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Kinetic Studies on the Reactions of Hydroxyl Radicals with Diethers and Hydroxyethers

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Rate constants for the reactions of OH radicals with a series of diethers and hydroxyethers have been determined at 298 ± 2 K. Rate measurements were made using a pulsed laser photolysis resonance fluorescence technique at total pressures of ~100 Torr and a conventional photolytic relative rate method at atmospheric pressure. The temperature dependencies of the rate constants for four diethers were also studied over the temperature range 230−372 K using pulsed laser photolysis resonance fluorescence. The rate data for reaction of OH with the diethers show significant deviations from simple structure−activity relationships. Evidence is presented that suggests that these deviations may be a consequence of stabilization of the reaction transition states by hydrogen bonding.

Introduction

Polyfunctional oxygenated compounds, such as diethers and hydroxyethers, have increasing applications as water soluble solvents and fuel additives. The release of these species into the atmosphere is likely to have effects on tropospheric ozone levels and also lead to the formation of other secondary pollutants. Consequently, a detailed understanding of the kinetics and mechanisms of the atmospheric degradation of these compounds is required.

The major fate of oxygenated organic compounds released into the troposphere is through reaction with hydroxyl radicals. To date, relatively few studies have been carried out on the gas-phase reactions of hydroxyl radicals with polyfunctional oxygenated organic,[1−3] although rate data for the reactions of OH radicals with various polyalcohols,[4] polyethers,[5] and hydroxyethers[4,6−8] have been reported. The purpose of this work was to determine rate constant data for the reaction of OH radicals with a series of diethers and hydroxyethers using both a laser flash photolysis technique and a conventional relative rate method. The results yield estimates of the atmospheric lifetimes and provide structure−reactivity information on the reactions.

Experimental Section

(a) Relative Rate. Relative rate studies were carried out at atmospheric pressure in an FEP Teflon cylindrical reaction vessel (volume ~50 L) surrounded by fluorescent lamps. Twenty Philips TUV 15 W germicidal lamps were used as the source of radiation at 254 nm, and the light intensity was varied by switching off various sets of lamps. Electric fans, positioned below the reaction vessel, were used to ensure a uniform reaction temperature, which was monitored by two chromel/alumel thermocouples placed within the chamber. Measured amounts of reagents were flushed from calibrated Pyrex bulbs into the reaction vessel by a stream of zero-grade nitrogen (Air Products); the vessel was then filled to its full capacity with ultrapure air (Air Products). The photolysis of ozone in the presence of water vapor was used as the source of OH radicals:

$$O_3 + h\nu\ (\lambda = 254\text{ nm}) \rightarrow O(^1D) + O_2 \qquad (1)$$

$$O(^1D) + H_2O \rightarrow OH + OH \qquad (2)$$

Mixtures of O_3, H_2O, and oxygenated organic and reference compounds in air were photolyzed for about 15 min at 298 ± 2 K with $[\text{Substrate}]_0$ and $[\text{Reference}]_0 = 1-10$ ppm; $[O_3]_0 = 100-1000$ ppm; $[H_2O]_0 = 2000-10\,000$ ppm, (1 ppm = 2.46×10^{13} molecules cm^{-3} at 298 K and 760 Torr total pressure). The reference compounds used were $(C_2H_5)_2O$, $(n\text{-}C_3H_7)_2O$, $(n\text{-}C_4H_9)_2O$, and C_2H_5OH.

Ozone was produced by passing zero-grade oxygen (Air Products) through an ozone generator (Monitor Labs) directly into the reaction chamber. All pressure measurements were made using MKS Baratron capacitance manometers, and ozone concentrations were determined by a Monitor Labs 8810 UV photometric ozone analyzer following dilution of the reaction mixtures. The reactants were allowed to mix for at least 30 min prior to the start of photolysis. Samples of the reaction mixtures were drawn through a Valco gas sampling valve for quantitative analysis by gas chromatography (Shimadzu Model 14A) at approximately 2 min intervals. Chromatographic separation was achieved by using a 30 m wide-bore (0.53 mm i.d.) capillary column packed with either Carbowax or SE-54. The columns were operated over the temperture range 40−80 °C using nitrogen as the carrier gas and flame ionization detection.

