Reaction Rate Coefficients of OH Radicals and Cl Atoms with Ethyl Propanoate, *n*-Propyl Propanoate, Methyl 2-Methylpropanoate, and Ethyl *n*-Butanoate

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Kinetics of the reactions of OH radicals and Cl atoms with four saturated esters have been investigated. Rate coefficients for the gas-phase reactions of OH radicals with ethyl propanoate (k_1), *n*-propyl propanoate (k_2), methyl 2-methylpropanoate (k_3), and ethyl *n*-butanoate (k_4) were measured using a conventional relative rate method and the pulsed laser photolysis−laser induced fluorescence technique. At (296 ± 2) K, the rate coefficients obtained by the two methods were in good agreement. Significant curvatures in the Arrhenius plots have been observed in the temperature range 243−372 K for k_1, k_3, and k_4. The rate coefficients for the reactions of the four esters with Cl atoms were determined using the relative rate method at (296 ± 2) K and atmospheric pressure. The values obtained are presented, compared with the literature values when they exist, and discussed. Reactivity trends and atmospheric implications for these esters are also presented.

1. Introduction

Esters, as many other volatile organic compounds (VOCs), are emitted into the atmosphere as primary pollutants from a wide number of anthropogenic and biogenic sources. In particular, they are widely used as solvents in industry and in the manufacture of perfumes and flavorings, and they are also produced in nature by vegetation.[1] A number of esters have pleasant odors and are present in fruits and other natural sources, and they are also often added to fragrances and consumer products. Esters can also be produced in the atmosphere from the degradation of ethers.[2−4] Recently, Niedojadlo et al.[5] and Legreid et al.[6] have reported quantitative measurements of esters in ambient air in Wuppertal (Germany) and Zürich (Switzerland) with mixing ratios ranging from 0.01 to 3.14 ppbV.

It is well established that the main gas-phase removal process of esters in the troposphere is the reaction with OH radicals, the reactions with O_3 and NO_3 (essentially for the unsaturated esters) and Cl atoms (in coastal areas and the marine boundary layer of the troposphere) being other important degradation pathways.[7] Hence, to assess the impact of these VOCs on air quality, a detailed understanding of the kinetics and mechanisms of their atmospheric degradation is required.

In this work, we report the rate coefficients for OH radical reactions with ethyl propanoate (ethyl propionate, $CH_3CH_2C(O)OCH_2CH_3$) (k_1), *n*-propyl propanoate (*n*-propyl propionate, $CH_3CH_2C(O)OCH_2CH_2CH_3$) ($k_2$), methyl 2-methylpropanoate (methyl isobutyrate, $(CH_3)_2CHC(O)OCH_3$) (k_3), and ethyl *n*-butanoate (ethyl butyrate, $CH_3CH_2CH_2C(O)OCH_2CH_3$) ($k_4$)

$$OH + CH_3CH_2C(O)OCH_2CH_3 \rightarrow \text{products} \quad (k_1) \tag{1}$$

$$OH + CH_3CH_2C(O)OCH_2CH_2CH_3 \rightarrow \text{products} \quad (k_2) \tag{2}$$

$$OH + (CH_3)_2CHC(O)OCH_3 \rightarrow \text{products} \quad (k_3) \tag{3}$$

$$OH + CH_3CH_2CH_2C(O)OCH_2CH_3 \rightarrow \text{products} \quad (k_4) \tag{4}$$

The kinetic study of the title reactions was performed in the temperature range 243−372 K for reactions 1 and 3 and between 253 and 372 K for reactions 2 and 4 at around 100 Torr total pressure, using the pulsed laser photolysis−laser induced fluorescence (PLP−LIF) technique and also using a relative method at (296 ± 2) K and 760 Torr of purified air.

In addition, the reactions of chlorine atoms with these esters were investigated using a relative method at (296 ± 2) K in 760 Torr of air

$$\text{C1} + \text{ethyl propionate} \rightarrow \text{products} \quad (k_5) \tag{5}$$

$$\text{C1} + n\text{-propy1 propionate} \rightarrow \text{products} \quad (k_6) \tag{6}$$

$$\text{C1} + \text{methyl isobutyrate} \rightarrow \text{products} \quad (k_7) \tag{7}$$

$$\text{C1} + \text{ethyl butyrate} \rightarrow \text{products} \quad (k_8) \tag{8}$$

To the best of our knowledge, this work provides the first temperature dependence studies for the four reactions with OH radicals and the first determination of the rate coefficients at

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room temperature for the reactions with Cl atoms. The previous data reported in the literature for the reactions of this series of esters with atmospheric oxidants at room temperature are those reported by Campbell et al.[8] for the reaction of ethyl propionate with OH; Wallington et al.[9] for the reactions of ethyl propionate, ethyl butyrate, and *n*-propyl propionate with OH; Ferrari et al.[10] for the reaction of ethyl butyrate with OH; Wyatt et al.[11] for the reaction of methyl isobutyrate with OH; and Langer et al.[12] for the reaction of ethyl propionate with NO_3. These previous values were obtained at room temperature.

The results obtained in this work are compared with previous measurements when possible and discussed in terms of the reactivity trends. Also, on the basis of the experimental data obtained in this work and previously from the literature, the tropospheric lifetimes of the four esters are estimated.

