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Kinetic Studies on the Reactions of Hydroxyl Radicals with a Series of Alkoxy Esters

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Rate coefficients for the gas-phase reactions of hydroxyl radicals with a series of alkoxy esters of structure $RC(O)O(CH_2)_nOR'$, where R = H, CH_3, R′ = CH_3, C_2H_5, and n = 1−2, have been determined with use of relative and absolute rate methods. Relative rate measurements were performed in a Teflon reaction chamber at 298 ± 2 K and atmospheric pressure. Absolute rate measurements were made with pulsed laser photolysis−laser induced fluorescence over the temperature range 263−372 K at pressures of ∼100 Torr. The kinetic data are used to derive Arrhenius expressions for the reactions and tropospheric lifetimes for the alkoxy esters. The reactivity of the alkoxy esters is discussed in light of the current understanding of the atmospheric chemistry of oxygenated organic compounds.

Introduction

Multifunctional oxygenated organic compounds, such as alkoxy esters, are increasingly being employed as water-soluble solvents and fuel additives. Ethoxyethyl acetate, $CH_3C(O)OCH_2CH_2OC_2H_5$, for example, is used in paints and cleaning solutions.[1] The use of these volatile organic compounds (VOCs) can lead to significant emissions into the atmosphere where they are likely to contribute to the formation of ozone and other secondary pollutants. Another source of alkoxy esters in the atmosphere is the tropospheric degradation of diethers which are also employed as solvents and have considerable potential for use as fuel additives.[2−4] To fully assess the environmental impact of alkoxy esters, a detailed understanding of the kinetics and mechanisms for their atmospheric oxidation is required.

Gas-phase reaction with hydroxyl (OH) radicals is the principal, if not dominant, atmospheric fate of the vast majority of saturated oxygenated VOCs. As a result there have been many kinetic studies of the reactions of hydroxyl radicals with monofunctional oxygenated compounds such as ethers, alcohols, ketones, and esters.[4] In contrast only a limited number of studies have been performed on the reactions of multifunctional oxygenated compounds such as alkoxy esters.[1,4−7] The aim of this work was to investigate the kinetics of the reactions of hydroxyl radicals with a series of alkoxy esters of structure $RC(O)O(CH_2)_nOR'$, where R = H, CH_3, R′ = CH_3, C_2H_5, and n = 1, 2. The names and formulas of the alkoxy esters are shown in Figure 1. Rate coefficients have been determined at room temperature, using a conventional relative rate technique, and over the temperature range 263−372 K, using the absolute rate technique of pulsed laser photolysis−laser induced fluorescence (PLP-LIF). The kinetic data are used to derive Arrhenius expressions for the reactions and compared to the values obtained for other oxygenated hydrocarbons. The atmospheric implications of the results are also discussed.

Experimental Section

Relative rate studies were conducted in a Teflon reaction chamber at University College Dublin. Absolute rate measurements were made with use of the PLP-LIF technique at LCSR-CNRS Orléans. Both experimental systems have been described in previous papers from these laboratories[8,9] and are only briefly outlined here.

Relative Rate Measurements. Reactions were carried out at 298 ± 2 K and atmospheric pressure in a collapsible 50 L FEP (fluorine−ethene−propene) Teflon reaction chamber. The chamber was surrounded by 10 Philips TUV 15 W germicidal lamps which provided a source of irradiation at 254 nm for OH radical generation from the photolysis of O_3 in the presence of water vapor. The substrate and reference compounds were introduced into the reactor by flushing measured amounts from calibrated Pyrex bulbs with a stream of high-purity synthetic air (Air Products). The reactor was then filled to around 80% capacity with synthetic air and the remaining volume filled with synthetic air containing 1−5% v/v ozone, produced by passing synthetic air through an ozone generator. Water (triply distilled, 0.5 mL) was injected directly into the chamber. The initial concentrations of ozone and water vapor were 50−100 and 1000−10000 ppm, respectively (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 1 atm of pressure). The initial concentrations of substrate and reference compounds were in the range 15−95 ppm.

The reactions were initiated by switching on the lamps to photolyze ozone. The gas mixtures were sampled at several stages during the reactions and analyzed by using gas chromatography with flame ionization detection (Shimadzu 8A). Chromatographic separation was achieved by using a 15 m

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$HC(O)OCH_2OCH_3$ Methoxymethyl formate	$CH_3C(O)OCH_2OCH_3$ Methoxymethyl acetate	$HC(O)OCH_2OC_2H_5$ Ethoxymethyl formate	$CH_3C(O)OCH_2OC_2H_5$ Ethoxymethyl acetate
$HC(O)OCH_2CH_2OCH_3$ Methoxyethyl formate	$CH_3C(O)OCH_2CH_2OCH_3$ Methoxyethyl acetate	$HC(O)OCH_2CH_2OC_2H_5$ Ethoxyethyl formate	$CH_3C(O)OCH_2CH_2OC_2H_5$ Ethoxyethyl acetate

Figure 1. Names and formulas of the alkoxy esters studied in this work.

wide-bore (0.53 mm i.d.) capillary column packed with carbowax and operated over the temperature range 50−70 °C, using nitrogen as the carrier gas. The relative change in concentration of substrate and reference compounds was derived from integration of the chromatogram peaks.

