; information on the few available atmospheric measurements for the unsaturated esters in all of the environmental compartments, air, aqueous phase, and soil, can be found in refs 6 and 7. Ambient air levels of vinyl acetate of 0.07−0.57 ppm, for example, have been detected in Houston, Texas air (Gulf Coast area) during June and July 1974.[8] These values should not be considered as representative of typical ambient air concentrations since a number of manufacturers of vinyl acetate are located in Texas City. This compound has also been detected in air samples taken at the Kin-Buc waste disposal site located near Edison, New Jersey at a concentration of 0.5 μg m^{-3} (0.00014 ppm).[9] The large range and types of products for which the unsaturated esters are used to manufacture indicates that indoor releases of the esters may be significant and there have been a few reports of their detection in indoor environments.[6,7] Vinyl acetate, for example, has been reported as a dominant compound emitted by a carpet with PVC backing from tests performed in an environmental chamber.[10] The results of the present study will, therefore, be of use in assessing both the outdoor and indoor fate and the environmental impact of atmospheric releases of these esters.

The unsaturated esters investigated here all have relatively high vapor pressures[6] which indicates that when emitted to the ambient atmopshere they will exist mainly as vapors. The esters do not absorb sunlight in the atmospheric actinic region and will therefore be degraded by reaction with OH and NO_3 radicals and ozone, whereby, based on what is known on the photooxidation of OVOCs,[11] reaction with photochemically produced OH radicals will be the dominant oxidation route and determine to a large extent any contribution they may make to the formation of tropospheric ozone and secondary aerosol formation (SOA). Therefore, knowledge of the rate coefficients for the OH-radical initiated oxidation reactions of the unsaturated esters will assist in determining their effect and potential impact on the air quality of the troposphere.

The kinetic studies on the reactions of OH radicals with methyl methacrylate (k_1), butyl methacrylate (k_2), butyl acrylate (k_3), and vinyl acetate (k_4) presented here have been performed in an environmental chamber using the relative kinetic technique over the temperature range 287−313 K.

$$\mathrm{OH + CH_2{=}C(CH_3)C(O)OCH_3 \rightarrow products} \qquad k_1$$

$$\mathrm{OH + CH_2{=}C(CH_3)C(O)O(CH_2)_3CH_3 \rightarrow products} \qquad k_2$$

$$\mathrm{OH + CH_2{=}CHC(O)O(CH_2)_3CH_3 \rightarrow products} \qquad k_3$$

$$\mathrm{OH + CH_3C(O)OCH{=}CH_2 \rightarrow products} \qquad k_4$$

The only previous temperature-dependent rate study on the above reactions available in the literature is that from Teruel et al.[12] on the reaction of OH radicals with MMA, which was performed using the pulsed laser photolysis−laser induced fluorescence (PLP−LIF) technique in the temperature range of 255−351 K. Rate coefficients determined at room temperature and atmospheric pressure using the relative kinetic technique have been reported previously for the reactions of OH radicals with MMA, BMA,[13] and BA.[14] The kinetics of the reaction of OH with MMA has also been studied at room temperature in a discharge flow system at low pressure under pseudo-first-order conditions, where the OH concentration was monitored by laser-induced fluorescence and helium was used as the carrier gas.[15] In the same study, a rate coefficient is reported for the reaction of OH with vinyl acetate, however, the compound which is depicted in the manuscript is methyl acrylate, therefore, there is some confusion as to which compound was actually investigated. To the best of our knowledge there are no temperature dependence studies on the reactions of OH radicals with BMA, BA, and VA, and this study reports the first temperature dependence of the OH-rate coefficients, k_2, k_3 and k_4.

The data are necessary for the realistic representation of the chemistry of these compounds in tropospheric models, which assess their impact on air quality. The results are discussed in terms of the effect that the position of the methyl substituent, ester functionality, and double bond have on the reactivity of the compounds toward OH radicals. This study complements ongoing work in our laboratories to understand the factors that contribute to the reactivity of unsaturated VOCs toward different tropospheric oxidants ($O(^3P)$),[16] OH,[12−14,17] and Cl[17]).

Experimental Section

All of the experiments were performed in a 1080 L quartz-glass reaction chamber over the temperature range of 287−313 K at a total pressure of 760 ± 10 Torr synthetic air (760 Torr = 101.325 kPa). A detailed description of the reactor can be found elsewhere,[18] and only a brief description is given here. A pumping system consisting of a turbo-molecular pump backed by a double-stage rotary fore pump was used to evacuate the reactor to 10^{-3} Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40W, with a maximum at 254 nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White-type multiple-reflection mirror system with a base length of 5.91 ± 0.01 m for sensitive "in situ" long path absorption monitoring of reactants and products in the IR 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. The reactor can be temperature regulated in the range 283−313 K with a precision of ±1 K.

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

$$\mathrm{H_2O_2} + h\nu \rightarrow \mathrm{2OH} \tag{1}$$

Typical photolysis times ranged from 10 to 20 min.