2. Experimental Section

2.1. Relative Measurements. A conventional relative rate method was used to obtain the rate coefficients for the reactions of OH radicals and Cl atoms with four esters at (296 ± 2) K in 760 Torr of air. The experimental setup consisted of a greaseless vacuum system, a 200 L collapsible Teflon bag, and a gas chromatograph (CG-FID, Star 3600 CX, Varian) coupled with flame ionization detection. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of ultrapure air, and it was then filled to its full capacity at atmospheric pressure with ultrapure air. The Teflon bag was surrounded by two types of lamps, Sylvania G30W providing irradiation at $\lambda = 254$ nm and Philips TL20W/05 for the UV light centered at 360 nm. OH radicals were generated through the photolysis of H_2O_2 at 254 nm, while Cl atoms were produced using the photolysis of Cl_2 at 360 nm. The concentrations of the organic compounds (reactants and references) were monitored over the course of the reaction by GC-FID. Gas samples were automatically collected from the chamber and introduced via a heated sampling loop of 0.25 mL capacity to the gas chromatograph containing a DB-1 capillary column (J&W Scientific, 30 m, 0.25 mm i.d., 5 μm film). The column was operated with several temperature programs between 303 and 433 K, according to the reference and the organic compounds used; helium was used as the carrier gas.

Relative rate coefficients were determined by comparing the rate coefficients for the reaction of OH radicals or Cl atoms with the esters to that with reference compounds

$$\mathrm{X} + \text{ester} \rightarrow \text{products} \qquad k_i$$

$$\mathrm{X} + \text{reference} \rightarrow \text{products} \qquad k_{\mathrm{Ref}}$$

with X being OH radicals or Cl atoms. Provided that both reactant and reference compounds are lost only by reaction with OH or Cl, it can be shown that

$$\ln([\text{ester}]_0/[\text{ester}]_t) = (k_i/k_{\mathrm{Ref}}) \times \ln([\mathrm{Ref}]_0/[\mathrm{Ref}]_t)$$

where $[\text{ester}]_0$, $[\text{ester}]_t$, $[\text{ref}]_0$, and $[\text{ref}]_t$ are the concentrations of the ester and reference compounds at times 0 and t, respectively; k_i ($i = 1-8$) are the second-order rate coefficients for reactions 1−8; and k_{ref} is the second-order rate coefficient for the reaction of the reference compound with OH radicals or Cl atoms.

The rate coefficients k_{1-4} for the reactions 1−4 of OH with the four esters were obtained relative to the rate coefficient of OH with *n*-butane and iso-butane in the case of ethyl propionate, relative to iso-butane in the case of methyl isobutyrate, and relative to *n*-pentane for ethyl butyrate and *n*-propyl propionate. The concentration range of the different esters and reference compounds was 39−142 ppm (1 ppm = 2.46×10^{13} molecules cm^{-3}). The H_2O_2 concentrations used were in the range 200−250 ppm, and H_2O_2 was introduced into the bag by a Hamilton syringe through a stream of ultrapure air. The reactant mixtures containing esters, reference compounds, and H_2O_2 were stable when left in the dark in the chamber for about 2 h. Moreover, no photolysis of both esters and references was observed when irradiated for more than 20 min with the combined set of lamps used in this study. After these checks, conducted before each run, the rate coefficients were derived from the kinetic measurements carried out by irradiating the reactant mixtures (ester, reference, and H_2O_2) for typical durations of 1 h 30 min to 2 h 30 min.

The rate coefficients for the reactions of Cl atoms with the four esters, k_{5-8}, were obtained relative to the rate coefficients of Cl with methanol and ethane in the case of ethyl propionate and methyl isobutyrate, relative to methanol, *n*-propane, and ethane in the case of ethyl butyrate, and relative to *n*-propane and ethane for *n*-propyl propionate. The concentration range of the different esters and reference compounds was 16−119 ppm. The Cl_2 concentrations used were in the range 46−82 ppm. Measured amounts of Cl_2 were flushed from a calibrated Pyrex bulb into the chamber. No side reactions such as dark reactions (in the presence and absence of Cl_2) or photolysis of reagents were observed under our experimental conditions. The kinetic measurements were carried out during a photolysis time range of 2−4 h.

2.2. Absolute Measurements. The pulsed laser photolysis−laser induced fluorescence (PLP−LIF) experimental setup and methodology used in this investigation have been presented in detail previously.[13] Therefore, the description given below is limited to the features necessary to understand the current experiments.

OH radicals were generated by photolysis of H_2O_2 at $\lambda = 248$ nm (KrF excimer laser). The concentration of OH radicals was monitored at various reaction times ranging from about 10 μs to 19 ms, by pulsed laser-induced fluorescence. A frequency-doubled dye laser pumped by a Nd:YAG laser was used to excite the OH radicals at $\lambda = 282$ nm, and fluorescence from OH radicals was detected by a photomultiplier tube fitted with a 309 nm narrow bandpass filter. The output pulse from the photomultiplier was integrated for a preset period by a gated charge integrator. Typically, the fluorescence signal resulting from 100 probe laser shots was measured for 10−15 different delay times and averaged to generate OH concentration−time profiles over at least three lifetimes. H_2O_2 was introduced into the reaction cell by passing a small flow of helium through a glass bubbler containing a solution of H_2O_2. Esters were premixed with helium in a 10 L glass bulb to form a 0.23−2.4% mixture at total pressure of about 800 Torr. The gas mixture, the photolytic precursor (H_2O_2), and the bath gas (He) were flowed through the cell with a linear velocity in the range 3−10 cm s^{-1}. Each photolysis/probe sequence interrogated a fresh gas mixture, and reaction products did not build up in the cell. The reactant concentrations were calculated from their mass flow rates, the temperature, and the pressure in the reaction cell. All flow rates were measured with mass flow meters calibrated by measuring the rate of pressure increase in a known volume.

The pressure in the cell was measured with a capacitance manometer connected at the entrance of the cell.