Absolute Rate Measurements. Reactions were carried out in a temperature-controlled Pyrex reaction cell using the PLP-LIF technique. Hydroxyl radicals were generated by photolysis of H_2O_2 at 248 nm with use of a KrF excimer laser. The concentration of OH radicals was measured with pulsed laser induced fluorescence, using a Nd:YAG pumped frequency doubled dye laser triggered at a variable delay time after the photolysis pulse. The photolysis and probe pulses travel through the center of the cell perpendicular to the gas flow. The transmitted fluorescence of the OH radicals was monitored by photomultiplier, integrated by a gated charge integrator, and transferred to a computer for signal averaging and analysis. The signals from 100 probe laser shots were averaged to obtain one data (concentration, time) point. An OH concentration versus time profile was obtained by averaging signals for delay times from about 10 μs to 30 ms, using a delay time generator. Typically 8 to 15 delays were sampled to map out OH concentration−time profiles over at least three lifetimes. Alkoxy esters were premixed with helium in a 10 L glass bulb and flowed through the cell along with the OH radical photolytic precursor (H_2O_2), and the bath gas (helium). The concentrations of the reactants 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.

Materials. Helium (UHP certified to >99.995%, Alphagas) was used without purification. The H_2O_2 solution (70 wt % in water) obtained from Interox Chemie was concentrated by bubbling helium through it for several days prior to use and constantly during the PLP-LIF experiments. Nitrogen (Zero-grade 99.95%) and Synthetic Air (Zero-grade, 21% mol oxygen, balance nitrogen, 99.95%) were from Air Products. *n*-Propanol (>99%), *n*-butanol (>99%), methoxyethyl acetate (>99%), and ethoxyethyl acetate (99%) were from Aldrich. The other alkoxy esters were synthesized in Dublin. Methoxymethyl formate and ethoxymethyl formate were synthesized by the reaction of the corresponding chloroethers, $ClCH_2OCH_3$ and $ClCH_2OC_2H_5$, respectively, with sodium formate at 50 °C. Methoxymethyl acetate and ethoxymethyl acetate were prepared by the reaction of $ClCH_2OCH_3$ and $ClCH_2OC_2H_5$, respectively, with sodium acetate at 50 °C. The alkoxy formates $HC(O)OCH_2CH_2OCH_3$ and $HC(O)OCH_2CH_2OC_2H_5$ were synthesized by the reaction of formic acid with the corresponding glycol ethers, $HOCH_2CH_2OCH_3$ and $HOCH_2CH_2OC_2H_5$, in a molar ratio of 4:1 at 140 °C for 3−4 h. In all cases the resulting products were separated by fractional distillation and the purity determined to be >99% as indicated by NMR and IR spectroscopy.

Results

Relative Rate Measurements. Relative rate coefficients for the reaction of OH radicals with the alkoxy esters (substrates) were determined by comparing their rates of decay to that of a reference compound whose rate coefficient with OH is accurately known:

$$\mathrm{OH} + \text{substrate} \rightarrow \text{products} \qquad k_s$$

$$\mathrm{OH} + \text{reference} \rightarrow \text{products} \qquad k_r$$

where k_s and k_r represent rate coefficients for the reaction of OH with the substrate and reference compounds, respectively. Provided that the reactant and reference compounds were consumed only by reaction with OH radicals it can be shown that

$$\ln\frac{[\text{substrate}]_0}{[\text{substrate}]_t} = \frac{k_s}{k_r}\ln\frac{[\text{reference}]_0}{[\text{reference}]_t} \qquad \text{(I)}$$

where the subscripts 0 and t indicate the beginning of the experiment and time *t*, respectively. Under the reaction conditions employed the concentrations of the substrate and reference compounds were found to decay by 20−50% during the experiments. At least three different experiments were carried out for each compound. Concentrations of substrate and reference compounds were measured as a function of time and plots in the form of eq I were used to determine k_s. The plots, shown in Figure 2, exhibit excellent linearity and have near-zero intercepts. Rate coefficients for the reaction of OH radicals with the alkoxy esters were determined with $n\text{-}C_3H_7OH$ and $n\text{-}C_4H_9OH$ as reference compounds and with $k_r(\mathrm{OH} + n\text{-}C_3H_7OH) = 5.53 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_r(\mathrm{OH} + n\text{-}C_4H_9OH) = 8.57 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, based on the evaluation of Atkinson.[10] A summary of the experimental conditions employed and the obtained slopes k_s/k_r is given in Table 1. The calculated rate coefficients, k_s, are listed in Table 3. The quoted errors are twice the standard deviation arising from the least-squares fit of the data and do not include an estimate of the error in the reference rate coefficients, k_r. The errors in k_r can add a further 30% to the uncertainty of the rate coefficients reported in these relative rate studies.[10]