In the presence of OH radicals, the esters and the reference compounds are consumed by the following reactions:

$$\mathrm{OH + ester \rightarrow products} \tag{2}$$

$$\mathrm{OH + ref \rightarrow products} \tag{3}$$

Provided that the reference compound and the reactant are lost only by reactions 2 and 3, then it can be shown that:

$$\ln\left\{\frac{[\mathrm{ester}]_0}{[\mathrm{ester}]_t}\right\} = \frac{k_{\mathrm{ester}}}{k_{\mathrm{ref}}}\ln\left\{\frac{[\mathrm{ref}]_0}{[\mathrm{ref}]_t}\right\} \tag{I}$$

where $[\mathrm{ester}]_0$, $[\mathrm{ref}]_0$, $[\mathrm{ester}]_t$ and $[\mathrm{ref}]_t$ are the concentrations of the ester and reference compound at times $t = 0$ and t, respectively, and k_{ester} and k_{ref} are the rate coefficients of reactions 2 and 3, respectively.

The relative rate technique relies on the assumption that both the ester and reference organics are removed solely by reaction

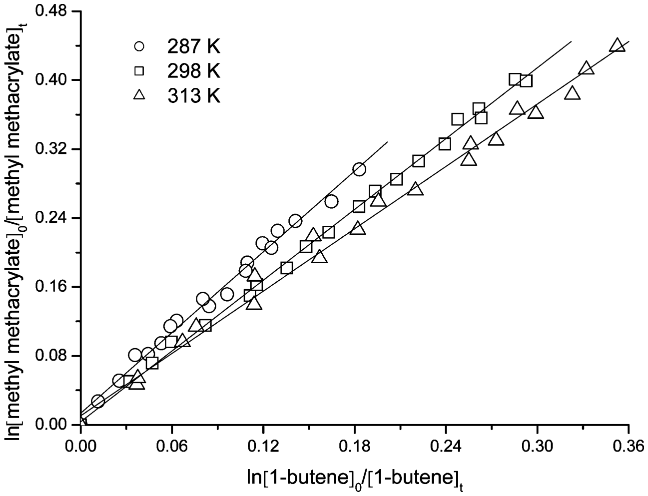

Figure 1. Plot of the kinetic data for the reaction of methyl methacrylate with OH radicals obtained at 287, 298, and 313 K, using 1-butene as reference hydrocarbon.

with OH radicals. To verify this assumption, various tests were performed to assess the reaction of the reactants with hydrogen peroxide, photolysis, and wall losses. Reaction between hydrogen peroxide and the esters and reference compounds was found to be negligible over the time period of the experiments. Photolysis of the esters and reference compounds in the absence of the OH source was likewise found to be negligible. Finally, no significant wall loss of the esters and references was observed on leaving the compounds in the dark in the reactor.

The initial concentrations used in the experiments for the esters and reference compounds in ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) were as follows: 0.3−0.9 for the esters; 1.39−1.86 for isobutene; 2.79 for 1-butene; the concentration of H_2O_2 was typically around 13 ppm.

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): methyl methacrylate at 1169; butyl methacrylate at 1167; butyl acrylate at 1070; vinyl acetate at 1148; isobutene at 891 and 1-butene at 912.

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%), methyl methacrylate (Aldrich, 99%), butyl methacrylate (Aldrich, 99%), butyl acrylate (Aldrich, 99%), vinyl acetate (Aldrich, 99%), isobutene (Messer Griesheim, 99%), 1-butene (Messer Griesheim, 99%) and H_2O_2 (Interox, 85% w/w).

Results and Discussion

Relative kinetic studies were performed at one atmosphere total pressure on the reactions of OH with MMA, BMA, BA and VA at temperatures of 287, 294, 298, 303, and 313 K. Figures 1−4 show examples of the kinetic data obtained relative to 1-butene at 287, 298, and 313 K and plotted according to eq I. In all cases, reasonable linear correlations with near zero intercepts were obtained. Table 1 lists the rate coefficient ratios obtained at each temperature from linear least-squares analyses of the kinetic data plotted according to eq I, the absolute rate coefficients obtained for OH with the esters derived from the rate ratios and the Arrhenius parameters obtained from the Arrhenius plots of the rate data shown in Figure 5. The rate coefficient ratios are each from a minimum of at least three experiments. To put the rate coefficients for the reaction of OH with the esters on an absolute basis rate coefficients for the respective temperatures derived from the following Arrhenius expression (in cm^3 $molecule^{-1}$ s^{-1} units) were used: k (OH + 1-butene) = 6.55×10^{-12} exp (4.67/T) cm^3 $molecule^{-1}s^{-1}$.[4] In the cases of BA and VA, measurements were also made at 298 K relative to the reaction of OH with isobutene. To put these measurements on an absolute footing a rate coefficient of k (OH + isobutene) = 5.14×10^{-11} cm^3 $molecule^{-1}$ s^{-1} was used.[19]