Absolute rate coefficients were determined under pseudofirst-order conditions with the concentration of esters in excess over that of the OH radicals ($[\text{ester}]_0 \gg [\text{OH}]_0$). Typically, the initial OH radical concentration ($[\text{OH}]_0$) was in the range (0.6−59.4) $\times 10^{10}$ molecules cm^{-3}. The rate of disappearance of the OH radical followed a simple exponential rate law

$$[\text{OH}]_t = [\text{OH}]_0 e^{-k't} \text{ where } k' = k_i[\text{ester}] + k'_0$$

and k_i represents the rate coefficient for the reaction of OH with the four esters, so that $i = 1-4$ and k'_0 is the first-order rate coefficient for OH removal in the absence of ester due to the diffusion of OH radicals out of the detection zone and the reaction between OH radicals and their precursor (H_2O_2). Further, k_i can be obtained from the slope of the plots of $k'-k'_0$ vs $[\text{ester}]_0$ considering the following equation

$$k' - k'_0 = k_i[\text{ester}]_0$$

Experiments were carried out in the temperature range 243−372 K for ethyl propionate and methyl isobutyrate reactions and between 253 and 372 K for ethyl butyrate and *n*-propyl propionate. The total pressure was between 101 and 104 Torr of helium for all experiments. The ester and H_2O_2 concentrations were in the range (0.18−18.1) $\times 10^{14}$ molecules cm^{-3} and (0.9−17.3) $\times 10^{13}$ molecules cm^{-3}, respectively.

2.3. Materials. The helium carrier gas (Alpha Gas UHP certified to >99.9995%), synthetic air (AGA 99.999%), Cl_2 (Alpha Gas 99.5%), ethane (Alpha Gas ≥99%), *n*-propane (Alpha Gas ≥99%), *n*-butane (Phillips 66 ≥99% - Phillips Petroleum Company), and iso-butane (Phillips 66 ≥99% - Phillips Petroleum Company) were used without further purification. The 50 wt. % H_2O_2 solution, from Sigma-Aldrich, was concentrated by bubbling helium through the solution to remove water for several days prior to use and constantly during the experiment. Methanol (Normapur ≥99.9%), *n*-pentane (Fluka ≥99.5%), ethyl propionate (Aldrich 99%), methyl isobutyrate (Alfa Aesar 98%), ethyl butyrate (Alfa Aesar 99%), and *n*-propyl propionate (Alfa Aesar 99%) were degassed by repeated freeze−pump−thaw cycles and purified by vacuum distillation before use.

3. Results and Discussion

3.1. Rate Coefficient Measurements.

3.1.1. Relative Measurements. The second-order rate coefficients for reactions 1−4 were measured at (296 ± 2) K in 760 Torr of air. Figure 1 shows an example of $\ln([\text{ester}]_0/[\text{ester}]_t)$ as a function of $\ln([\text{ref}]_0/[\text{ref}]_t)$ plots obtained during this work. The rate coefficients (in cm^3 molecule^{-1} s^{-1}) of the reaction of OH with the references used in this work were taken from Calvert et al.[14] as $k(\text{OH} + n\text{-butane}) = 2.36 \times 10^{-12}$, $k(\text{OH} + \text{isobutane}) = 2.12 \times 10^{-12}$, and $k(\text{OH} + n\text{-pentane}) = 3.96 \times 10^{-12}$ at 298 K. The linearity of the data and the fact that the plots show practically zero intercepts suggest that the contribution of secondary reactions could be considered negligible. The recommended rate coefficient values obtained by averaging the values from different experiments are the following

$$k_1 = (2.4 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (4.4 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (2.0 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_4 = (5.7 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation (σ_{n-1}) arising from the average of the values obtained in the independent experiments and do not include the corresponding statistical error in the reference rate constant. The uncertainties in the rate coefficients do not take into account potential systematic errors in the reference rate constants, which could be as high as 15−20%. Table 1 shows experimental conditions, reference compounds, and k_i/k_{ref} for each experiment.

The second-order rate coefficients for reactions 5−8 were also measured at (296 ± 2) K in 760 Torr of air. Figure 2 shows example plots of $\ln([\text{ester}]_0/[\text{ester}]_t)$ as a function of $\ln([\text{ref}]_0/[\text{ref}]_t)$. The rate coefficients of the reaction of Cl (in cm^3 molecule^{-1} s^{-1}) with the references used in this work were taken from Atkinson et al.[15] as $k(\text{Cl} + CH_3OH) = 5.5 \times 10^{-11}$, $k(\text{Cl} + C_2H_6) = 5.9 \times 10^{-11}$, and $k(\text{Cl} + C_3H_8) = 1.4 \times 10^{-10}$ at 298 K. The same considerations regarding the linearity of the data points and zero intercepts of the plots apply in this case as for the OH reactions. The recommended rate coefficient values obtained by averaging the values from different experiments were the following

$$k_5 = (3.7 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_6 = (8.2 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_7 = (4.2 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_8 = (10 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation (σ_{n-1}) arising from the average of the values obtained in the independent experiments and do not include the corresponding statistical error in the reference rate constant. The uncertainties in the rate

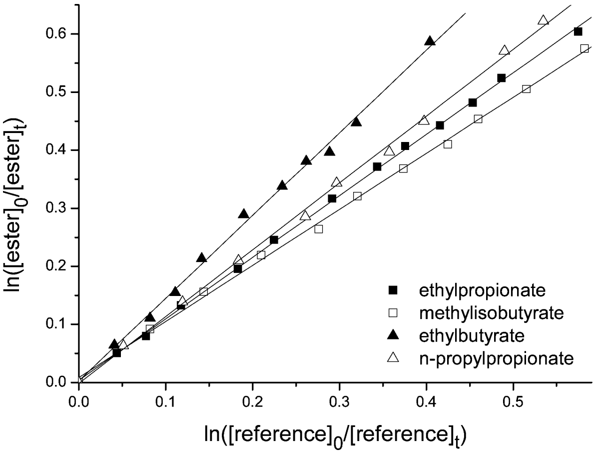

Figure 1. Relative rate data for the OH reactions with the investigated esters.