(b) Absolute Rate. Absolute rate studies were performed using the technique of pulsed laser photolysis−laser-induced fluorescence. The apparatus has been described recently in detail,[9,10] and only a brief description is given here. The reaction cell, made of Pyrex, could be heated or cooled to regulate the temperature. Hydroxyl radicals were produced by photolysis of H_2O_2 at $\lambda = 248$ nm (KrF excimer laser) and their concentrations measured using pulsed laser induced fluorescence using a Nd:YAG-pumped frequency-doubled dye laser which was triggered at a variable delay time after the photolysis pulse. The probe pulse excites the Q_11, Q_11', and R_23 lines in the (1,0)

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band of the (A $^2\Sigma^+$, $v' = 1$) ← (X $^2\Pi$, $v'' = 0$) transition of the OH radical at around 282 nm. Gaseous mixtures of H_2O_2, the reactant hydrocarbon, and the carrier gas, helium, were flowed through the cell in a mutually orthogonal direction to the photolysis and probe laser beams. Both the photolysis and the probe lasers were operated at a repetition rate of 10 Hz. The intersection of the lasers in the center of the cell defined the observation volume. A photomultiplier (PM) tube equipped with a bandpass filter (309.4 nm peak transmission, fwhm = 7.6 nm) was used to collect the resultant fluorescence of the OH radical corresponding to (A $^2\Sigma^+$, $v' = 1$) → (X $^2\Pi$, $v'' = 1$) and (A $^2\Sigma^+$, $v' = 0$) → (X $^2\Pi$, $v'' = 0$) transitions and discriminated against the scattered probe laser light. The PM tube was positioned below the reaction volume and coaxial with the gas flow.

For OH radical kinetic studies, the output pulse from the PM tube was integrated for a preset period by a gated charge integrator. The integrated signal was digitized and sent to a microcomputer for averaging and analysis. Typically, the signals from 100 probe laser shots were averaged to obtain one data (concentration versus time) point. The detection limit under these conditions was about 2×10^8 molecules cm^{-3} (S/N =1). Plots of OH concentration versus time were obtained by averaging signals for delay times from about 10 μs to 30 ms using a delay time generator. In kinetic runs, typically 10−15 delays were sampled to map out an OH profile over at least three lifetimes. This procedure was repeated several times in order to obtain a value for the pseudo-first-order rate constant at each substrate concentration. The reaction mixture was flowed slowly through the cell, so that each photolysis/probe sequence interrogated a fresh gas mixture and reaction products did not build up in the cell.

The gas mixture containing the oxygenate, the photolytic precursor (H_2O_2), and the bath gas (approximately 100 Torr of helium) was flowed through the cell with a linear velocity ranging between 5 and 20 cm s^{-1}. The concentrations of reactants and the bath gas were calculated from their mass flow rates, temperature, and the pressure in the reaction cell. All flow rates were measured with mass flowmeters calibrated by measuring the rate of pressure increase in a known volume. The cell pressure was measured with a capacitance manometer connected adjacent to the cell entrance.

(c) Materials. Helium carrier gas (UHP certified to >99.9995% (Alphagas)) was used without purification. The 70 wt % H_2O_2 solution obtained from Interox Chemie was concentrated by bubbling helium through the solution to remove water for several days prior to use and constantly during the course of the laser photolysis experiments. It was admitted into the reaction cell by passing a small flow of helium through a glass bubbler containing H_2O_2. All the alcohols and ethers employed in these studies were obtained from Aldrich Chemical Company (stated purities ≥ 99 mol %). All the oxygenated compounds were further purified by repeated freeze−pump−thaw cycles and fractional distillation prior to use.

Results

Relative rate constants for the reaction of OH radicals with the oxygenated organic substrates were determined by comparing the rate of reaction with the following reference compounds: $(C_2H_5)_2O$, $(n\text{-}C_3H_7)_2O$, $(n\text{-}C_4H_9)_2O$, and C_2H_5OH.

$$\mathrm{OH} + \mathrm{Substrate} \rightarrow \mathrm{Products} \qquad (3)$$

$$\mathrm{OH} + \mathrm{Reference} \rightarrow \mathrm{Products} \qquad (4)$$

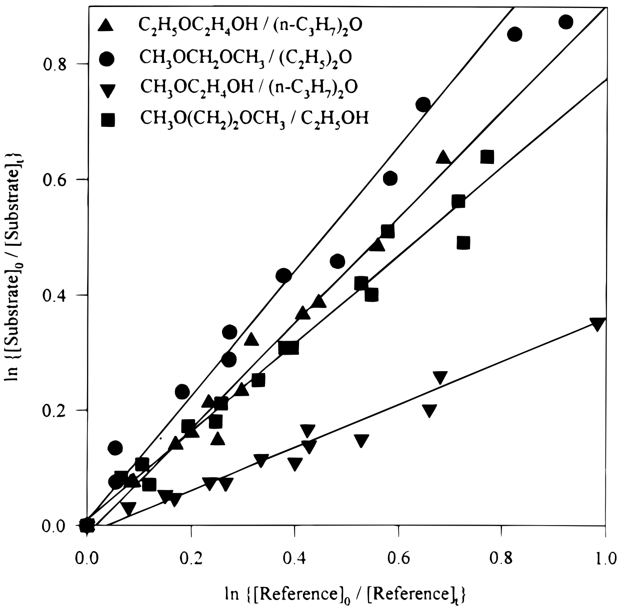

Figure 1. Concentration−time data for the reaction of OH radicals with diethers and hydroxyethers at 298 ± 2 K.