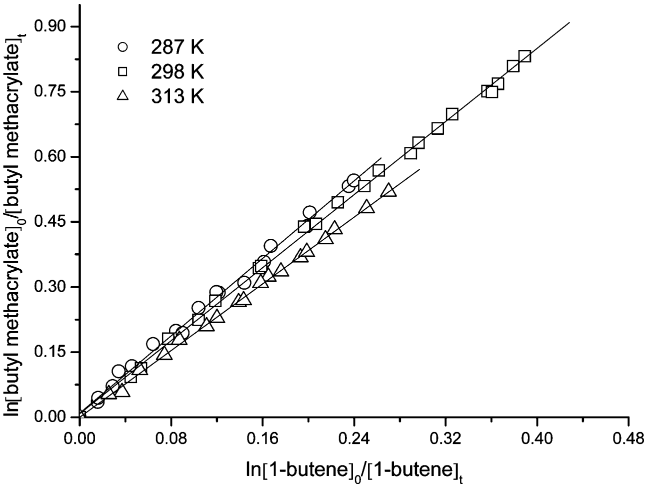

Figure 2. Plot of the kinetic data for the reaction of butyl methacrylate with OH radicals obtained at 287, 298, and 313 K, using 1-butene as reference hydrocarbon.

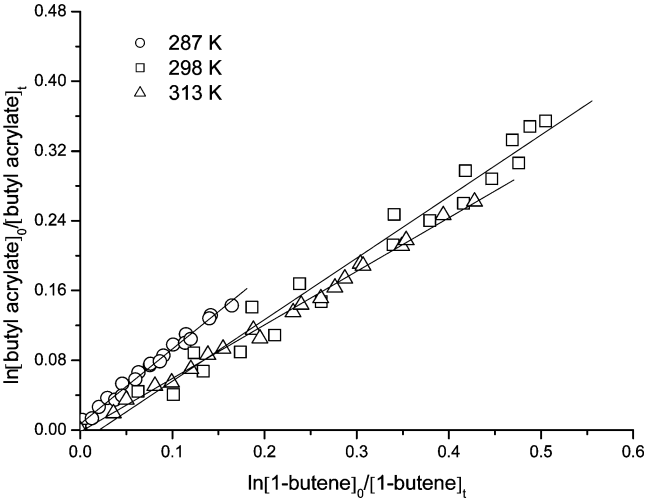

Figure 3. Plot of the kinetic data for the reaction of butyl acrylate with OH radicals obtained at 287, 298, and 313 K, using 1-butene as reference hydrocarbon.

The errors given for the rate coefficient ratios in Table 1 are the two least-squares standard deviations ($\pm 2\sigma$) from the linear regression analyses plus an additional 20% to cover uncertainties associated with the values of the reference rate coefficients.

As can be seen in Table 1 in instances where both reference compounds have been used, i.e., at 298 K, the rate coefficients derived from the experiments for the reaction are in excellent agreement. We therefore prefer to quote values for the reactions at this temperature as an average of the values determined with both reference hydrocarbons. These values are listed below and are also given in Table 2.

For all of the four esters, the reaction rate coefficients were found to decrease slightly with increasing temperature in the range 287−313 K. The k_{ester} values of Table 1 are plotted in Arrhenius form in Figure 5 for the four reactions. The following Arrhenius expressions adequately describe the data

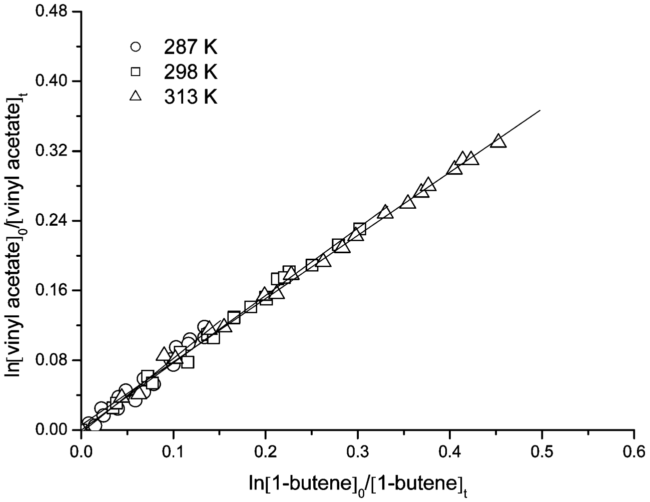

Figure 4. Plot of the kinetic data for the reaction of vinyl acetate with OH radicals obtained at 287, 298, and 313 K, using 1-butene as reference hydrocarbon.

