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Kinetic Studies on the Reactions of Hydroxyl Radicals with Cyclic Ethers and Aliphatic Diethers

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Rate coefficients for the reactions of hydroxyl radicals with a series of cyclic ethers and aliphatic diethers have been determined at 298 ± 2 K. Experiments were performed using a photolytic relative rate method at atmospheric pressure and the absolute rate technique of pulsed laser photolysis−laser induced fluorescence. The temperature dependence of the rate coefficients for the cyclic ethers was also studied over the temperature range 263−372 K. The rate coefficients show significant deviations from simple structure−activity relationships. The reactivity of the aliphatic diethers toward hydroxyl radicals is discussed in terms of the initial formation of a hydrogen-bonded adduct which then undergoes an intramolecular H atom transfer via five-, six-, and seven-membered-ring structures. The reactivity of cyclic ethers is also discussed in relation to adduct formation. However, because of steric restrictions, it is unlikely that the hydrogen-bonded adducts readily undergo H atom transfer via ring formation.

Introduction

Ethers are emitted into the atmosphere by various anthropogenic sources. Aliphatic ethers are widely used as fuel additives and are increasingly employed as solvents to replace chlorocarbons and aromatic hydrocarbons.[1] Although not used as fuel additives, cyclic ethers are extensively used as solvents in industry. For example 1,4-dioxane is employed as a solvent for cellulose acetate, resins, oils, and waxes[2] and 1,3-dioxolane is used as an industrial solvent.[3] The release of these volatile organic compounds (VOCs) into the atmosphere is likely to contribute to the formation of ozone and other components of photochemical smog, particularly in urban areas. To understand and evaluate the impact that these compounds will have on the environment, a detailed understanding of the kinetics and mechanisms for their atmospheric degradation is required.

The primary atmospheric fate of ethers following their release into the atmosphere is reaction with hydroxyl radicals in the gas phase.[4] Several kinetic studies of the OH-initiated degradation of aliphatic ethers,[5] cyclic ethers,[6] and diethers[7,8] have been reported in the scientific literature. However, analysis of the data reveals unexpected patterns of reactivity, particularly for multifunctional compounds.[8] To elucidate further details on the reactivity of ethers, we have determined rate coefficients for the reaction of OH radicals with a series of cyclic ethers and the aliphatic diethers $CH_3O(CH_2)_3OCH_3$ and $CH_3O(CH_2)_4OCH_3$, using relative and absolute rate measurements. The chemical structures of the ethers are shown in Figure 1. Knowledge of the rate coefficients enables the estimation of the atmospheric lifetimes of these compounds. These data together with mechanistic information allow us to predict their effect on tropospheric ozone levels and the formation of other secondary pollutants.

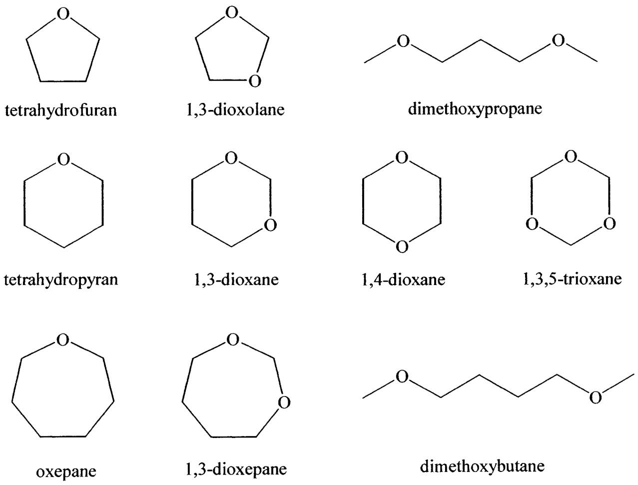

Figure 1. Chemical structures of the ethers studied in this work.