Absolute Rate Measurements. All absolute rate kinetic experiments were carried out under pseudo-first-order conditions, with $[\text{substrate}]_0 > 100[\mathrm{OH}]_0$. Under these conditions the reactions of OH with primary reaction products were negligible. In the absence of perturbations due to secondary reactions, the following simple rate law holds for loss of the hydroxyl radicals:

$$[\mathrm{OH}]_t = [\mathrm{OH}]_0 \exp(-k't)$$

where $k' = k_s[\text{substrate}] + k'_0$. The rate coefficient k'_0 represents the first-order loss of OH in the absence of substrate and depends on the reaction of OH with its precursor ($k(\mathrm{OH} + H_2O_2)$) and the diffusion from the detection zone. None of the compounds investigated in this study absorb significantly at 248 nm, and hence reaction of OH radicals with photofragments of the organic compounds did not contribute to OH loss. All compounds studied were purified to better than 99% thus minimizing the possible reaction of OH with impurities. Plots of $(k' - k'_0)$ versus substrate concentration were obtained for each of the compounds at a number of reaction temperatures in the range

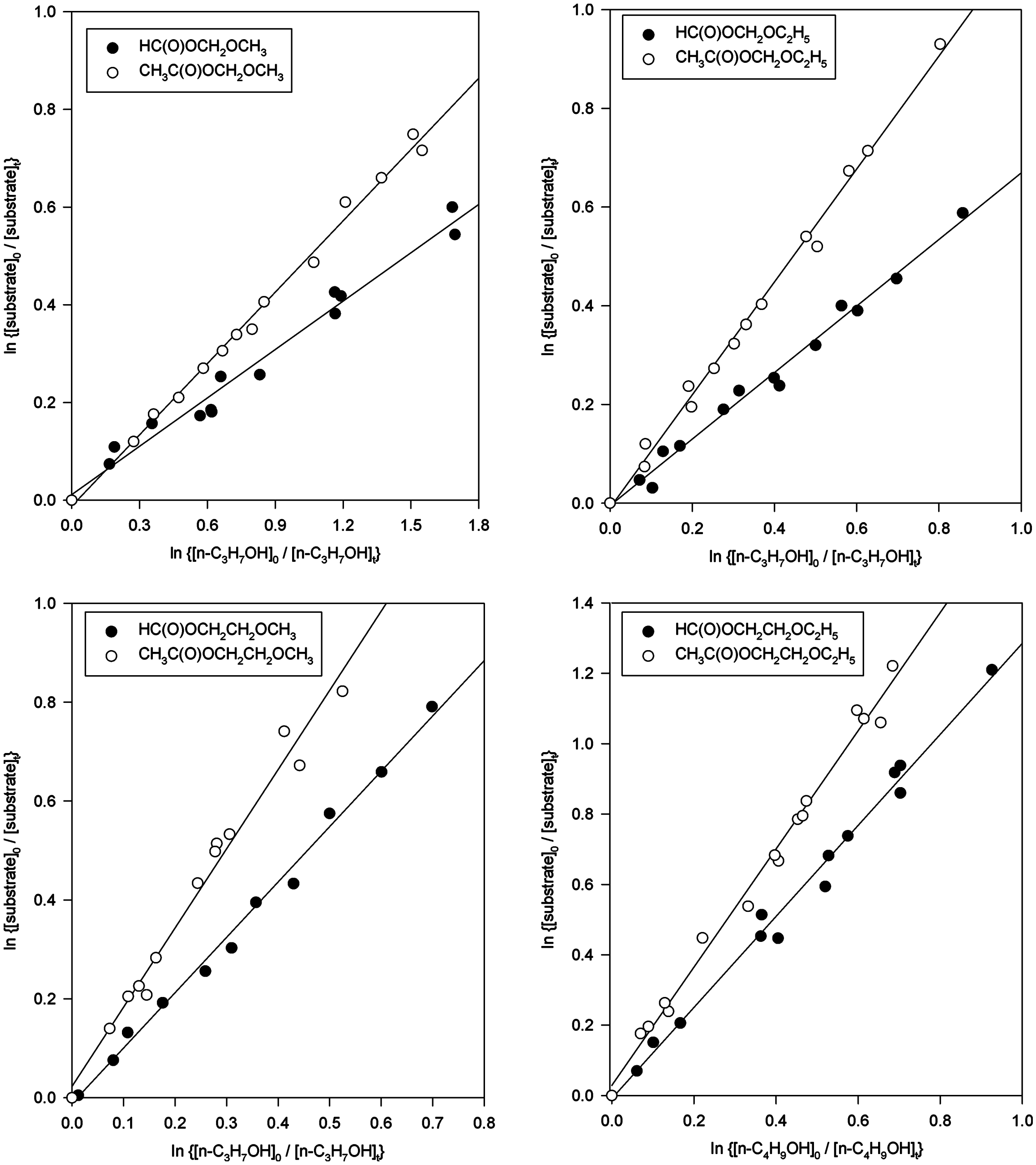

Figure 2. Relative rate plots for the reaction of OH radicals with alkoxy esters at 298 ± 2 K.