in the temperature range 287−313 K with k in units of cm^3 molecule^{-1} s^{-1}:

$$k_1(\mathrm{OH{+}MMA}) = (1.97 \pm 0.95) \times 10^{-12} \exp[(921 \pm 52)/T]$$

$$k_2(\mathrm{OH{+}BMA}) = (16.5 \pm 10.5) \times 10^{-12} \exp[(413 \pm 34)/T]$$

$$k_3(\mathrm{OH{+}BA}) = (0.44 \pm 0.25) \times 10^{-12} \exp[(1177 \pm 56)/T]$$

$$k_4(\mathrm{OH{+}VA}) = (4.06 \pm 2.02) \times 10^{-12} \exp[(540 \pm 49)/T]$$

The errors in the activation term and the pre-exponential factor are the 2σ random statistical errors from fits to the data presented in Table 1 and plotted in Figure 5. There are no prior experimental determinations of the Arrhenius parameters for the reactions of OH with butyl methacrylate, butyl acrylate, and vinyl acetate, hence, this is the first temperature dependence study for these reactions. Teruel et al.[12] have investigated the temperature-dependence of the reaction of OH radicals with methyl methacrylate (k_1) in the range 255−351 K using the PLP−LIF technique; this study also included investigations of the temperature dependence of the reactions of OH with methyl acrylate (MA) and ethyl acrylate (EA). In Figure 6, the data obtained by Teruel et al. between 255 and 351 K for the reaction of OH with methyl methacrylate are compared with the results obtained in this work between 287 and 313 K. It can be observed that the rate coefficients obtained by Teruel et al. and the reported activation energy ($E_a/R = -821 \pm 55$ K) are in very good agreement with the experimental results determined in this study.

The values of rate coefficients and activation energies obtained in the present work appear entirely consistent with the available literature data for the reactions of OH radicals with other unsaturated esters ($E_a/R = -300$ to -1000 K),[12,20] unsaturated aldehydes ($E_a/R = -333$ to -510 K)[21] and alkenes ($E_a/R = -500$ K).[4,22]

A low pre-exponential factor and a negative temperature dependence for the rate coefficients (k_1, k_2, k_3, and k_4), together with the product distribution reported for the reactions of OH radicals with methyl methacrylate, butyl methacrylate,[13] and butyl acrylate[14] suggest that the dominant reaction pathway is radical addition to form an association complex, which may decompose back to reactants or be collisionally stabilized, whereby the OH preferably attacks the terminal carbon of the double bond.[23] This is the generally accepted mechanism for OH radical addition to alkenes [4,24,25] and also that which is observed for the reactions of OH radicals with other unsaturated compounds.[22]

The following rate coefficients have been obtained at 298 K for the reaction of OH with MMA, BMA, BA, and VA:

$$k_1 = (4.30 \pm 0.98) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_2 = (6.63 \pm 1.42) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_3 = (2.17 \pm 0.48) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_4 = (2.48 \pm 0.61) \times 10^{-11}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Table 2 shows a comparison of the room temperature rate coefficients obtained in this work with literature values obtained mainly at room temperature and atmospheric pressure using different experimental techniques. Rate coefficients for the reactions of OH with the esters have been estimated using the US EPA AOPWIN program[26] which is based upon the structure−activity relationship (SAR) method described in Kwok and Atkinson.[27] The estimated rate coefficients are also listed in Table 2.

With the exception of the value reported by Saunders et al.[15] the other rate coefficients reported for the reaction of OH radicals with methyl methacrylate (k_1), at room temperature measured using both absolute[12] and relative techniques [12,13] are in excellent agreement with the value determined here using the relative kinetic method. Saunders et al. used the discharge flow-laser induced fluorescence (DF−LIF) technique to measure the rate coefficient for the reaction of OH with MMA at 1 Torr total pressure of helium. It has been argued by Teruel et al.[12] that the difference may be due to the low pressure used in the Saunders et al. study and that the rate coefficient measurements were not in the high-pressure-limiting regime.

As can be seen in Table 2, the value of k_2 (butyl methacrylate + OH) obtained at 298 K in this work is in very good agreement with the previously reported value[13] obtained at 298 K and 750 Torr total pressure using the relative kinetic method and gas chromatography/flame ionization detection (RR−GC/FID) for the analyses. Similarly, the value obtained for k_3 (butyl acrylate + OH) in this work is in a very good agreement with the previous value[14] obtained at 298 K and 750 Torr total pressure using the RR−GC/FID technique with different sources of OH radicals; photolysis of H_2O_2 and CH_3ONO.

A rate coefficient of (2.5 ± 0.4) × 10^{-11} cm^3 molecule^{-1} s^{-1} has been reported by Saunders et al.[15] for the reaction of OH with vinyl acetate at 298 K which is in excellent agreement with the value determined in this study. However, although the authors state that the rate coefficient is for OH with vinyl acetate ($CH_3C(O)OCH{=}CH_2$) the molecule actually depicted in the manuscript is methyl acrylate ($CH_2{=}CHC(O)OCH_3$). Until this discrepancy is clarified, we suggest that our determination should be considered as the first unequivocal reported room-temperature rate coefficient for the reaction of OH radicals with vinyl acetate. The SAR estimation method gives rate coefficients for the reactions of OH with MMA, BMA, and BA which are factors of between 2 and 3 lower than the actual measured values showing that the method inadequately predicts the reactivity of a double bond adjacent to the carbonyl group of the ester group and needs adjustment. However, the SAR rate prediction for the reaction of OH with VA, where the double bond is adjacent to the alkoxy oxygen in the ester group, agrees excellently with the value measured in this study. The SAR method also accurately predicts the rate coefficients for the reactions of OH