Experimental Section

Relative Rate Studies. The apparatus used in this relative rate study consisted of a collapsible 50 L FEP (fluorine−ethene−propene) Teflon reaction chamber coupled to a gas chromatograph for chemical analysis. The chamber was surrounded by 10 Philips TUV 15 W germicidal lamps which provided a source of irradiation at 254 nm. Two electric fans were positioned below the reactor to help maintain a constant temperature, which was monitored by a chromel/alumel thermocouple. The reaction chamber was kept in the dark to prevent

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photolysis of reactants prior to irradiation. Measured amounts of substrate and reference compounds were flushed from calibrated Pyrex bulbs into the reaction chamber by a stream of zero-grade air (Air Products). Hydroxyl radicals were generated by the photolysis of ozone in the presence of water vapor:

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

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

Ozone was produced by passing zero-grade air (Air Products) through an ozone generator (Monitor Labs) directly into the reaction chamber at a flow rate of 1 L min^{-1} for 10 min. Water (0.1 mL triply distilled) was injected directly into the reaction chamber. When all reactants had been added to the chamber, it was subsequently filled to maximum capacity at ca. 1 atm pressure and kept in the dark for 20 min to allow complete mixing of the reactants. A homogeneous reaction mixture was confirmed by constant, reproducible gas chromatographic analysis.

Mixtures of substrate, reference, O_3, and H_2O were photolyzed for around 10 min over the course of the experiment at 298 ± 2 K with $[\text{substrate}]_0 = [\text{reference}]_0 = 20-60$ ppm, $[O_3] \sim 50$ ppm, and $[H_2O] = 2000$ ppm, where 1 ppm $= 2.46 \times 10^{13}$ molecule cm^{-3} at 298 K and 760 Torr total pressure.

A Shimadzu 8A gas chromatograph, incorporating a flame ionization detector, was used for all analysis. The carrier gas was oxygen-free nitrogen (Air Products). The flow rates of the "flame" gases, compressed air (Irish Industrial Gases Ltd.) and hydrogen (Irish Industrial Gases Ltd.), were controlled and adjusted by means of two pressure regulators for optimal detector response. Chromatographic separation was achieved by using a 15 m wide-bore (0.53 mm i.d.) capillary column packed with either Carbowax or CP-Sil 19CB. The columns were operated over the temperature range 40−70 °C.

Absolute Rate Studies. Absolute rate studies were carried out using the technique of pulsed laser photolysis−laser induced fluorescence (PLP−LIF). Only a brief description of the system is given here as more detailed accounts are already provided elsewhere.[9,10] Hydroxyl radicals were produced by photolysis of H_2O_2 at 248 nm (KrF excimer laser, Lambda Physik LPX 105i):

$$H_2O_2 + h\nu\ (\lambda = 248\ \text{nm}) \rightarrow OH + OH \quad (3)$$

The energy of the photolysis laser was of the order 2−15 mJ per pulse in the cell and the duration of the pulse was equal to 23 ns, full width at half-maximum (fwhm). The OH concentrations were measured by laser induced fluorescence (LIF) using a Nd:YAG (Continuum) pumped frequency doubled dye laser which was triggered at a variable time after the photolysis pulse. The probe pulse excited the Q_11, Q_11^1 and the R_23 lines in the (1,0) of the $(A^2\Sigma^+, v' = 1) \leftarrow (X_2\Pi, v'' = 0)$ transition of the OH radical at around 282 nm. Hydrogen peroxide (70 wt % in water) was concentrated by bubbling helium through the solution for several days prior to use to remove water. Measured amounts of the ether vapor were released into a calibrated glass bulb and then allowed to mix with H_2O_2 and the bath gas (approximately 100 Torr helium) before being flowed vertically through the cell with a linear velocity ranging between 5 and 20 cm s^{-1}. The concentration of reactants and the bath gas were calculated from their mass flow rates, the temperature, and the pressure in the cell. All flow rates were measured with mass flow meters calibrated by measuring the rate of pressure increase in a known volume. The cell pressure was measured with a capacitance manometer positioned adjacent to the entrance of the cell. Typically, 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 (Standford Research Systems DG 535). Typically 8−15 delays were sampled to map out an OH profile over at least three lifetimes.