TABLE 1: Experimental Conditions Employed in the Relative Rate Study with the Measured Rate Coefficient Ratios (k_s/k_r)

substrate	substrate concn (ppm)	reference	reference concn (ppm)	k_s/k_r[a]
$HC(O)OCH_2OCH_3$	30−70	n-C_3H_7OH	30−70	0.33 ± 0.03
$CH_3C(O)OCH_2OCH_3$	40−65	n-C_3H_7OH	30−75	0.51 ± 0.03
$HC(O)OCH_2OC_2H_5$	45−70	n-C_3H_7OH	45−70	0.67 ± 0.04
$CH_3C(O)OCH_2OC_2H_5$	20−45	n-C_3H_7OH	20−45	1.14 ± 0.05
$HC(O)OCH_2CH_2OCH_3$	55−95	n-C_3H_7OH	55−95	1.12 ± 0.06
$CH_3C(O)OCH_2CH_2OCH_3$	25−40	n-C_3H_7OH	30−55	1.60 ± 0.14
$HC(O)OCH_2CH_2OC_2H_5$	45−60	n-C_4H_9OH	40−60	1.29 ± 0.08
$CH_3C(O)OCH_2CH_2OC_2H_5$	15−25	n-C_4H_9OH	15−40	1.68 ± 0.07

[a] Errors are twice the standard deviation and represent precision only.

263−372 K. All plots exhibited excellent linearity. Rate coefficient values for the reaction of OH with substrate were calculated from least-squares fits of the data and found to be independent of changes in pressure, flow rate, and photolysis fluence. The rate coefficients obtained at the different reaction temperatures are listed in Table 2 along with the experimental conditions employed. Rate coefficients for each of the alkoxy esters are plotted in Arrhenius form in Figure 3, with the preexponential factors (*A*) and activation energies (*E*) reported in Table 2.

Discussion

Comparison with Previous Studies. The measured rate coefficients for the reaction of OH radicals with alkoxy esters

TABLE 2: Experimental Conditions Employed in the Absolute Rate Measurements with the Measured Rate Coefficients (*k*) and Associated Arrhenius Parameters

alkoxy ester	T^a	[substrate]^b	k^c	A^d	$(E/R)^e$
$HC(O)OCH_2OCH_3$	263	0.9−8.2	1.82 ± 0.07	1.4 ± 0.4	−(56 ± 97)
	273	0.7−7.9	1.77 ± 0.08		
	298	0.7−7.3	1.62 ± 0.10		
	323	0.7−6.7	1.61 ± 0.10		
	348	0.6−6.2	1.67 ± 0.13		
	372	0.5−5.8	1.73 ± 0.10		
$CH_3C(O)OCH_2OCH_3$	263	0.6−6.3	3.08 ± 0.07	1.8 ± 0.4	−(134 ± 75)
	273	0.7−6.1	3.06 ± 0.06		
	298	0.6−5.5	2.70 ± 0.07		
	323	0.4−5.0	2.77 ± 0.10		
	348	0.4−4.8	2.78 ± 0.08		
	372	0.4−4.4	2.61 ± 0.10		
$HC(O)OCH_2OC_2H_5$	263	0.7−6.7	5.51 ± 0.16	1.6 ± 0.3	−(317 ± 64)
	273	0.6−6.4	5.09 ± 0.20		
	298	0.6−6.0	4.54 ± 0.19		
	323	0.6−5.5	4.14 ± 0.21		
	348	0.5−5.2	3.94 ± 0.19		
	372	0.5−4.9	3.90 ± 0.21		
$CH_3C(O)OCH_2OC_2H_5$	263	0.5−5.4	7.79 ± 0.28	1.9 ± 0.8	−(380 ± 144)
	273	0.5−5.2	8.40 ± 0.37		
	298	0.5−4.8	6.39 ± 0.43		
	323	0.3−4.4	5.79 ± 0.22		
	348	0.3−4.1	5.61 ± 0.16		
	372	0.3−3.9	5.53 ± 0.30		
$HC(O)OCH_2CH_2OCH_3$	273	0.6−6.8	7.49 ± 0.47	2.2 ± 1.0	−(324 ± 142)
	298	0.5−6.2	6.60 ± 0.14		
	323	0.5−5.8	5.75 ± 0.23		
	368	0.5−5.1	5.57 ± 0.24		
$CH_3C(O)OCH_2CH_2OCH_3$	273	0.2−3.3	8.95 ± 0.78	2.9 ± 1.5	−(309 ± 162)
	298	0.3−3.0	7.83 ± 0.31		
	333	0.2−2.6	7.79 ± 0.29		
	372	0.2−2.4	6.38 ± 0.30		
$HC(O)OCH_2CH_2OC_2H_5$	263	0.2−2.6	14.30 ± 0.54	2.9 ± 1.2	−(405 ± 132)
	273	0.2−2.5	12.07 ± 0.70		
	298	0.2−2.3	11.38 ± 0.45		
	333	0.2−2.0	9.28 ± 0.38		
	368	0.2−1.8	9.09 ± 0.27		
$CH_3C(O)OCH_2CH_2OC_2H_5$	273	0.1−1.8	15.53 ± 0.68	1.4 ± 0.6	−(642 ± 148)
	298	0.3−1.7	12.10 ± 0.29		
	333	0.1−1.5	9.37 ± 0.61		
	368	0.1−1.4	8.55 ± 0.43		

[a] In units of K. [b] In units of 10^{14} molecule cm^{-3}. [c] In units of 10^{-12} cm^3 molecule^{-1} s^{-1}, errors are twice the standard deviation and represent precision only. [d] In units of 10^{-12} cm^3 molecule^{-1} s^{-1}, $\Delta A = 2A\sigma \ln A$. [e] In units of K, $\Delta E/R = 2\sigma_{E/R}$.