Provided that reaction with OH is the only significant loss process for both substrate and reference compounds, it can be shown that

$$\ln\{[\mathrm{Substrate}]_0/[\mathrm{Substrate}]_t\} = k_3/k_4 \ln\{[\mathrm{Reference}]_0/[\mathrm{Reference}]_t\} \qquad (\mathrm{I})$$

where the subscripts 0 and t indicate concentrations before irradiation and at time t, respectively. Direct photolytic loss of the substrate and reference compounds was unimportant, and the reaction mixtures were stable in the dark for at least 5 h. Reactions of the products with O_3 were shown to be negligible. Under the reaction conditions employed the substrate and reference compound were found to decay by approximately 50% during the experiments. Data for the runs were plotted in the form of eq I and showed the expected linear relationship. Typical data for the experiments are shown in Figure 1. The slope of the plots provide values of k_3/k_4 which were independent of relative reactant concentration, reaction time, and light intensity, in agreement with the proposed mechanism. A possible source of error in the determinations of k_3/k_4 is the reaction of O(^{1}D) with the substrate and reference compounds. The rate constant for the reaction of O(^{1}D) with H_2O, $k_2 = 2.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[11] is sufficiently high that, under the experimental conditions employed with [H_2O] ≥ 100-[Substrate]$_0$ or 100[Reference]$_0$, O(^{1}D) is effectively scavenged in reaction 2. Variation in water vapor from 2−10 Torr had no measurable effect on the value of k_3/k_4, thus providing support for this assumption.

At least three individual runs were carried out with each substrate using diethyl ether, di-n-propyl ether, di-n-butyl ether, or C_2H_5OH as the reference compound. In order to test the internal consistency of the rate constant ratio data, each of the reactants was also run against another member of the series. In all cases the relative rate values were in excellent agreement with the results obtained using one of the reference compounds. The rate constants for reaction of OH radicals with the oxygenated compounds were calculated from the rate constant ratios k_3/k_4 using values of $k_4(\mathrm{OH} + (C_2H_5)_2O) = 13.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k_4(\mathrm{OH} + (n\text{-}C_3H_7)_2O) = 18.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k_4(\mathrm{OH} + (n\text{-}C_4H_9)_2O) = 28.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and $k_4(\mathrm{OH} + C_2H_5OH) = 3.27 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 ± 2 K, taken from Atkinson,[2,3] Table 1.

The errors quoted 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 constants, k_4. The errors in k_4 probably add a further 25% to the uncertainty of the rate constants reported in these relative rate studies.

All absolute rate kinetic experiments were carried out under pseudo-first-order conditions with $[\text{Substrate}]_0 > 100[\text{OH}]_0$. Typically the initial OH concentration, $[\text{OH}]_0$, was around 1×10^{11} molecules cm^{-3}. Following OH formation in the pulsed laser photolysis of H_2O_2,

$$H_2O_2 + h\nu\ (\lambda = 248\ \text{nm}) \rightarrow OH + OH \qquad (5)$$

the radical is lost via the following processes:

$$OH + \text{Substrate} \rightarrow \text{Products} \qquad (3)$$

$$OH + H_2O_2 \rightarrow \text{Products} \qquad (6)$$

$$OH \rightarrow \text{diffusion out of the detection zone} \qquad (7)$$

Hence

$$-d[OH]/dt = (k_3[\text{Substrate}] + k_6[H_2O_2] + k_7)[OH]$$

and

$$[OH]_t = [OH]_0 e^{-k't}$$

where $k' = k_3[\text{Substrate}]_0 + k_6[H_2O_2] + k_7$.

The decay rate constant k'_0 ($k'_0 = k_6[H_2O_2] + k_7$) is the first-order OH radical disappearance rate in the absence of the oxygenated organic and typically had values in the range 100−500 s^{-1}. Loss of the OH radical, in the presence of substrate, was exponential over at least three lifetimes, and plots of ($k' - k'_0$) versus the substrate concentrations at 298 ± 1 K showed excellent linearity. Representative data for various ethers and hydroxyethers are shown in Figure 2. Values of k_3 were obtained from the least squares fits of the data and are listed in Table 1. The experimentally determined rate constants were shown to be independent of gas flow rates through the reactor or changes in the total pressure of the system. None of the oxygenates under investigation absorb radiation with a wavelength 248 nm, and hence reaction of OH with photofragments of the organic compounds cannot contribute to OH loss. As expected, variations in the photolysis fluence had no effect on the determined rate constants. All the compounds studied were purified to better than 99.5%, and hence loss of OH radicals by reaction with impurities in the gas mixtures is expected to be insignificant.