TABLE 1: Rate Coefficients Ratios, k_{ester}/k_{ref} and Arrhenius Parameters for the Gas Phase Reactions of OH Radicals with Methyl Methacrylate (MMA), Butyl Methacrylate (BMA), Butyl Acrylate (BA) and Vinyl Acetate (VA) Determined at Different Temperatures[a] [19]

T (K)	k_{ester}/k_{ref}	$k_{ester} \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	reactant	E_a/R(K)	$A/10^{-12}$ (cm^3 molecule^{-1} s^{-1})
			Methyl Methacrylate		
287	1.43 ± 0.03	4.88 ± 1.22		−921 ± 52	1.97 ± 0.95
294	1.40 ± 0.02	4.51 ± 0.98			
298	1.37 ± 0.02	4.30 ± 0.98			
303	1.32 ± 0.02	4.04 ± 0.88			
313	1.29 ± 0.01	3.76 ± 0.86			
			Butyl Methacrylate		
287	2.23 ± 0.04	7.60 ± 1.60		−413 ± 34	16.5 ± 10.5
294	2.16 ± 0.04	6.94 ± 1.42			
298	2.11 ± 0.02	6.63 ± 1.42			
303	2.06 ± 0.03	6.31 ± 1.36			
313	1.92 ± 0.02	5.59 ± 1.36			
			Butyl Acrylate		
287	0.80 ± 0.02	2.72 ± 0.61		−1177 ± 105	0.44 ± 0.25
294	0.75 ± 0.03	2.42 ± 0.55			
298	0.42 ± 0.01[b]	2.09 ± 0.50[b]			
298	0.71 ± 0.03	2.23 ± 0.46			
303	0.67 ± 0.02	2.06 ± 0.45			
313	0.67 ± 0.02	1.95 ± 0.42			
			Vinyl Acetate		
287	0.78 ± 0.03	2.66 ± 0.66		−540 ± 49	4.06 ± 2.02
294	0.80 ± 0.04	2.56 ± 0.61			
298	0.50 ± 0.01[b]	2.49 ± 0.59[b]			
298	0.79 ± 0.02	2.48 ± 0.63			
303	0.79 ± 0.02	2.41 ± 0.52			
313	0.78 ± 0.02	2.28 ± 0.49			

[a] Except where indicated the measurements have been made relative to the reaction of OH with 1-butene. [b] Measurement made using isobutene as reference compound.

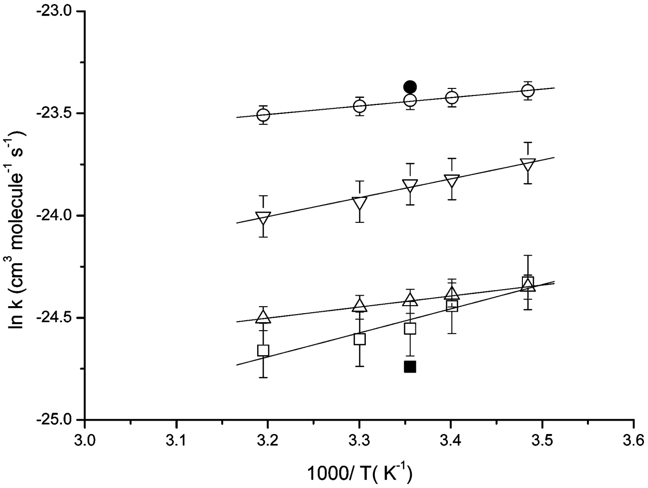

Figure 5. Arrhenius plots of the kinetic data obtained in this study between 287 and 313 K for the reactions of OH with methyl methacrylate (▽); butyl methacrylate (○); butyl acrylate (□) and vinyl acetate (△). The 298 K single values from ref 13 (●) and ref 14 (■) are also shown.

with other unsaturated esters, such as allyl acetate ($CH_3C(O)OCH_2CH{=}CH_2$) and isopropenyl acetate ($CH_3C(O)OC(CH_3){=}CH_2$),[20] where the double bond is also on the side of the alkoxy oxygen in the ester group.

The rate coefficients for the reactions of OH radicals with unsaturated esters reported here are of the same order as the rate coefficients reported for the reactions of OH with other unsaturated oxygenated organic compounds,[4,11,22] however, the position of the double bond in the unsaturated esters and its substituent has distinct effects on the reactivity of the esters toward OH radicals. To aid in the discussion, averaged values of rate coefficients for the reaction of OH with unsaturated esters reported in this study and in the literature are given in Table 3.