TABLE 1: Rate Coefficient Ratios, k_i/k_{Ref}, and the Obtained Second-Order Rate Coefficients for the Reactions of OH with the Studied Esters at (296 ± 2) K and 760 Torr of Air

ester	$[ester]_0$ (ppm)	reference	$[ref]_0$ (ppm)	number of runs	k_{ester}/k_{Ref} [a]	$k_{ester}/10^{-12}$ (cm^{-3} $molecule^{-1}$ s^{-1}) [a]
ethyl propionate	47	butane	142	1	1.06 ± 0.01	2.50 ± 0.02
	63	isobutane	59	1	1.09 ± 0.02	2.30 ± 0.07
					Average	**2.4 ± 0.1** [b]
n-propyl propionate	47	pentane	41	2	1.15 ± 0.03	4.55 ± 0.12
	39		40		1.08 ± 0.03	4.28 ± 0.12
					Average	**4.4 ± 0.2** [b]
methyl isobutyrate	59	isobutane	62	2	0.94 ± 0.02	1.99 ± 0.04
	63		51		0.97 ± 0.03	2.05 ± 0.06
					Average	**2.0 ± 0.1** [b]
ethyl butyrate	41	pentane	65	2	1.42 ± 0.05	5.62 ± 0.20
	39		40		1.44 ± 0.03	5.70 ± 0.12
					Average	**5.7 ± 0.2** [b]

[a] The errors quoted for the k_{ester}/k_{Ref} values are twice the standard deviation arising from the least-squares fit of the straight lines and do not include the corresponding statistical error in the reference rate constant. The errors quoted for k_i in the individual experiments are calculated multiplying the errors quoted for k_{ester}/k_{Ref} by k_{Ref}. [b] Errors quoted as $2\sigma_{n-1}$ from the average of the two runs.

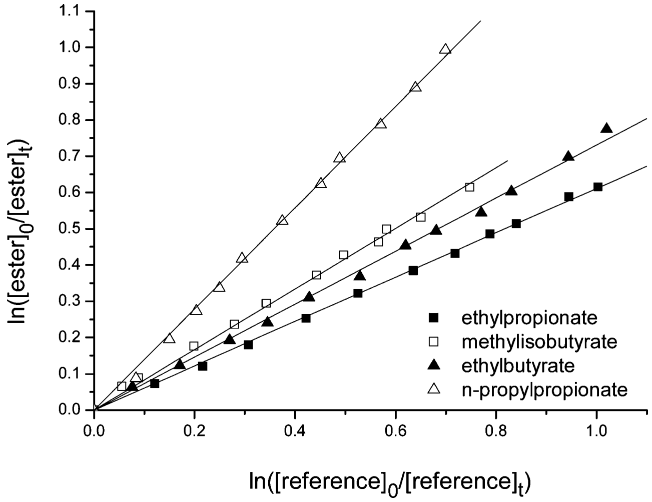

Figure 2. Relative rate data for the Cl reactions with the investigated esters.

coefficients do not take into account potential systematic errors in the reference rate constants, which could be as high as 15−20%. Table 2 shows experimental conditions, reference compounds, and k_i/k_{Ref} for each experiment.

3.1.2. Absolute Measurements. The absolute rate coefficients k_1 and k_3 were measured in the temperature range 243−372 K, whereas k_2 and k_4 were measured between 253 and 372 K. All experiments were carried out in 100−104 Torr (of helium) under pseudofirst-order conditions in which the concentration of the esters was at least 70 times larger than that of the OH radicals. The OH decays were found to be exponential over at least three lifetimes while k'_0 and k' were in the ranges 88−422 s^{-1} and 161−3954 s^{-1}, respectively. The variation of the photolysis fluence by a factor of ≈10 (2.3−27 mJ cm^{-2}) had no effect on the determined rate coefficients indicating that there was no noticeable contribution of photofragments to the OH consumption. The ester samples were purified to better than 99%, and hence loss of OH radicals by reaction with impurities is expected to be insignificant.

Figure 3 shows as an example a plot of $(k' - k'_0)$ as a function of methyl isobutyrate concentration at different temperatures. The experimental conditions and the values obtained for k_1−k_4 are presented in Table 3. The rate coefficients, taken as the average of all values obtained at (298 ± 2) K are

$$k_1 = (2.1 \pm 0.2) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_2 = (4.2 \pm 0.3) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_3 = (1.7 \pm 0.1) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_4 = (5.1 \pm 0.5) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

The errors quoted for k_1−k_4 are $2\sigma_{n-1}$ from the average of the independent determinations and do not include systematic errors. These values are in good agreement with those obtained by the relative method. Figure 4 shows the measured rate coefficients for the studied reactions plotted as a function of the reciprocal of temperature. Significant curvature is evident in the Arrhenius plots for k_1, k_3, and k_4 in the range 243−273 K. Hence, the Arrhenius parameters for k_1, k_3, and k_4 were derived from a limited temperature range below 298 K. Two expressions are given for k_2, respectively, in the temperature ranges 253−298 K and 253−372 K. The least-squares analysis of the ln k_i versus $1/T$ plots lead to the following expressions of k_i (in units of cm^3 $molecule^{-1}$ s^{-1}) below 298 K

$$k_1 = (0.59 \pm 0.21) \times 10^{-13} \exp[(1064 \pm 98)/T] \quad \text{in the range } T = 243-298\ \text{K}$$

$$k_2 = (12.5 \pm 4.9) \times 10^{-13} \exp[(358 \pm 110)/T] \quad \text{in the range } T = 253-298\ \text{K}$$

$$k_3 = (2.82 \pm 0.68) \times 10^{-13} \exp[(541 \pm 65)/T] \quad \text{in the range } T = 243-298\ \text{K}$$

$$k_4 = (4.0 \pm 1.9) \times 10^{-13} \exp[(761 \pm 131)/T] \quad \text{in the range } T = 253-298\ \text{K}$$

Uncertainties are $2A\sigma_{\ln A}$ and $2\sigma_{E/R}$ for A and E/R, respectively. No significant curvature was observed for ln k_2 versus $1/T$ plot