Rate constants for the reaction of OH radicals with $CH_3OCH_2OCH_3$, $C_2H_5OCH_2OC_2H_5$, $CH_3OCH_2CH_2OCH_3$, and $C_2H_5OCH_2CH_2OC_2H_5$ were determined over the temperature range 230−372 K using the laser photolysis−laser-induced fluorescence technique. Figure 3 shows plots of the pseudo-first-order rate constant versus substrate concentration as a function of temperature for $CH_3OCH_2OCH_3$. Similar plots were obtained for the three other ethers in the series, and the measured rate constants are plotted in Arrhenius form in Figure 4. All of the plots show slight curvature and indicate that the rate constants have small negative temperature dependencies. The data are better expressed in terms of $k = A'T^2e^{-E/RT}$; $CH_3OCH_2OCH_3$, $A' = (4.0 \pm 1.0) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, $E/R = -(7.8 \pm 0.7) \times 10^2$ K; $C_2H_5OCH_2OC_2H_5$, $A' = (4.2 \pm 0.5) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, $E/R = -(12.0 \pm 0.4) \times 10^2$ K; $CH_3OCH_2CH_2OCH_3$, $A' = (5.3 \pm 0.5) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, $E/R = -(12.2 \pm 0.2) \times 10^2$ K; $C_2H_5OCH_2CH_2OC_2H_5$, $A' = (5.8 \pm 1.1) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}, $E/R = -(14.0 \pm 0.5) \times 10^2$ K.

TABLE 1: Rate Constants for the Reaction of OH Radicals with Diethers and Hydroxyethers at 298 ± 2 K

oxygenated compound	$10^{12}\,k_{OH}{}^{a}$/cm^3 molecule^{-1} s^{-1}	technique[b]	reference
$CH_3OCH_2OCH_3$	5.3 ± 0.5	RR	Wallington *et al.*[13]
	4.9 ± 0.6	RR	Sauer *et al.*[14]
	4.9 ± 0.8	RR	this work
	4.6 ± 0.1	PLP-LIF	this work
$CH_3OC(CH_3)_2OCH_3$	3.9 ± 0.2	FP-RF	Dagaut *et al.*[5]
	3.6 ± 0.6	RR	this work
	4.7 ± 0.2	PLP-LIF	this work
$C_2H_5OCH_2OC_2H_5$	16.8 ± 1.6	FP-RF	Dagaut *et al.*[5]
	20.4 ± 1.4	RR	this work
	20.6 ± 0.1	PLP-LIF	this work
$CH_3OCH_2CH_2OCH_3$	28.1 ± 1.0	RR	this work
	26.7 ± 3.1	PLP-LIF	this work
$CH_3OCH_2CH(CH_3)OCH_3$	14.3 ± 1.5	FP-RF	Dagaut *et al.*[5]
	28.4 ± 1.8	RR	this work
	34.0 ± 0.8	PLP-LIF	this work
$C_2H_5OCH_2CH_2OC_2H_5$	57.9 ± 5.3	RR	this work
	57.9 ± 2.4	PLP-LIF	this work
1,4-dioxane	10.9 ± 0.5	FP-RF	Dagaut *et al.*[15]
	9.7 ± 0.7	RR	this work
	12.6 ± 0.3	PLP-LIF	this work
$CH_3OCH_2CH_2OH$	12.5 ± 0.7	FP-RF	Dagaut *et al.*[6]
	10.9 ± 0.5	RR	Stemmler *et al.*[7]
	14.1 ± 2.8	RR	this work
	11.4 ± 1.0	PLP-LIF	this work
$C_2H_5OCH_2CH_2OH$	14.5 ± 0.4	LP-RF	Hartmann *et al.*[8]
	18.7 ± 2.0	FP-RF	Dagaut *et al.*[6]
	14.5 ± 0.4	RR	Stemmler *et al.*[7]
	17.4 ± 3.1	RR	this work
	21.2 ± 0.7	PLP-LIF	this work
$CH_3OCH_2CH(CH_3)OH$	17.9 ± 1.6	RR	this work
	19.2 ± 0.9	PLP-LIF	this work
$(CH_3)_2CHOCH_2CH_2OH$	22.6 ± 1.8	RR	this work
	18.5 ± 0.7	PLP-LIF	this work

[a] Errors are twice the standard deviation and represent precision only. [b] RR, relative rate; PLP-LIF, pulsed laser photolysis−laser-induced fluorescence; FP-RF, flash photolysis−resonance fluorescence; LP-RF, laser photolysis−resonance fluorescence.