Regarding the structure−reactivity relationships of the unsaturated esters studied, H-substitution by electron donor groups like $-CH_3$ or other alkyl groups in the α,β-unsaturated ester increases quite significantly the reactivity of the compounds toward electrophilic attack of OH radicals irrespective of whether the double bond is on the carbonyl group or alkoxy oxygen atom side of the ester entity. This can be seen for the alkoxy oxygen side of the ester entity when comparing the higher reactivity of isopropenyl acetate ($CH_3C(O)OC(CH_3){=}CH_2$) toward OH radical attack, where a rate coefficient of 6.96×10^{-11} cm^3 molecule^{-1} s^{-1} has been reported by Le Calve et al.,[20] with the value of 2.48×10^{-11} cm^3 molecule^{-1} s^{-1} determined for the reaction of OH with vinyl acetate ($CH_3C(O)OCH{=}CH_2$) in this study. A similar increase of approximately a factor of 3 is observed upon methyl substitution when the double bond is on the carbonyl side of the ester entity, e.g., the rate coefficient for the reaction of OH with methyl methacrylate ($CH_2{=}C(CH_3)C(O)OCH_3$) is 4.30×10^{-11} cm^3 molecule^{-1} s^{-1} (this work) whereas that of OH with methyl acrylate ($CH_2{=}CHC(O)OCH_3$) is 1.3×10^{-11} cm^3 molecule^{-1} s^{-1} [12] and the rate coefficient for the reaction of OH with butyl methacrylate ($CH_2{=}C(CH_3)C(O)O(CH_2)_3CH_3$) is 6.63×10^{-11} cm^3 molecule^{-1} s^{-1} (this work) whereas that of OH with butyl acrylate ($CH_2{=}CHC(O)O(CH_2)_3CH_3$) is 2.17×10^{-11} cm^3 molecule^{-1} s^{-1} (this work). This effect can be largely attributed to the positive inductive effect of the CH_3 radical, which increases the charge density on the double-bonded carbon atom and hence increases the susceptibility of the double bond toward OH radical electrophilic attack.

The large deactivating effect of halogen-containing substituents toward OH radical addition when directly attached to a double bond is well established. However, the electron-

TABLE 2: Comparison of Room Temperature Rate Coefficients Obtained in This Work for the Reaction of OH Radicals with Unsaturated Esters with Literature Values

ester	$k \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	technique[a]	ref	SAR[b] $k \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})
methyl methacrylate	4.30 ± 0.98	RR–FTIR	this work	1.83
	3.9 ± 0.4	PLP–LIF	12	
	4.2 ± 1.1	RR–GC	12	
	4.15 ± 0.32	RR–GC	13	
	2.6 ± 0.5	DF–LIF	15	
butyl methacrylate	6.63 ± 1.42	RR–FTIR	this work	2.27
	7.08 ± 0.75	RR–GC	13	
butyl acrylate	2.17 ± 0.48	RR–FTIR	this work	1.38
	1.80 ± 0.26	RR–GC	14	
vinyl acetate	2.48 ± 0.61	RR–FTIR	this work	2.63
	2.5 ± 0.4	DF–LIF	15	

[a] PLP–LIF: pulsed laser photolysis/laser induced fluorescence. RR–GC: relative rate/gas chromatography. DF–LIF: discharge flow/laser induced fluorescence. RR–FTIR: relative rate/fourier transform infrared spectroscopy. [b] Calculated using the AOPWIN program from ref 26.

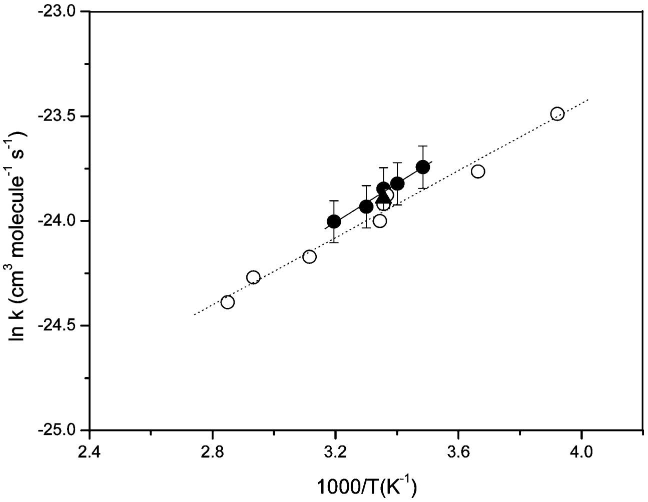

Figure 6. Arrhenius plots of the temperature dependent kinetic data obtained for the reaction OH with methyl methacrylate from (i) the present study and (ii) the study of Teruel et al. (dashed line).[12] For comparison the room temperature rate coefficient from Blanco et al. is also shown (▲).[13]

withdrawing effect of halogen substitution when on the alkoxy side of an ester functionality appears to be only marginal. This can be observed if we compare the small difference between the rate coefficients for the reactions of $CH_2{=}CHC(O)OCH_2CH_3$ (1.65×10^{-11} cm^3 molecule^{-1} s^{-1})[12] and $CH_2{=}CHC(O)O(CH_2)_2C_4F_9$ (1.1×10^{-11} cm^3 molecule^{-1} s^{-1})[28] with OH radicals. The ester functional group very effectively sheilds the double bond from the deactivating effect of the $C_4F_9^-$ group.