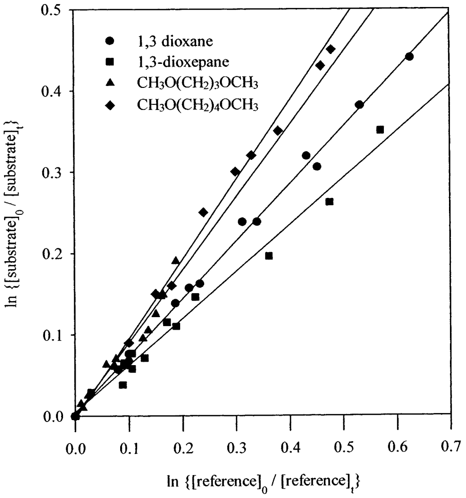


Figure 2. Relative rate plots for the reaction of OH radicals with cyclic ethers and diethers at 298 ± 2 K.

Materials. Helium carrier gas (UHP certified to >99.9995%, Alphagas) was used without further purification. Hydrogen peroxide (70 wt % in water) was obtained from Interox Chemie. All the ethers and reference compounds used in this study were obtained from Aldrich Chemical Co. (stated purities >97%) and used without further purification. Samples of the compounds were stored in evacuated glass vessels and subjected to freeze−pump−thaw cycles prior to use.

Results

Relative rate coefficients for the reaction of OH radicals with the ethers (substrates) were determined by comparing their rates of decay with the following reference compounds: $CH_3CH(OH)CH_2OCH_3$, tetrahydrofuran, $CH_3OCH_2CH_2OH$, $CH_3(CH_2)_3OH$, $C_2H_5O(CH_2)_2OC_2H_5$, and $(n\text{-}C_4H_9)_2O$.

$$OH + \text{substrate} \rightarrow \text{products} \quad (4)$$

$$OH + \text{reference} \rightarrow \text{products} \quad (5)$$

Provided that both compounds are only lost by the reaction with OH radicals, and the dilution due to sampling is negligible, it can be shown that

$$\ln\{[\text{substrate}]_0/[\text{substrate}]_t\} = k_4/k_5 \ln\{[\text{reference}]_0/[\text{reference}]_t\} \quad (I)$$

where the subscripts 0 and *t* indicate concentrations at the beginning and at 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 individual runs were carried out with each compound. Plots in the form of eq I were found to be linear with near-zero intercepts. Representative data are shown in Figure 2. Rate coefficients for the reaction of OH radicals with the ethers were calculated from the rate coefficient

TABLE 1: Rate Coefficient Ratios k_4/k_5 Determined in This Work

ether	ref compd	k_4/k_5[a]
tetrahydrofuran	$CH_3CH(OH)CH_2OCH_3$	0.97 ± 0.07
1,3-dioxolane	tetrahydrofuran	0.73 ± 0.03
tetrahydropyran	$CH_3CH(OH)CH_2OCH_3$	0.62 ± 0.03
1,3-dioxane	tetrahydrofuran	0.71 ± 0.03
1,4-dioxane	$CH_3OCH_2CH_2OH$	0.83 ± 0.06
1,3,5-trioxane	$CH_3(CH_2)_3OH$	0.66 ± 0.06
oxepane	$CH_3CH(OH)CH_2OCH_3$	0.99 ± 0.07
1,3-dioxepane	$(CH_3)_2CH(OH)CH_2OCH_3$	0.58 ± 0.04
$CH_3O(CH_2)_3OCH_3$	$C_2H_5O(CH_2)_2OC_2H_5$	0.88 ± 0.09
$CH_3O(CH_2)_4OCH_3$	$(n\text{-}C_4H_9)_2O$	1.01 ± 0.04