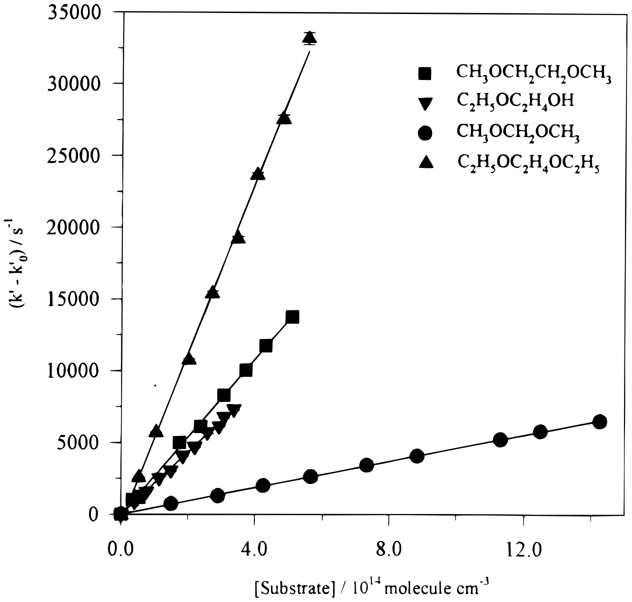

Figure 2. Plots of (k' - k'_0) versus substrate concentration for the reaction of OH radicals with diethers and hydroxyethers at 298 ± 1 K.

Discussion

The rate constants obtained in this study for the reactions of OH radicals with oxygenated organics at 298 ± 2 K are

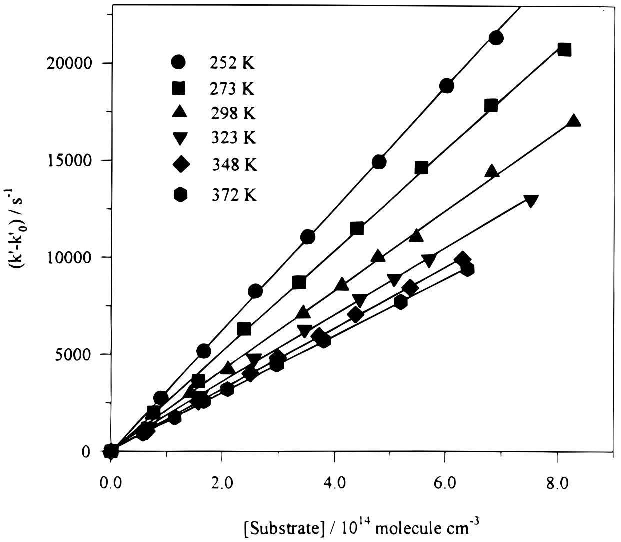

Figure 3. Plots of ($k' - k'_0$) versus substrate concentration as a function of temperature for $CH_3OCH_2OCH_3$.

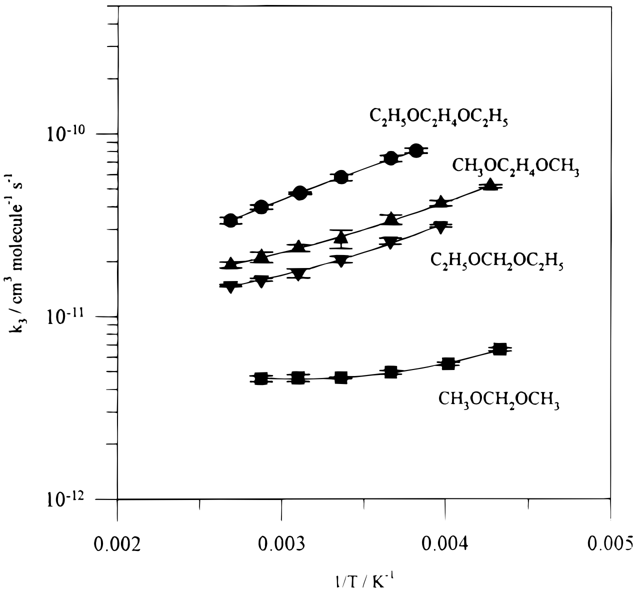

Figure 4. Arrhenius plots of the of the rate constant data for the reaction of OH radicals with diethers. The error bars of the individual points are 2σ and do not include systematic errors.

compared with previously reported data in Table 1. Good agreement between the relative and absolute rate constant measurements in this work is evident. The rate constant values determined for the reaction of OH with dimethoxymethane are in close agreement with the recent relative rate measurements of Wallington *et al.*[13] and Sauer *et al.*[14] The rate data obtained by Dagaut *et al.*[5] for diethers are consistently lower than the rate coefficients measured in the present study, although the data for 1,4-dioxane[15] obtained by this group are in line with the present work. For 2-methoxyethanol, the rate constants determined by Dagaut *et al.*[6] and Stemmler *et al.*[7] are in good agreement with the present data. However, for 2-ethoxyethanol, the rate constant obtained by Stemmler *et al.*[7] is about 25% lower than the values determined by Dagaut *et al.*[6] and that obtained in this work. The reasons for these discrepancies are not readily apparent.