TABLE 2: Rate Coefficient Ratios, k_i/k_{Ref}, and the Obtained Second-Order Rate Coefficients for the Reactions of Cl with the Studied Esters at (296 ± 2) K and 760 Torr of Air

ester	$[ester]_0$ (ppm)	reference	$[ref]_0$ (ppm)	$[Cl_2]_0$ (ppm)	number of runs	k_{ester}/k_{Ref}	$k_{ester}/10^{-11}$ (cm^3 $molecule^{-1}$ s^{-1})[a]
ethyl propionate	62	methanol	69	61	2	0.68 ± 0.02	3.74 ± 0.11
	42		101	82		0.65 ± 0.02	3.58 ± 0.11
	48	ethane	79	69	2	0.63 ± 0.02	3.71 ± 0.11
	31		79	63		0.62 ± 0.01	3.66 ± 0.05
						Average	**3.7 ± 0.1**[b]
n-propyl propionate	41	ethane	80	52	2	1.39 ± 0.05	8.20 ± 0.30
	43		75	54		1.40 ± 0.02	8.26 ± 0.12
	36	propane	68	48	2	0.61 ± 0.01	8.50 ± 0.18
	34		87	57		0.57 ± 0.02	7.98 ± 0.28
						Average	**8.2 ± 0.4**[b]
methyl isobutyrate	20	methanol	98	46	2	0.75 ± 0.04	4.13 ± 0.22
	23		119	51		0.81 ± 0.02	4.46 ± 0.11
	21	ethane	40	46	2	0.70 ± 0.04	4.13 ± 0.24
	21		40	54		0.67 ± 0.01	3.95 ± 0.06
						Average	**4.2 ± 0.4**[b]
ethyl butyrate	16	methanol	75	53	1	2.03 ± 0.08	11.17 ± 0.44
	30	propane	59	51	2	0.72 ± 0.02	10.08 ± 0.28
	35		70	54		0.74 ± 0.01	10.36 ± 0.14
	41	ethane	80	52	1	1.60 ± 0.07	9.44 ± 0.41
						Average	**10 ± 1**[b]

[a] The errors quoted for the k_{ester}/k_{Ref} values are twice the standard deviation arising from the least-squares fit of the straight lines and do not include the corresponding statistical error in the reference rate constant. The errors quoted for k_i in the individual experiments are calculated multiplying the errors quoted for k_{ester}/k_{Ref} by k_{Ref}. [b] Errors quoted as $2\sigma_{n-1}$ from the average of the four runs.

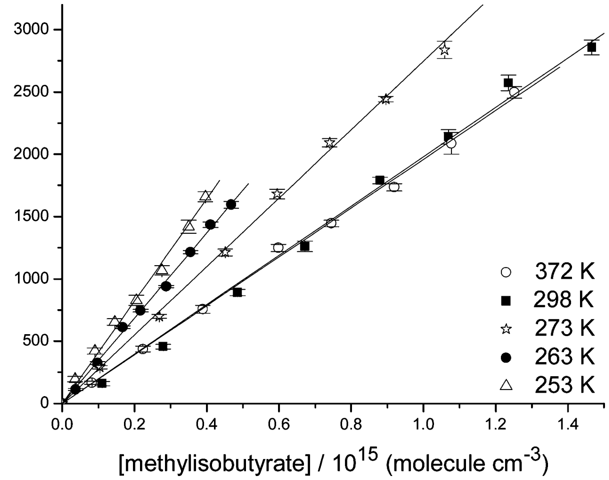

Figure 3. Absolute rate data for the OH reaction with methyl isobutyrate at different temperatures.

in the range 253−372 K; however, a fit of the simple Arrhenius and modified Arrhenius expressions to the data gives $k_2 = (15.4 \pm 2.8) \times 10^{-13} \exp[(299 \pm 52)/T]$ and $k_2 = 2.15 \times 10^{-18}T^2 \exp(916/T)$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

3.1.3. Discussion. Table 4 presents the OH reaction rate coefficients and the Arrhenius parameters for the four esters obtained in this work and those reported earlier in the literature. The reaction of OH with ethyl propionate has been investigated earlier by Campbell and Parkinson[8] and Wallington et al.[9] using, respectively, a relative rate method and flash photolysis−resonance fluorescence technique. While the measurements reported by Wallington et al.[9] and those obtained in this work are in excellent agreement, the value of k_1 reported by Campbell and Parkinson[8] is approximately 30% lower. The rate coefficient values for OH reaction with organics determined by Campbell and Parkinson[8] are suspect due to questions concerning the validity of the experimental technique they used. Hence, it seems likely that this latter measurement was subject to substantial systematic error. The value of k_2 obtained in this work is in very good agreement with the only study reported so far on the reaction of OH with propyl propionate from Wallington et al.[9] Very good agreement is also observed between this work and that of Wyatt et al.[11] for the reaction of OH with methyl isobutyrate. Wyatt et al.[11] used a relative rate method and three references (2-butanone, 2,2,4-trimethyl pentane, and 3-pentanone) to derive the k_3 value at (297 ± 3) K and atmospheric pressure of air. For k_4, the value reported by Ferrari et al.[10] using a relative rate method is ≈25% lower than the ones obtained by Wallington et al.[9] and this work.

The measurements of Wallington et al.[9] obtained at total pressures of 25−50 Torr of Ar and those from this work conducted in 100−760 Torr (of helium and air, respectively) indicate the absence of any pressure dependence of the rate coefficients of the reactions investigated in this work above 25 Torr.

To our best knowledge, the temperature-dependence parameters for the four reactions investigated here have not been reported prior to this work. As shown in Figure 4, where the rate coefficients are plotted in the Arrhenius form, the three plots of k_1, k_3, and k_4 versus $1/T$ show a significant curvature in the temperature range investigated (243−372 K). Besides, all plots exhibit a negative temperature dependence below 298 K. Such a negative dependence has been also observed for the reaction of OH radicals with other esters.[9,16−19] This temperature dependence behavior has been reported for the OH reaction with other oxygenated organic compounds which has been, at least, partly attributed to the occurrence of an alternative channel in parallel to the direct H-atom abstraction.