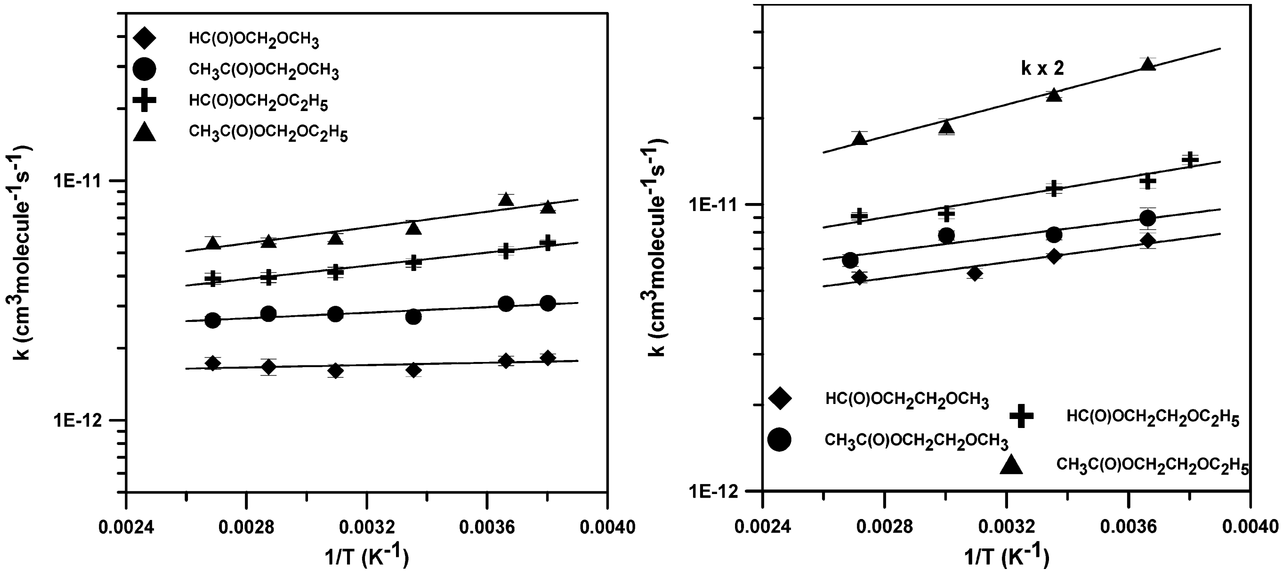

Figure 3. Arrhenius plots of kinetic data obtained for the reaction of OH radicals with alkoxy esters, using the absolute rate method.

at 298 ± 2 K obtained in this work are summarized in Table 3. In general, there is very good agreement between the rate coefficients determined with both absolute and relative rate techniques. Although there is a small discrepancy between the

TABLE 3: Rate Coefficients for the Reaction of OH Radicals with Alkoxy Esters at 298 ± 2 K

alkoxy ester	k^a	technique^b	ref
$HC(O)OCH_2OCH_3$	1.82 ± 0.17	RR	this work
	1.62 ± 0.10	PLP-LIF	this work
$CH_3C(O)OCH_2OCH_3$	2.82 ± 0.17	RR	this work
	2.70 ± 0.07	PLP-LIF	this work
$HC(O)OCH_2OC_2H_5$	3.71 ± 0.22	RR	this work
	4.54 ± 0.19	PLP-LIF	this work
$CH_3C(O)OCH_2OC_2H_5$	6.30 ± 0.28	RR	this work
	6.39 ± 0.43	PLP-LIF	this work
$HC(O)OCH_2CH_2OCH_3$	6.19 ± 0.33	RR	this work
	6.60 ± 0.14	PLP-LIF	this work
$CH_3C(O)OCH_2CH_2OCH_3$	8.85 ± 0.77	RR	this work
	7.83 ± 0.31	PLP-LIF	this work
$HC(O)OCH_2CH_2OC_2H_5$	11.06 ± 0.70	RR	this work
	11.38 ± 0.45	PLP-LIF	this work
$CH_3C(O)OCH_2CH_2OC_2H_5$	14.40 ± 0.66	RR	this work
	12.10 ± 0.29	PLP-LIF	this work
	13 ± 2	PLP-RF	Hartmann et al.[6]
	10.56 ± 1.31	RR	Williams et al.[5]

[a] In units of 10^{-12} cm^3 molecule^{-1} s^{-1}. The relative rate coefficients do not include an estimate of the errors in k_r which can add up to 30% to the uncertainty in the values. [b] PLP-LIF, pulsed laser photolysis−laser induced fluorescence; RR, relative rate; PLP-RF, pulsed laser photolysis−resonance fluorescence.