All the available evidence suggests that the products formed from reaction of OH radicals with alcohols and ethers are consistent with hydrogen atom abstraction by OH from the reactants.[1−3] The reaction with alcohols may involve abstraction from both C−H and O−H bonds, although the former process is more favored on thermodynamic grounds. The results from several investigations indicate that abstraction from the alcohol group in CH_3OH accounts for around 15% of the products at room temperature;[16] however, this contribution to the overall rate constant for reaction of OH radicals with longer chain aliphatic alcohols is likely to be less significant. The rate constants obtained as a function of temperature for the four diethers investigated in this work and those previously reported for aliphatic alcohols and ethers containing a $-CH_2-$ group[1−3] show small negative temperature dependencies. It is probable that these facile bimolecular reactions have near zero activation energies and negative temperature dependent pre-exponential factors. When plotted in Arrhenius form, the overall rate constants previously reported for the ethers[2,3,9] and diethers investigated in this work show distinct curvature over a limited temperature range. This is probably due to the rate constants for reaction at separate sites in the molecule having slightly different temperature dependencies.

The kinetic data for the reactions of OH radicals with hydroxyethers and diethers, given in Table 1, can be used to test the structure−activity relationship (SAR) developed by Atkinson[1,17−19] to estimate OH radical rate constants for hydrogen atom abstraction reactions from organic compounds. In general, the rate constants estimated by this method are in good agreement with experimental data, particularly for compounds containg one functional group. Calculation of H atom abstraction rate constants for C−H and O−H bonds is based on the estimation of $-CH_3$, $-CH_2-$, $>CH-$, and $-OH$ group rate constants, assuming that the group rate constants are dependent on the identity of the substituents attached to the group. At room temperature, the group rate constants are given by: $k(CH_3-X) = k_{prim}F(X)$, $k(Y-CH_2-X) = k_{sec}F(X)\,F(Y)$, $k\left(\begin{smallmatrix}Y\\Z\end{smallmatrix}{>}CH-X\right) = k_{tert}F(X)\,F(Y)\,F(Z)$, $k(X-OH)$ (X = alkyl group) $= k_{abst}(-OH)$, where k_{prim}, k_{sec}, k_{tert}, $k_{abst}(-OH)$ are the rate constants per CH_3-, $-CH_2-$, $>CH-$, and $-OH$ groups for $X = Y = Z = -CH_3$, with $F(-CH_3) = 1.00$ by definition. The experimentally determined rate constants are compared with those calculated using the SAR treatment in Table 2, where at 298 K, $k_{prim} = 0.136 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k_{sec} = 0.934 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k_{tert} = 1.94 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, $k_{abst}(-OH) = 0.14 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, and $F(-CH_2-) = F(>CH-) = F(-C-) = 1.23$, $F(O-H) = 3.5$, and $F(-O-R)$ (R = alkyl) $= 8.4$.[19] Agreement between the experimental data and the SAR calculated values is, in general, rather poor. In particular, the calculated rate constants for compounds with $-CH_2-$ groups situated between ether groups show significant deviations from the experimental values. For compounds of structure $ROCH_2OR$ the calculated rate constants are considerably higher than those determined experimentally, whereas for $ROCH_2CH_2OR$ the calculated values are significantly lower than the experimental rate constants, with the exception of the cyclic diether 1,4-dioxane, where the SAR provides a rate constant that is around a factor of 3 higher than that observed experimentally. Deviations between the measured and estimated rate constants for hydroxyethers and diethers 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 constants for alcohols and ethers.[19] This is not surprising since ether and hydroxy groups have been shown to exhibit long-range activating effects with respect to OH radical reactions,[12,20,21] and hence deviations from a simple structure−activity relationship are likely to occur.