This work provides the first kinetic studies for the reactions of Cl with ethyl propionate, propyl propionate, methyl isobutyrate, and ethyl butyrate. An examination of the reactivity of the studied esters toward Cl atoms shows that *n*-propyl propionate ($CH_3CH_2C(O)OCH_2CH_2CH_3$) is two times more reactive than ethyl propionate ($CH_3CH_2C(O)OCH_2CH_3$), $k = 8.2 \times 10^{-11}$ and 3.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. Both have higher reactivity with Cl compared to that of methyl propionate ($CH_3CH_2C(O)OCH_3$), $k = 1.51 \times 10^{-11}$ cm^3 mol-

TABLE 3: Summary of Experimental Conditions and the Measured OH Reaction Rate Coefficients with Ethyl Propionate, *n*-Propyl Propionate, Methyl Isobutyrate, and Ethyl Butyrate, in the Temperature Range 243−372 K

T (K)	[ethyl propionate][a]	k_1[b]	[propyl propionate][a]	k_2[b]	[methyl isobutyrate][a]	k_3[b]	[ethyl butyrate][a]	k_4[b]
243	0.33−3.23	4.69 ± 0.24			0.59−6.22	2.64 ± 0.10		
253	0.35−4.74	4.11 ± 0.20	0.24−2.47	5.19 ± 0.16	0.57−5.86	2.35 ± 0.08	0.25−2.47	7.90 ± 0.26
263	0.61−9.70	3.40 ± 0.12	0.25−2.56	5.04 ± 0.22	0.64−6.54	2.16 ± 0.06	0.25−2.85	7.57 ± 0.28
263	0.37−4.68	3.43 ± 0.12	0.23−2.39	4.77 ± 0.22	0.57−5.73	2.23 ± 0.10	0.26−2.79	6.98 ± 0.18
273	1.04−12.17	2.75 ± 0.08	0.23−2.31	4.45 ± 0.18	0.51−5.40	2.09 ± 0.04	0.23−2.66	6.39 ± 0.08
298	1.47−12.50	2.14 ± 0.12	0.21−2.21	3.93 ± 0.12	1.09−18.13	1.67 ± 0.10	0.54−7.70	4.86 ± 0.18
298	1.17−14.30	2.21 ± 0.06	0.22−2.11	4.28 ± 0.17	1.04−18.09	1.73 ± 0.06	0.45−6.39	5.33 ± 0.16
298	1.11−16.20	2.03 ± 0.08	0.22−2.23	4.23 ± 0.11	1.66−17.92	1.79 ± 0.06	0.21−2.48	5.11 ± 0.11
323			0.21−2.13	3.69 ± 0.08	0.98−16.24	1.60 ± 0.08	0.51−6.99	4.71 ± 0.26
324	1.07−14.20	2.14 ± 0.10						
348	0.89−13.00	2.09 ± 0.12	0.19−1.94	3.66 ± 0.20	0.95−15.07	1.68 ± 0.06	0.47−6.51	4.60 ± 0.22
372	0.82−12.52	1.95 ± 0.06	0.18−1.87	3.55 ± 0.17	1.28−14.09	1.76 ± 0.04	0.40−5.03	4.68 ± 012
372	0.72−12.87	1.97 ± 0.08	0.18−1.77	3.53 ± 0.22	1.66−14.49	1.74 ± 0.04	0.46−6.07	4.52 ± 0.18

[a] ($/10^{14}$) molecules cm^{-3}. [b] ($/10^{-12}$) cm^3 molecule^{-1} s^{-1}. The uncertainties given for k_i are 2σ precision from the fit to the data and do not include systematic errors.