TABLE 4: Experimental and Calculated Rate Coefficients for the Reaction of OH Radicals with Alkoxy Esters at 298 ± 2 K and the Corresponding Atmospheric Lifetimes

compd	$k_{expt}{}^a$	$k_{SAR}{}^b$	lifetime^c (h)
$HC(O)OCH_2OCH_3$	1.7	5.9	163
$CH_3C(O)OCH_2OCH_3$	2.8	14	99
$HC(O)OCH_2OC_2H_5$	4.1	13	68
$CH_3C(O)OCH_2OC_2H_5$	6.4	21	43
$HC(O)OCH_2CH_2OCH_3$	6.4	12	43
$CH_3C(O)OCH_2CH_2OCH_3$	8.3	13	33
$HC(O)OCH_2CH_2OC_2H_5$	11.2	18	25
$CH_3C(O)OCH_2CH_2OC_2H_5$	13.3	20	21

[a] Average experimental rate coefficient based on this work (units of 10^{-12} cm^3 molecule^{-1} s^{-1}). [b] Predicted rate coefficient based on the SAR method (units of 10^{-12} cm^3 molecule^{-1} s^{-1}).[11] [c] Lifetime = $1/(k_{OH}[OH])$, where $[OH] = 1 \times 10^6$ molecule cm^{-3}.[24]

absolute and relative rate coefficients obtained for $HC(O)OCH_2OC_2H_5$ and $CH_3C(O)OCH_2CH_2OC_2H_5$, where the differences are slightly larger than the quoted experimental errors, the values are still within 10% of each other. The high level of agreement between both methods used in this study provides confirmation of their reliability, and consequently, it is recommended that an average of the absolute and relative rate coefficients be used for all of the alkoxy esters. With the exception of ethoxyethyl acetate, this work is the first reported study of the kinetics of the reaction of OH with the alkoxy esters. The values obtained in this study for the reaction of OH with ethoxyethyl acetate are in reasonable agreement with that previously reported by Hartmann et al.,[6] who employed a laser photolysis−resonance fluorescence technique. The rate coefficient obtained by Williams et al.[5] in a relative rate study is slightly lower than all the other reported values.

Trends in Reactivity. The kinetic data obtained for the alkoxy esters can be used to test the structure−activity relationship (SAR) developed by Kwok and Atkinson[11] for the estimation of rate coefficients for the reaction of OH radicals with organic compounds. A detailed discussion of the principles and methods used for calculating the rate coefficients is given in the original literature.[11] As shown in Table 4, agreement between the experimental and SAR calculated values for the rate coefficients is, in general, rather poor. The calculated values are considerably higher than the experimental results for all the alkoxy esters investigated. Deviation between the measured and estimated rate coefficients for the alkoxy esters may be expected, since the SAR treatment employed only considers α-substituent groups. Problems have previously been encountered in obtaining agreement between calculated and experimentally measured rate coefficients for multifunctional ethers.[8,9] Clearly, this is also true for the alkoxy esters. Porter et al.[8] suggested that the lack of agreement between the experimental rate data and the rate coefficients calculated with the SAR method for reaction of OH with oxygenated organic compounds may be related to the formation of cyclic transition states involving hydrogen bonding between the attacking OH radical and the oxygen atom of the hydroxy, ether, or carbonyl groups.

In an attempt to rationalize the experimental results for the alkoxy esters, it is useful to compare their reactivity with the corresponding monofunctional esters and ethers. The rate coefficients for the compounds used in the comparison are listed in Table 5. The structures of the alkoxy esters are essentially the same as those of the corresponding alkyl esters but contain an extra O atom in the hydrocarbon chains. The structures of the ethers are analogous to those of the alkoxy esters but with a CH_3 unit replacing the $HC(O)O-$ and $CH_3C(O)O-$ groups in alkoxy formates and alkoxy acetates, respectively.

The available kinetic and product yield data indicate that the reaction of OH radicals with esters mainly involves hydrogen atom abstraction from the alkoxy group.[12,13,19,20] The rate coefficients for reaction of OH with a series of *n*-alkyl acetates show that the alkoxy groups in these compounds are slightly more reactive than the corresponding alkyl group in alkanes, although they are significantly less reactive than those in ethers.[4] Thus, the $-OCH_3$ group in methyl acetate[13] is approximately twice as reactive as a $-CH_3$ group in ethane[10] but about seven times less reactive than the $-OCH_3$ group in dimethyl ether.[4]