TABLE 2: Experimental and Calculated Rate Constants for the Reaction of OH Radicals with Diethers and Hydroxyethers at 298 ± 2 K and the Corresponding Atmospheric Lifetimes

substrate	$10^{12}k_{\mathrm{expt}}{}^{a,b}$	$10^{12}k_{\mathrm{SAR}}{}^{a,c}$	$10^{12}k_{\mathrm{GR}}{}^{a,d}$	lifetime^{e}/h
$CH_3OCH_2OCH_3$	4.8	68	14	58
$CH_3OC(CH_3)_2OCH_3$	4.2	3	5	66
$C_2H_5OCH_2OC_2H_5$	20.5	82	24	14
$CH_3OCH_2CH_2OCH_3$	27.4	22	20	10
$CH_3OCH_2CH(CH_3)OCH_3$	31.2	32	18	8.9
$C_2H_5OCH_2CH_2OC_2H_5$	57.9	35	30	4.8
1,4-dioxane	11.2	39	32	25
$CH_3OCH_2CH_2OH$	12.8	15	14	22
$C_2H_5OCH_2CH_2OH$	19.3	22	19	14
$CH_3OCH_2CH(CH_3)OH$	18.6	19	15	15
$(CH_3)_2CHOCH_2CH_2OH$	20.6	30	18	13

[a] In units of cm^3 molecule^{-1} s^{-1}. [b] Rate data from this work. [c] Kwok and Atkinson.[19] [d] Dagaut *et al.*[6] [e] Lifetime = $1/k_{OH}[OH]$; $[OH] = 1 \times 10^6$ molecule cm^{-3}.

TABLE 3: Group Reactivities in Alcohols and Ethers[a,b]

group R	ROH	ROR′	RH
α, CH_3	0.94^{1}	1.5^{8}	
C_2-C_4, CH_3	0.37^{2}	0.48^{9}	0.17^{3}
$>C_4$, CH_3	0.17^{3}	0.17^{3}	
α, CH_2	2.9^{4}	6.1^{10}	
C_2-C_4, CH_2	2.6^{5}	3.4^{11}	1.4^{3}
$>C_4$, CH_2	1.4^{3}	1.4^{3}	
α, CH	4.6^{6}	4.6^{12}	2.9^{3}
C_2-C_4, CH	4.6^{7}	4.6^{13}	

[a] Derived from rate data for the reaction of OH radicals with aliphatic alcohols and ethers,[2,3] in units of 10^{12} cm^3 molecule^{-1} s^{-1}. [b] Calculated from (*1*) CH_3OH, (*2*) $(CH_3)_3COH$, (*3*) average reactivity in alkanes,[19] (*4*) C_2H_5OH, (*5*) n-C_3H_7OH to n-$C_5H_{11}OH$, (*6*) $(CH_3)_2CHOH$, (*7*) assumed to have same reactivity as an α CH in ROH, (*8*) CH_3OCH_3, (*9*) $CH_3OC(CH_3)_3$, (*10*) $C_2H_5OC_2H_5$, (*11*) n-$(C_3H_7)_2O$ to n-$(C_5H_{11})_2O$, (*12*) $(CH_3)_2CHOCH(CH_3)_2$, (*13*) assumed to have the same reactivity as an α CH in ROR′.

Dagaut *et al.*[6] have proposed a somewhat different method for predicting OH radical rate constants for reaction with difunctional oxygenates. This analysis is based on group reactivity coefficients determined from experimental rate data for the reaction of OH radicals with aliphatic monoalcohols and monoethers which inherently take account of the long-range effects of the hydroxy and ether groups. The group reactivity (GR) values for $-CH_3$, $-CH_2-$, and $>CH-$ groups in alcohols and ethers given in Table 3 are similar to those used previously by Dagaut *et al.*,[6] but are based on a much wider data base.[2,3] Comparison of the differences between the GR values for the oxygen-containing compounds and those for unsubstituted alkanes provides a measure of the increase in reactivity due to the presence of hydroxy and ether groups. In order to calculate rate constants for polyfunctional oxygen-containing compounds, Dagaut *et al.*[6] proposed that the rate constants for the individual $-CH_3$, $-CH_2-$, and $>CH-$ groups are additive, but reactivity increases are not transmitted across ether linkages. Thus, the reactivity of groups positioned between two functional groups is calculated as the sum of the rate constant for the group based on one of the functional groups plus the increase in the rate constant due to the other functional group over and above that observed for an alkane. As can be seen from the data in Table 2, the predicted rate constants based on group reactivity values are in considerably better agreement with the experimental rate constants than those calculated on the basis of the SAR method. However, serious discrepancies are still apparent for compounds containing $-CH_2-$ groups between the ether groups.