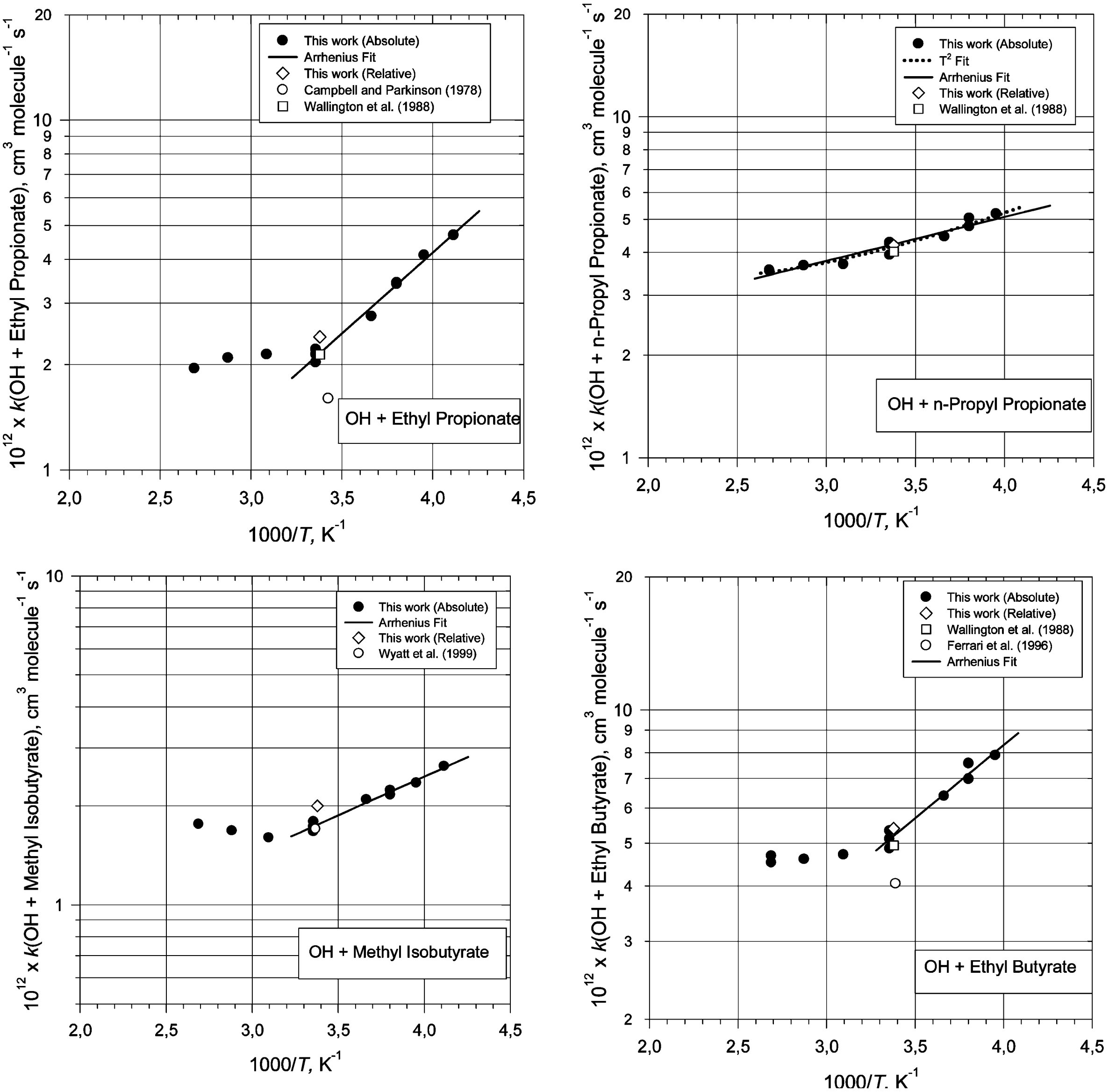

Figure 4. OH + Esters: plot of k_i (i = 1−4) as function of 1/T obtained in this work. The available literature data are also shown (see text).

ecule^{-1} s^{-1},[20] indicating that the increase of the reactivity is basically due the additional contribution of the −OR group of the ester. Interestingly, the reactivity of ethyl butyrate ($CH_3CH_2CH_2C(O)OCH_2CH_3$) measured in this work is essentially the same as that of ($CH_3CH_2C(O)OCH_2CH_2CH_3$), k = 10 × 10^{-11} and 8.2 × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively. Both are higher than that of ethyl propionate ($CH_3CH_2C(O)OCH_2CH_3$) which implies, for this specific example, that the

TABLE 4: Rate Coefficients of the Reactions of OH with Ethyl Propionate, Propyl Propionate, Methyl Isobutyrate, and Ethyl Butyrate from This Work and the Literature

ester	T_{room} (K)	k_{Troom} (10^{-12} cm^3 molecule^{-1} s^{-1})	T range (K)	A (10^{-13} cm^3 molecule^{-1} s^{-1})	E/R (K^{-1})	method[c]	reference
ethyl propionate ($CH_3CH_2C(O)OCH_2CH_3$)	298	2.1 ± 0.2	243−298[a]	0.59 ± 0.21	−(1064 ± 98)	PLP−LIF	this work
	296 ± 2	2.4 ± 0.1	−	−	−	RR	this work
	292	1.60 ± 0.34	−	−	−	RR[d]	8
	296	2.14 ± 0.30	−	−	−	FP−RF	9
propyl propionate ($CH_3CH_2C(O)OCH_2CH_2CH_3$)	298	4.2 ± 0.3	253−372	15.4 ± 2.8	−(299 ± 52)	PLP−LIF	this work
			253−298	12.5 ± 4.9	−(358 ± 110)	PLP−LIF	this work
	296 ± 2	4.4 ± 0.2	−	−	−	RR	this work
	296	4.02 ± 0.32	−	−	−	FP−RF	9
methyl isobutyrate ($(CH_3)_2CHC(O)OCH_3$)	298	1.7 ± 0.1	243−298[a]	2.82 ± 0.68	−(541 ± 65)	PLP−LIF	this work
	296 ± 2	2.0 ± 0.1	−	−	−	RR	this work
	297 ± 3	1.7 ± 0.4	−	−	−	RR[e]	11
ethyl butyrate ($CH_3CH_2CH_2C(O)OCH_2CH_3$)	298	5.1 ± 0.5	253−298[b]	4.0 ± 1.9	(−761 ± 131)	PLP−LIF	this work
	296 ± 2	5.7 ± 0.2	−	−	−	RR	this work
	296	4.94 ± 0.38	−	−	−	FP−RF	9
	295 ± 2	4.05 ± 0.38	−	−	−	RR[f]	10

[a] Experiments conducted in the range 243−372 K (see text). [b] Experiments conducted in the range 253−372 K (see text). [c] PLP−LIF: Pulsed Laser Photolysis−Laser Induced Fluorescence; RR: Relative rate; FP−RF: Flash Photolysis−Resonance Fluorescence. [d] Placed on an absolute basis using k(n-butane) = 2.36 × 10^{-12} cm^3 molecule^{-1} s^{-1}. [e] Placed on an absolute basis using k(2-butanone) = 1.15 × 10^{-12}, k(2,2,4-trimethyl pentane) = 3.59 × 10^{-12}, and k(3-pentanone) = 2.0 × 10^{-12} cm^3 molecule^{-1} s^{-1}. [f] Placed on an absolute basis using k(n-octane) = 7.81 × 10^{-12} cm^3 molecule^{-1} s^{-1}.