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

TABLE 2: Rate Coefficients for the Reaction of OH Radicals with Cyclic Ethers and Aliphatic Diethers at 298 ± 2 K

ether	k[a]	technique[b]	ref
tetrahydrofuran	17.8 ± 1.6	FP−RF	Wallington et al.[13]
	16.2 ± 2.3	FP−RF	Ravishankara et al.[14]
	18.0 ± 0.7	RR	this work
	16.7 ± 0.7	PLP−LIF	this work
1,3-dioxolane	11.1 ± 0.3	PLP−LIF	Le Calvé[15]
	8.8 ± 0.9	PR−UV	Sauer et al.[3]
	11.8 ± 0.5	RR	this work
tetrahydropyran	13.8 ± 0.7	FP−RF	Dagaut et al.[6]
	11.5 ± 0.6	RR	this work
	12.3 ± 0.4	PLP−LIF	this work
1,3-dioxane	9.2 ± 0.4	FP−RF	Dagaut et al.[6]
	11.4 ± 0.5	RR	this work
	10.3 ± 0.4	PLP−LIF	this work
1,4-dioxane	10.9 ± 0.5	FP−RF	Dagaut et al.6
	9.7 ± 0.7	RR	Porter et al.[8]
	12.6 ± 0.3	PLP−LIF	Porter et al.[8]
	12.4 ± 0.4	RR	Maurer et al.[2]
	9.5 ± 0.8	RR	this work
	12.2 ± 0.4	PLP−LIF	this work
1,3,5-trioxane	5.9 ± 0.2	LP−RF	Zabarnick et al.[16]
	6.0 ± 1.0	RR	Platz et al.[17]
	5.7 ± 0.7	RR	this work
	5.3 ± 0.2	PLP−LIF	this work
1,3-dioxepane	18.0 ± 0.7	RR	this work
	16.7 ± 0.7	PLP−LIF	this work
$CH_3O(CH_2)_3OCH_3$	55.6 ± 2.0	RR	Porter[18]
	47.5 ± 1.3	PLP−LIF	this work
	51.0 ± 5.2	RR	this work
$CH_3O(CH_2)_4OCH_3$	32.0 ± 3.5	RR	Porter[18]
	30.7 ± 0.8	PLP−LIF	this work
	29.1 ± 1.2	RR	this work

[a] Units are 10^{-12} cm^3 molecule^{-1} s^{-1}. Errors are twice the standard deviation and represent precision only. [b] FP−RF, flash photolysis−resonance fluorescence; RR, relative rate; PLP−LIF, pulsed laser photolysis−laser induced fluorescence; PR−UV, pulsed radiolysis−ultraviolet absorption; LP−RF, laser photolysis−resonance fluorescence.

ratios k_4/k_5 using the following values of k_5 (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}): $CH_3CH(OH)CH_2OCH_3$) = 18.6, tetrahydrofuran = 16.1, $CH_3OCH_2CH_2OH$ = 11.4, $CH_3(CH_2)_3OH$ = 8.6, $C_2H_5O(CH_2)_2OC_2H_5$) = 57.9, and $(n\text{-}C_4H_9)_2O$ = 28.8, taken from Porter et al.[8] and Atkinson.[4,11,12] A summary of the reference compounds and the rate coefficient ratios k_4/k_5 is given in Table 1. It should be noted that tetrahydrofuran was used as both a reactant and reference compound. All experimental rate coefficients are shown in Table 2, along with previously reported results. 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 coefficients, k_5. The errors in k_5 can add a further 25% to the uncertainty of the rate coefficients reported in these relative rate studies.

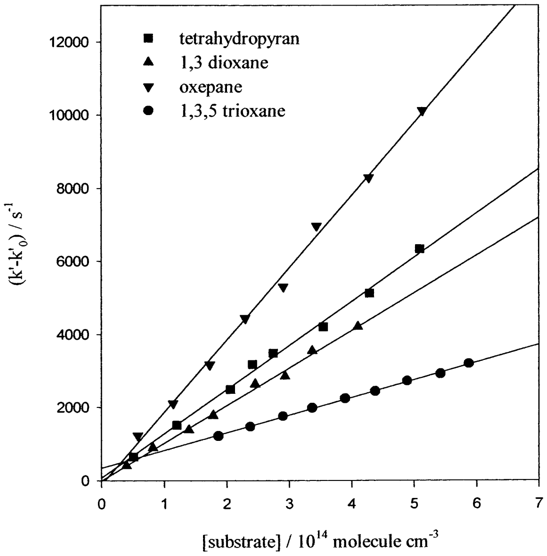


Figure 3. Plots of ($k' - k'_0$) versus substrate concentration for the reaction of OH radicals with cyclic ethers and diethers at 298 ± 2 K.