Kinetic data for the reaction of OH radicals with a large number of aliphatic alcohols and ethers have been reported.[1-3] The increase in reactivity shown for the reaction of OH radicals with CH_3OH or $(CH_3)_2O$, C_2H_5OH or $(C_2H_5)_2O$, and $(CH_3)_2CHOH$ or $((CH_3)_2CH)_2O$ compared to the corresponding alkanes can, at least in part, be rationalized in terms of the lowering of the C−H bond dissociation energies for a carbon atom bound to an oxygen atom in an alcohol or an ether. However, the available data shows that the rate constants for the reaction of OH radicals with straight chain alcohols and ethers increase fairly linearly with the alkyl chain length up to about five carbon atoms. Thus, the $-CH_2-$ groups in the C_2 to C_4 positions in these molecules show quite similar reactivities, with a gradual reduction in reactivity per $-CH_2-$ group as the chain length increases. The rate constants per $-CH_2-$ group are around a factor of 2 and 3 higher in the alcohols and ethers, respectively, than the corresponding alkanes.[12] Hence, the activating effect of the alcohol or ether group for reaction with OH radicals appears to extend over about four carbon atoms. For further increases in chain length, the reactivity of the $-CH_2-$ group is similar to that found in unsubstituted alkanes. The observed long-range activating effect of the alcohol and ether groups cannot be explained in terms of bond energy or inductive effects and indicates an alternative reaction pathway to the direct concerted hydrogen atom abstraction process observed for alkanes. It is proposed that this enhanced reactivity may be due to stabilization of the transition states for the reactions resulting from interaction of the attacking OH radical with the alcohol or ether group. Singleton *et al.*[22] have previously explained the rapid abstraction of the acidic hydrogen in acetic acid by OH radicals in terms of a six-membered-ring transition state that involves hydrogen bonding between the incoming OH radical and the acid carbonyl group. In a similar manner, Wallington and Kurylo[23] suggested that the enhanced reactivity of C−H bonds on the β carbon atoms of aliphatic ketones compared to C−H bonds with the same bond energy in hydrocarbons was possibly due to the formation of an addition complex involving formation of a six-membered ring in which the O atom of the attacking OH radical interacts with the O atom of the carbonyl group. However, it seems more reasonable that stabilization of the transition state for the reaction of OH with alcohols, ethers, and carbonyls occurs through a H-bonded transition state as suggested by Singleton *et al.*[22] rather than by an O−O interaction. Reaction of OH with a H atom at the α carbon of an alcohol or ether would involve a five-membered ring, while attack at the β and γ carbon atoms would give rise to six- and seven-membered-ring transition states, respectively. In terms of ring strain, it is likely that the six-membered-ring structure for reaction at the β carbon atom will provide a higher degree of stabilization than the five-membered ring formed by abstraction at the α carbon atom. The rate constants for H atom abstraction from α and β $-CH_2-$ groups in alcohols or ethers seem to be almost equal, although in terms of bond energies, abstraction at the α carbon would be favored. It is suggested that the near equal reactivity of the two sites is a consequence of the enhanced stabilization of a six-membered transition state for attack at the β position. As the ring size increases beyond six, ring strain is unlikely to increase significantly; however, the entropy term for ring formation will be less favorable. Hence, as abstraction takes place at sites increasingly more remote from the alcohol or ether group the stability acquired by the transition state via hydrogen bonding will become progressively smaller. Such a decrease in reactivity is apparent in the experimental data.

The relatively large increase in reactivity shown by diethers possessing two $-CH_2-$ groups between the ether groups compared to $ROCH_2OR$ may be related to the ability of these systems to form transition states with six-membered rings rather than only a five-membered ring for $ROCH_2OR$. Some support for this argument comes from the rate data for the reaction of OH radicals with 1,4-dioxane. The low value of the rate constant may be related to the steric restrictions of a stabilized transition state involving a six-membered-ring structure.

Reactions of hydroxyl radicals with the difunctional oxygenated organics studied in this work appear to be relatively facile, and hence reaction with OH radicals is expected to be the major atmospheric sink for these species. Photolysis or reactions with NO_3 radicals and O_3 are unlikely to be significant in comparison. The atmospheric lifetime of a compound with respect to reaction with hydroxyl radicals is a function of the bimolecular rate constant and the OH concentration in the troposphere (lifetime $= 1/k_{OH}[OH]$). Assuming a tropospheric concentration of 1×10^6 molecules cm^{-3} for OH radicals in moderately polluted atmospheres, the calculated lifetimes for the oxygenated organics investigated are shown in Table 2. These may be compared with lifetimes of 110, 34, and 23 h for butane, butanol, and diethyl ether, respectively.[1−3] These lifetime data indicate that the increased reactivity of alcohols and ethers with hydroxyl radicals compared to the unsubstituted alkanes leads to relatively short lifetimes for these species in the troposphere. The available data also suggest that bifunctional group oxygen-containing compounds are likely to be removed fairly rapidly during daylight hours via reaction with OH radicals. As a consequence, the products of the OH-initiated oxidation of these species will be important in local ozone formation and also possibly in the formation of long-lived nitrogen-containing compounds.

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