The α-carbon−hydrogen bond strengths in the alkoxy groups of esters have not been reported; however, the C−H bond dissociation energies at sites remote from the ester group are unlikely to vary from those found in alkanes since the carbonyl group is strongly electron withdrawing. Thus, it may be expected that the reaction of the electrophilic OH radical at the α-position of the alkoxy group in an ester may be considerably less reactive than with the corresponding group in an alkane. It is interesting to note that the rate coefficient for reaction of Cl atoms with the $-OCH_3$ group in methyl acetate is around 20 times smaller than the rate coefficient for reaction with a $-CH_3$ group in ethane.[21] Smith and Ravishankara[22] have recently discussed the reactions of OH radicals with carboxylic acids, aldehydes, and ketones in terms of the formation of hydrogen-bonded complexes. It was proposed that the initial step in the reaction involves the formation of a complex in which a hydrogen bond exists between the H-atom of the attacking OH radical and the O atom of the carbonyl group. A second hydrogen bond is then formed in the complex between the O atom of the OH radical and a H atom in the hydrocarbon chain, resulting in intramolecular hydrogen atom transfer via a cyclic transition state. It is suggested that the reactions of OH with esters also involve hydrogen-bonded complexes rather than a direct H-atom abstraction pathway. Hence, the deactivating inductive effect of the carbonyl group in esters is offset by the stabilizing effect of hydrogen bonding. In contrast, such stabilization of the transition state by hydrogen bonding is not possible in Cl atom reactions and provides an explanation for the observation that the reactivity of a $-OCH_3$ group in an ester is significantly

TABLE 5: Comparison of the Rate Coefficients (k_{OH} in Units of 10^{-12} cm^3 molecule^{-1} s^{-1}) for the Reaction of OH Radicals with Alkoxy Esters, Alkyl Esters, and Ethers at 298 ± 2 K

alkoxy ester	k^a	alkyl ester	k^b	ether	k^c
$HC(O)OCH_2OCH_3$	1.7	$HC(O)OC_2H_5$	0.9	$CH_3CH_2OCH_3$	8.2
$CH_3C(O)OCH_2OCH_3$	2.8	$CH_3C(O)OC_2H_5$	1.7	$CH_3CH_2OCH_3$	8.2
$HC(O)OCH_2OC_2H_5$	4.1	$HC(O)OC_3H_7$	1.8	$CH_3CH_2OC_2H_5$	13.6
$CH_3C(O)OCH_2OC_2H_5$	6.4	$CH_3C(O)OC_3H_7$	3.4	$CH_3CH_2OC_2H_5$	13.6
$HC(O)OCH_2CH_2OCH_3$	6.4	$HC(O)OC_3H_7$	1.8	$CH_3CH_2CH_2OCH_3$	12.3
$CH_3C(O)OCH_2CH_2OCH_3$	8.3	$CH_3C(O)OC_3H_7$	3.4	$CH_3CH_2CH_2OCH_3$	12.3
$HC(O)OCH_2CH_2OC_2H_5$	11.2	$HC(O)OC_4H_9$	3.5	$CH_3CH_2CH_2OC_2H_5$	17.7
$CH_3C(O)OCH_2CH_2OC_2H_5$	13.3	$CH_3C(O)OC_4H_9$	5.5	$CH_3CH_2CH_2OC_2H_5$	17.7

[a] Average experimental rate coefficient based on this work. [b] Values for formates taken from ref 12, values for acetates taken from ref 13. [c] Values for ethers taken from refs 4 and 14−18.

lower than the reactivity of a $-CH_3$ group in an alkane.[21] It is interesting to note that the rate coefficients for reaction of OH and Cl with alkyl formates are lower than those for reaction with alkyl acetates.[12,13,16] Presumably, replacement of the electron-donating methyl group in acetates by a hydrogen atom leads to an increase in the deactivating inductive effect of the carbonyl group.

The relatively high reactivity of ethers compared to the analagous alkanes has previously been discussed in detail[4,8,9,19] and has been rationalized, at least in part, in terms of the reduction in the C−H bond energy at the α-carbon atom. However, $-CH_2-$ groups at the β- and γ-positions in ethers also show increased reactivity compared to their reactivity in alkanes. Moriarty et al.[9] have explained the long-range activating effect of the ether functional group in a manner similar to that suggested for the enhanced reactivity shown by carbonyl compounds in which a hydrogen-bonded adduct is initially formed involving the OH radical and the oxygen atom of the ether followed by intramolecular H-atom transfer.

As shown in Table 5, in all cases, the OH rate coefficients measured for the alkoxy esters are higher than those of the corresponding alkyl esters but lower than those of the ethers. The measured temperature dependence of the rate coefficients for reaction of OH with all the alkoxy esters investigated in this study shows small negative activation energies. Similar results have been obtained for monofunctional esters[12,13] and ethers[15,17] and provide some support for formation of weakly bound complexes between the OH radical and the alkoxy esters which can either decompose back to reactant or eliminate H_2O.