All absolute rate kinetic experiments were carried out under pseudo-first-order conditions with $[\text{substrate}]_0 \gg [OH]_0$. Following OH formation from photolysis of H_2O_2, reaction 3, the radical can be lost via the following processes:

$$OH + \text{substrate} \rightarrow \text{products} \tag{4}$$

$$OH + H_2O_2 \rightarrow \text{products} \tag{6}$$

$$OH \rightarrow \text{diffusion out of the detection zone} \tag{7}$$

Hence

$$-d[OH]/dt = (k_4[\text{substrate}] + k_6[H_2O_2] + k_7)[OH]$$

and

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

where $k' = k_4[\text{substrate}] + k'_0$.

The rate coefficient k'_0 represents the first-order decay of OH radicals in the absence of substrate ($k'_0 = k_6[H_2O_2] + k_7$). Values for k'_0 were measured to be in the range 100−300 s^{-1}. Plots of ($k' - k'_0$) versus the substrate concentration at 298 ± 2 K exhibited excellent linearity. Representative data for some of the ethers are shown in Figure 3. Absolute rate coefficients, k_4, were derived from least-squares fits of the data and are listed in Table 2. The values for the rate coefficients were shown to be independent of changes in pressure, flow rate, and laser fluence. 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 97%, and therefore loss of OH radicals by reaction with impurities in the ethers is expected to be insignificant since the reaction of OH with the ethers is relatively facile. Furthermore, the high [substrate]/[OH] ratio ensures negligible contributions from reaction of OH with primary reaction products.

The temperature dependence of the rate coefficients was investigated for all cyclic ethers except 1,3-dioxolane, which had been studied before using the same experimental system.[15] Figure 4 shows plots of the pseudo-first-order rate coefficient

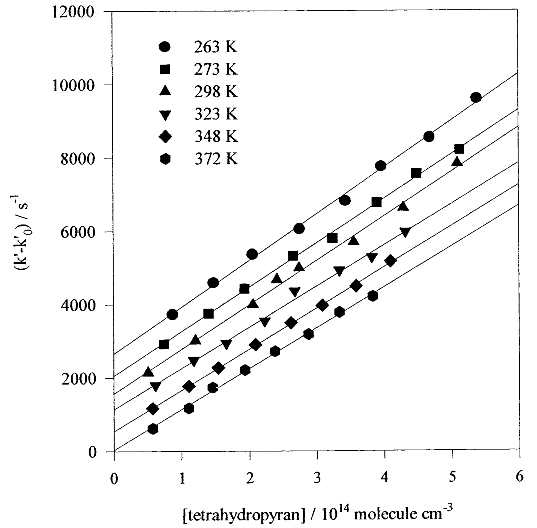


Figure 4. Plots of ($k' - k'_0$) versus substrate concentration as a function of temperature for tetrahydropyran. For reasons of clarity, values for 263−348 K have been vertically offset by 500 units in a consecutive manner.

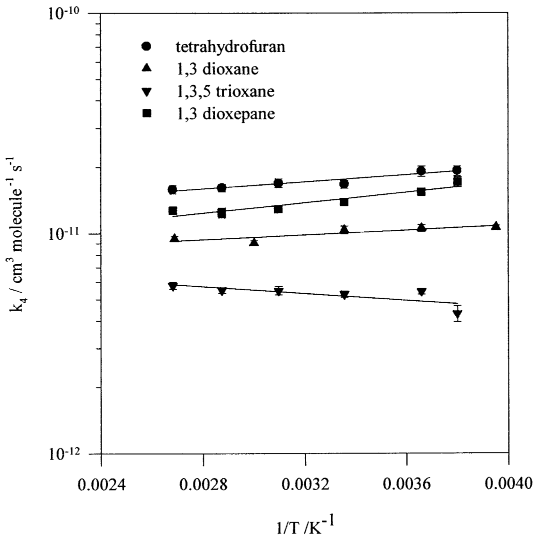


Figure 5. Arrhenius plots of kinetic data obtained for the reaction of OH radicals with cyclic ethers and diethers. The error bars of the individual points are twice the standard deviation and do not include systematic errors.