From the above discussion, it is evident that a double bond on the alkoxy oxygen side of the ester unit ($-C(O)OCH{=}CH_2$) is more receptive toward OH radical attack than a double bond on the carbonyl side of the ester unit ($CH_2{=}CHOC(O)O^-$), e.g., the rate coefficient for the reaction of OH with vinyl acetate of 2.48×10^{-11} cm^3 molecule^{-1} s^{-1} from this work is almost 2× higher than the rate coefficient of 1.3×10^{-11} cm^3 molecule^{-1} s^{-1} for the reaction of OH with methyl acrylate (Table 3). This observation can be explained by the activation of the double bond toward OH addition by the conjugation effect of the lone pair electrons on the oxygen atom of the vinyl acetate ester group with the olefinic π electron system. In contrast, the negative inductive effect of the carbonyl group adjacent to the double bond in methyl acrylate deactivates the double bond toward OH addition as has been observed in a comparison of the rate coefficients for the reactions of OH radicals with unsaturated aldehydes with those of the corresponding alkenes.[29]

Mellouki et al.[11] have calculated group rate coefficients for the CH_x ($x = 1$, 2, or 3) groups in alkyl esters as a function of their position in the alkyl group chain relative to the functional group. Their calculations were based on the assumption that the reactivities of the groups on either side of the ether and carbonyl groups of the ester functionality are reasonably independent and additive. It is interesting to test if these CH_x group rate coefficients derived for the alkyl esters are consistent with the rate coefficients reported here and in other studies for the unsaturated esters. The difference between the rate coefficient for OH with ethyl acrylate ($CH_2{=}CHC(O)OCH_2CH_3$)[12] and OH with methyl acrylate[12] would give a group rate coefficient for the $-CH_2-$ unit in ethyl acrylate of around 3.6×10^{-12} cm^3 molecule^{-1} s^{-1}. Using the group CH_x rate coefficients given in Mellouki et al.[11] results in a value of 1.4×10^{-12} cm^3 molecule^{-1} s^{-1} more than a factor of 2 lower. Similarly, the difference between the rate coefficient for OH with butyl acrylate ($CH_2{=}CHC(O)O(CH_2)_3CH_3$),[14] (this work) and OH with methyl acrylate[12] would give a collective group rate coefficient for the $-CH_2CH_2CH_2-$ unit in butyl acrylate of around 7.0×10^{-12} cm^3 molecule^{-1} s^{-1}. Using the group CH_x rate coefficients given in Mellouki et al.[11] results in a value of 4.9×10^{-12} cm^3 molecule^{-1} s^{-1}, which is still lower but probably acceptable within the experimental errors of the method. However, the difference becomes very crass on comparing methyl methacrylate with butyl methacrylate. The difference between the rate coefficient for OH with butyl methacrylate ($CH_2{=}C(CH_3)C(O)O(CH_2)_3CH_3$) (this work), and OH with methyl methacrylate (this work) would give a collective group rate coefficient for the $-CH_2CH_2CH_2-$ unit in butyl methacrylate of around 2.6×10^{-11} cm^3 molecule^{-1} s^{-1}. Using the group CH_x rate coefficients given in Mellouki et al.[11] results in a value of only 4.9×10^{-12} cm^3 molecule^{-1} s^{-1} for the $-CH_2CH_2CH_2-$ unit.

If the rate coefficients used in the above comparisons are correct, then the group CH_x rate coefficients calculated for the alkyl esters by Mellouki et al.[11] are clearly not valid for the unsaturated esters when the double bond is on the carbonyl side of the ester functional group. Either the CH_x groups are more activated in the unsaturated esters than in the alkyl esters or the inductive effect of the alkoxy groups $-O(CH_2)_xCH_3$ can positively affect the reactivity of the double bond on the carbonyl side of the ester group. If the latter is true, then the reactivities of the groups on either side of the ether and carbonyl groups will not be independent of one another for this class of compound. Further studies on the kinetics of the reaction of OH with unsaturated esters using different techniques would

TABLE 3: Comparison of Averaged Rate Coefficients for the Reactions of OH Radicals with Unsaturated Esters at 298 K

compound	$k \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})	compound	$k \times 10^{11}$ (cm^3 molecule^{-1} s^{-1})
$CH_2{=}CHC(O)OCH_3$	1.3[a]	$CH_3C(O)OCH{=}CH_2$	2.48[b]
$CH_2{=}CHC(O)OCH_2CH_3$	1.65[a]	$CH_3C(O)OC(CH_3){=}CH_2$	6.96[d]
$CH_2{=}CHC(O)O(CH_2)_3CH_3$	2.17[b]	$CH_3C(O)OCH_2CH{=}CH_2$	2.71[d]
$CH_2{=}C(CH_3)C(O)OCH_3$	4.30[b]		
$CH_2{=}C(CH_3)C(O)O(CH_2)_3CH_3$	6.63[b]		
$CH_2{=}CHC(O)O(CH_2)_2C_4F_9$	1.1[c]		

[a] From ref 12. [b] This work. [c] From ref 28. [d] From ref 20.