In principle, it should be possible to rationalize the reactivity of alkoxy esters by assuming that their overall reactivity is a combination of the effects of the ester and ether functional groups. To a first approximation, it is reasonable to expect that the $-OCH_3$ and $-OC_2H_5$ groups in the alkoxy esters have the same reactivities as those in the symmetric ethers CH_3OCH_3 and $CH_3CH_2OCH_2CH_3$, respectively. Hence, the contribution to the overall rate coefficients for these groups in the alkoxy esters will be, in units of 10^{-12} cm^3 molecule^{-1} s^{-1}, $k_{OH}(-OCH_3) = 1.4$ and $k_{OH}(-OC_2H_5) = 6.8$.[4] Rate coefficient data for the reactions of OH with $HC(O)OCH_2CH_3$ and $CH_3C(O)OCH_2CH_3$ provide values of $k_{OH}(HC(O)OCH_2-) = 0.5$[12] and $k_{OH}(CH_3C(O)OCH_2-) = 1.5$,[13] in units of 10^{-12} cm^3 molecule^{-1} s^{-1}. The measured rate coefficients for $HC(O)OCH_2OCH_3$ (1.7×10^{-12} cm^3 molecule^{-1} s^{-1}) and $CH_3C(O)OCH_2OCH_3$ (3.3×10^{-12} cm^3 molecule^{-1} s^{-1}) are close to the simple sum of the rate coefficients for the ester and ethers groups. Thus, it is possible that the reactivity of the $-CH_2-$ group in these molecules is largely influenced by the ester group and the presence of the ether group only causes an increase in reactivity of the $-CH_3$ group remote from the ester group. Consideration of the rate coefficients for reaction of OH with ethoxymethyl formate and ethoxymethyl acetate provides support for this conclusion, although the reactivities of these alkoxy esters are somewhat less than predicted. An alternative approach in attempting to rationalize the reactivities of the alkoxymethyl formates and acetates is to compare the reactivity of the $-OCH_2O-$ group in the alkoxy esters with that in the diether $CH_3OCH_2OCH_3$. Rather surprisingly, kinetic[3,8] and product distribution studies[2,3,23] on the reaction of OH with $CH_3OCH_2OCH_3$ show that the reactivity of the $-OCH_2O-$ group is similar to that found for a $-CH_2-$ group in an alkane, $k_{OH}(-CH_2-) = 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, [10] and around 5 times less reactive than the $-CH_2-$ group in diethyl ether.[4] It has been suggested that the relatively low reactivity of the $-OCH_2O-$ group in $CH_3OCH_2OCH_3$ is largely related to a strengthening of the C−H bond compared to the $-CH_2-$ group in diethyl ether.[9] It is hence possible that the low reactivity of the $-OCH_2O-$ group in the alkoxymethyl esters is also related to bond strength rather than the deactivating inductive effect of the ester group.

The reactivities of alkoxy esters containing the $-CH_2CH_2-$ group between the ether and ester functionalities may usefully be considered by assuming that the $-CH_2OCH_3$ and $-CH_2OC_2H_5$ groups will have approximately the same reactivities as in the ethers $CH_3CH_2OCH_3$ and $CH_3CH_2OCH_2CH_3$ respectively: $k_{OH}(-CH_2OCH_3) = 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_{OH}(-CH_2OC_2H_5) = 13 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The rate coefficients determined in this work for the alkoxyethyl formates and acetates show that the overall rate coefficients for these compounds can be estimated with a reasonable level of accuracy by assuming that the measured rate coefficient is the simple sum of the rate coefficients of the two groups $RC(O)OCH_2-$ and $-CH_2OR$. As mentioned previously, it is of interest to compare the reactivity of the $-C(O)OCH_2CH_2O-$ group in alkoxyethyl esters with the reactivity of the $-OCH_2CH_2O-$ group in dimethoxy ethane. The reactivity of the $-CH_2-$ groups in the diether is around twice the reactivity of a $-CH_2-$ group in a monoether.[2,3,8] It has been suggested that this enhancement in reactivity is due to activation of the H atoms as a result of the initial formation of a hydrogen-bonded adduct followed by formation of a cyclic transition state.[9] Presumably, the electron-withdrawing carbonyl group in the alkoxyethyl esters reduces the importance of adduct formation involving the ether group. As a consequence, only the $-CH_2-$ groups adjacent to the ether group, which have relatively low C−H bond energies, show the reactivity associated with α-CH_2- groups in monoethers. Wells et al.[1] reported a product study on the OH radical initiated oxidation of ethoxyethyl acetate. The major products detected are consistent with H-atom abstraction, with approximately the same degree of selectivity, from the two $-CH_2-$ groups either side of the ether linkage and hence provide support for the reactivity estimates calculated in this work.

Atmospheric Implications. Gas-phase reaction with hydroxyl radicals is expected to be the major loss process for alkoxy esters in the troposphere. The atmospheric lifetime of these compounds can be calculated by using the following expression: lifetime $= 1/k_{OH}[OH]$, where k_{OH} is the bimolecular rate coefficient and [OH] is the tropospheric concentration of OH radicals. Using the average value of k_{OH} obtained in this work and a 24 h average concentration of $[OH] = 1 \times 10^6$ molecule cm^{-3},[24] lifetimes for the alkoxy esters range from ca. 1 day for ethoxyethyl acetate to 7 days for methoxymethyl formate, Table 4. The relatively short lifetimes for the alkoxy esters indicate that, if released or formed in the atmosphere, they will undergo degradation in the troposphere and contribute to regional ozone formation.

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