($k' - k'_0$) versus substrate concentration as a function of temperature for tetrahydropyran. Similar plots were obtained for all other cyclic ethers in the series, and a selection of the measured rate coefficients is plotted in Arrhenius form in Figure 5. All plots except 1,3,5-trioxane show that the rate coefficients have small negative temperature dependencies. The preexponential factors (*A*) and activation energies (*E*) determined from these graphs are also listed in Table 3. Also shown for completeness are the preexponential factors and activation energies determined in other studies.

Discussion

Comparison with Previous Studies. The available rate coefficient data for the reaction of OH radicals with cyclic ethers and long-chain diethers are summarized in Table 2. In general the rate coefficients obtained in this study show good agreement with those in the literature. However, the relative rate coefficient for tetrahydrofuran obtained in this work is 10% higher than the absolute rate coefficients determined in this study and by Wallington et al.[13] The reason for this discrepancy is not clear. The relative rate coefficient for 1,3-dioxolane obtained in this work is in close agreement with that determined by Le Calvé[15] using the PLP−LIF method, but both of these values are significantly higher than the value obtained by Sauer et al.,[3] who employed a pulsed radiolysis technique. The rate coefficients for 1,3-dioxane and oxepane obtained by Dagaut et al.[6] using a flash photolysis−resonance fluorescence method are 20% lower than those measured in this study, while those for 1,4-dioxane and tetrahydrofuran obtained by the same group are more in line with the present work. For 1,3,5-trioxane the rate coefficients determined by Zabarnick et al.[16] using a laser photolysis−resonance fluorescence technique and Platz et al.[17] using a conventional relative rate technique agree well with the present work. There is no previously reported value for 1,3-dioxepane, but the values determined in this study are in line with expectations. The rate coefficients determined for $CH_3O(CH_2)_3OCH_3$ and $CH_3O(CH_2)_4OCH_3$ using the relative rate method are in good agreement with the values previously reported from this laboratory.[18] The only previous studies of

TABLE 3: Absolute Rate Coefficients for the Reaction of OH Radicals with Cyclic Ethers as a Function of Temperature and the Associated Arrhenius Parameters[a]

ether	temp[b]	*k*[c]	A[c]	(*E*/*R*)[b]
tetrahydrofuran	263	19.2 ± 1.0	9.7 ± 3.2	−(177 ± 67)
	273	19.1 ± 1.0		
	298	16.7 ± 0.7		
	323	16.9 ± 0.8		
	348	16.1 ± 0.6		
	372	15.8 ± 0.7		
1,3-dioxolane[d]			6.7 ±0.9	−(154 ± 36)
tetrahydropyran	263	13.0 ± 0.4	7.8 ± 1.0	−(130 ± 44)
	273	12.2 ± 0.3		
	298	12.3 ± 0.4		
	323	11.5 ± 0.5		
	348	11.3 ± 0.2		
	372	11.2 ± 0.3		
1,3-dioxane	253	10.6 ± 0.2	6.7 ± 1.2	−(121 ± 46)
	273	10.5 ± 0.4	9.4 ± 0.2[e]	(10 ± 60)[e]
	298	10.3 ± 0.4		
	333	9.03 ± 0.2		
	372	9.44 ± 0.2		
1,4-dioxane	263	15.2 ± 0.7	4.5 ± 2.5	−(332 ± 109)
	273	14.4 ± 0.6	8.3 ± 2.2[e]	(80 ± 90)[e]
	298	12.2 ± 0.4		
	323	11.4 ± 0.5		
	348	11.1 ± 0.6		
	372	10.8 ± 0.4		
1,3,5-trioxane	263	4.3 ± 0.4	9.6 ± 1.5	(184 ± 75)
	273	5.4 ± 0.2		
	298	5.3 ± 0.2		
	323	5.5 ± 0.2		
	348	5.5 ± 0.2		
	372	5.8 ± 0.2		
oxepane	263	19.7 ± 0.2	9.9 ± 1.3	−(184 ± 39)
	273	19.2 ± 0.9		
	298	18.7 ± 0.2		
	323	17.8 ± 0.4		
	348	16.5 ± 0.8		
	372	15.9 ± 1.1		
1,3-dioxepane	263	17.1 ± 0.9	5.9 ± 1.1	−(269 ± 94)
	273	15.4 ± 0.5		
	298	13.9 ± 0.4		
	323	12.9 ± 0.6		
	348	12.4 ± 0.6		
	372	12.7 ± 0.4		