TABLE 4: Estimated Tropospheric Lifetimes of the Unsaturated Esters Studied in This Work with Respect to Reaction with OH Radicals, Cl Atoms, NO$_3$ Radicals and O$_3$ Molecules

ester	τ_{OH} (hours)	τ_{Cl} (days)	τ_{NO3} (days)	τ_{O3} (days)
methyl methacrylate	3	4	6	2
butyl methacrylate	2	3		
butyl acrylate	6	5		
vinyl acetate	6	4		5

desirable in order to put the rate coefficients on a firmer experimental basis. A detailed product study would give the relative importance of the addition and abstraction reaction channels and show whether the CH$_x$ groups in unsaturated esters are more activated than in alkyl esters or if the $-O(CH_2)_xCH_3$ group is activating the double bond. Theoretical calculations could also be helpful in highlighting potential activating electronic effects in the reactions of OH with alkyl acrylate esters.

Tropospheric Implications

Unsaturated and saturated compounds are chemically removed from the troposphere, mainly, by their reactions with OH, NO$_3$, O$_3$, and halogen atoms. Where rate coefficients are available, tropospheric lifetimes at 298 K have been calculated for the reactions of the esters with these oxidants using the expression: $\tau_x = 1/k_x[X]$ where X = OH, NO$_3$, Cl, and O$_3$, and k_x is the appropriate rate coefficient and [X] is the average concentration of each oxidant. The results are listed in Table 4.

In these calculations, the following rate coefficient values were used: $k_{OH+MMA} = 4.30 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{OH+BMA} = 6.63 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{OH+BA} = 2.17 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{OH+VA} = 2.48 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (this work). $k_{Cl+MMA} = 2.86 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[30] $k_{Cl+BMA} = 3.77 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[31] $k_{Cl+BA} = 2.50 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[32] $k_{Cl+VA} = 2.68 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[32] $k_{NO3+MMA} = 3.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1},[33] $k_{O3+MMA} = 7.51 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1},[34] and $k_{O3+VA} = 3.2 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.[35]

The reactions of the unsaturated esters with O$_3$ are relatively slow. For example, assuming a 24-h average ozone concentration of 7×10^{11} molecule cm^{-3} [36] results in a tropospheric lifetime of ∼2 days for the loss of methyl methacrylate due to reaction with O$_3$. Kinetic data for reaction of the esters with NO$_3$ radicals, the main tropospheric oxidant at nighttime, has only been reported for methyl methacrylate; assuming a typical atmospheric NO$_3$ radical concentration (12-h averaged night-time) of 5×10^8 radical cm^{-3} [37] results in an atmospheric lifetime of 6 days for methyl methacrylate with respect to its reaction with NO$_3$. The tropospheric lifetimes of the studied esters due to the OH-reaction were calculated using an OH concentration (12-h averaged daytime) of 2×10^6 radicals cm^{-3}.[38] On the basis of the room-temperature rate coefficients obtained in this work, tropospheric lifetimes for these compounds are from 2 to 6 h.

In a recent kinetic study of the reactions of Cl atoms with methyl methacrylate, butyl methacrylate, butyl acrylate and vinyl acetate,[30−32] we have estimated tropospheric lifetimes from between 3 to 5 days for reactions based on a global Cl atom concentration of 1×10^4 atoms cm^{-3}.[39] However, in some marine regions, peak values of 1×10^5 atoms cm^{-3} have been observed.[40] Under such circumstances, the reaction of Cl with the esters can be a significant if not dominant loss process.

As mentioned earlier, photolysis is not an important atmospheric loss process for the esters since they do not absorb radiation at actinic wavelengths. Losses by uptake in surface and rainwater or cloud droplets are not important sinks for these compounds since they are highly volatile and sparingly soluble in water. Thus, the main tropospheric chemical removal of these unsaturated esters seems to be the reaction of OH radicals.

The relatively short atmospheric lifetimes indicate that these unsaturated oxygenated compounds will be oxidized rapidly by reaction with OH radicals near their anthropogenic origin where the oxidation can contribute to ozone and photooxidant formation in these areas.

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Supporting Information Available: Typical FTIR spectra for the experiments of MMA with OH radicals at different photolysis times (Figure 1) and relative kinetic plots of the reactions of OH with MMA, BMA, BA and VA at 298 K (Figures 2−5) using two reference hydrocarbons in the cases of BA and VA. This material is available free of charge via the Internet at http://pubs.acs.org.

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