TABLE 5: Estimated Atmospheric Lifetimes of the Studied Esters with Cl Atoms and OH and NO_3 Radicals

ester	k_{OH} ($/10^{-12}$)[a]	τ_{OH}[b] (days)	k_{Cl}($/10^{-12}$)[a]	τ_{Cl}[c] (days)	k_{NO3}($/10^{-17}$)[a]	τ_{NO3}[d] (years)
ethyl propionate	(2.1 ± 0.2)[e]	5.5	(37 ± 1)[e]	312	(3.3 ± 0.4)[f]	3.8
methyl isobutyrate	(1.7 ± 0.1)[e]	6.8	(42 ± 4)[e]	276	---	---
ethyl butyrate	(5.1 ± 0.5)[e]	2.3	(100 ± 10)[e]	116	---	---
n-propyl propionate	(4.2 ± 0.3)[e]	2.8	(82 ± 4)[e]	141	---	---

[a] All the k values are at 298 K and in units of cm^3 molecule^{-1} s^{-1}. [b] [OH] = 2 × 10^6 radicals cm^{-3} (ref 22). [c] [Cl] = 1 × 10^3 atoms cm^{-3} (ref 24). [d] [NO_3] = 5 × 10^8 radicals cm^{-3} (ref 23). [e] This work. [f] Ref 12.

addition of the $-CH_2-$ group to one side (R′ or −OR) of the ester molecule (R′C(O)OR) would impact the reactivity with Cl atoms in the same manner. However, while this remark can be made for $CH_3CH_2C(O)OCH_3$ and $CH_3C(O)OCH_2CH_3$, it cannot be applied to $CH_3CH_2CH_2C(O)OCH_2CH_3$ and $CH_3CH_2CH_2CH_2C(O)OCH_3$. While $CH_3CH_2C(O)OCH_3$ and $CH_3C(O)OCH_2CH_3$ have essentially the same reactivity (k = 1.51 × 10^{-11} and 1.76 × 10^{-11} cm^3 molecule^{-1} s^{-1}, respectively) and higher than that of $CH_3C(O)OCH_3$ (k = 0.22 × 10^{-11} cm^3 molecule^{-1} s^{-1}[21]), the reactivity of $CH_3CH_2CH_2CH_2C(O)OCH_3$ (k = 17 × 10^{-11})[20] seems to be higher than that of $CH_3CH_2CH_2C(O)OCH_2CH_3$ (k = 10 × 10^{-11}) and $CH_3CH_2C(O)OCH_2CH_2CH_3$ (k = 8.2 × 10^{-11}). The latter two, measured in this work, show approximately the same reactivity. This might be due to the effect of the RC(O)O− and ROC(O)− groups on the reactivity of chlorine atoms with esters.

The only mechanistic study reported so far on the oxidation of the title esters is that of Wyatt et al.[11] who have investigated the oxidation mechanism of the OH reaction with methyl isobutyrate in the presence of NO_x at atmospheric pressure. These authors have reported the formation of acetone and methyl pyruvate ($CH_3C(O)C(O)OCH_3$) in molar yields of 97 ± 1% and 3.3 ± 0.3%, respectively, from the OH radical initiated oxidation in one atmosphere of air in the presence of NO_x. The observation of acetone in a molar yield close to unity indicates that the majority of the reaction of OH with methyl isobutyrate proceeds via attack at the tertiary C−H bond leading to an alkoxy radical which decomposes via C−C bond scission to give acetone

$$(CH_3)_2CHC(O)OCH_3 + OH \rightarrow (CH_3)_2CC(O)OCH_3 + H_2O$$

$$(CH_3)_2CC(O)OCH_3 + O_2 + M \rightarrow (CH_3)_2C(OO)C(O)OCH_3 + M$$

$$(CH_3)_2C(OO)C(O)OCH_3 + NO \rightarrow (CH_3)_2C(O)C(O)OCH_3 + NO_2$$

$$(CH_3)_2C(O)C(O)OCH_3 \rightarrow CH_3C(O)CH_3 + CH_3OC(O)$$

3.3. Atmospheric Implications. In addition to reaction with OH, the esters could be removed from the atmosphere by reaction with O_3, NO_3, and Cl atoms. Considering the gas-phase loss processes, the lifetimes toward reaction with OH, Cl atoms, and NO_3 have been calculated for the four esters (when the rate constants were available) using an OH radical concentration (12 h daytime average) of 2 × 10^6 radicals cm^{-3},[22] a 12 h night time average of [NO_3] = 5 × 10^8 radicals cm^{-3},[23] and a 24 h average Cl concentration of 1 × 10^3 atoms cm^{-3}.[24] The lifetimes calculated using the relationship $\tau_x = 1/k_x[\mathrm{X}]$ with X = OH, Cl, and NO_3 are in the range of 2−7 days with respect to the reaction with OH radicals and 11−31 days with respect to the reactions with Cl atoms. Tropospheric degradation via reactions with the NO_3 radical seems to be negligible since the reactions with NO_3 with saturated esters are slow processes. Taking into account the UV spectra of unsaturated esters reported by Teruel et al.,[25] and that their chemical structure is similar to this series of compounds, we can assume that the esters studied in this work are photolytically stable in the actinic region of the solar spectrum, indicating that the tropospheric removal by photolysis can be considered negligible. The studied esters are expected to be sparingly soluble in water (e.g., Henry's law coefficients for methyl alkanoates are less than 10 M atm^{-1} at 298 K[26]). In addition, these compounds are highly volatile so, both, wet and dry deposition can be estimated of minor importance.

The estimated lifetimes indicate that the studied esters are likely to be rapidly removed in the gas phase, that the main process for the tropospheric degradation is reaction with OH radicals, Cl reactions being non-negligible, and that these compounds will be degraded near their emission sources. The OH and Cl concentrations vary substantially depending on the environment, location, and season. Cl atom reaction may be more significant in those areas with higher concentration of this atom. In fact, peak concentrations as high as 1×10^5 atoms cm^{-3}[27−29] are expected in the marine boundary layer at dawn and much earlier than OH where [OH] is 5×10^5 radicals cm^{-3}.

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