[a] Errors are twice the standard deviation and represent precision only. [b] In units of K. [c] In units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. [d] Data obtained by Le Calvé.[15] [e] Data obtained by Dagaut et al.[6]

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

ether	k_{expt}[a]	k_{SAR}[b]	lifetime[c] (h)
tetrahydrofuran	17	14	16
1,3-dioxolane	12[d]	17	28
tetrahydropyran	12	24	28
1,3-dioxane	11	29	25
1,4-dioxane	11	39	25
1,3,5-trioxane	5.5	24	51
oxepane	19	25	15
1,3-dioxepane	13	30	21
$CH_3OCH_2OCH_3$	4.9[e]	10	58
$CH_3O(CH_2)_2OCH_3$	27[e]	22	10
$CH_3O(CH_2)_3OCH_3$	50[f]	23	6
$CH_3O(CH_2)_4OCH_3$	30[f]	24	9

[a] Average experimental rate coefficient based on this work (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}). [b] Predicted rate coefficient based on SAR method (in units of 10^{-12} cm^3 molecule^{-1} s^{-1}).[22] [c] Lifetime = $1/k_{\mathrm{OH}}$[OH], where [OH] = 1×10^6 molecules cm^{-3}.[33] [d] Average of the rate data from the present relative rate study and the PLP−LIF study of Le Calvé.[15] [e] Average of the rate data from Porter et al.[8] and Wallington et al.[23] [f] Average of the data from the present relative rate studies and the PLP−LIF studies of Porter.[18]

the temperature dependence of the rate coefficients were performed by Dagaut et al.,[6] who reported Arrhenius parameters for 1,3-dioxane and 1,4-dioxane which are in reasonable agreement with this work

Trends in the Rate Coefficients for Diethers. The kinetic data obtained for the diethers, given in Table 2, can be used to test the structure−activity relationship (SAR) developed by Atkinson and co-workers[19−22] 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. As shown in Table 4, agreement between the experimental and SAR calculated values for the rate coefficients for the reactions of OH with ethers is, in general, rather poor. In particular, the calculated rate coefficients for compounds with $-CH_2-$ groups situated between two ether groups are at considerable variance with the experimental values. Diethers containing the $-OCH_2O-$ group are much less reactive than predicted by the SAR, even assuming that activation by two O atoms is equal to that from one O atom.[22] However, for $-O(CH_2)_nO-$ groups (where n = 2−4) the calculated rate coefficients are significantly lower than the experimental values. Differences between estimated and experimental rate coefficients for ethers may be expected since the SAR treatment only considers α-substituents and ether groups are known to show long-range activating effects with respect to OH radical reactions.[5,23−27]

The long-range activating effect of the ether group cannot be explained in terms of bond energy or inductive effects alone and indicates an alternative pathway to the direct concerted hydrogen abstraction process observed for alkanes. Porter et al.[8] have previously suggested that the enhanced reactivity shown by ethers may be due to the formation of a ring transition state resulting from the interaction of the attacking OH radical with the O atom of the ether group and adjacent $-CH_2-$ groups. Similarly, Smith and Ravishankara[28] have also recently discussed reactions of OH radicals with oxygenated organic compounds in terms of the formation of hydrogen-bonded complexes. The authors conclude that formation of such complexes can significantly influence the dynamics of the reactions by affecting the potential energy surface near the transition state. This could result in a lower activation energy for reaction and thus help to explain the small negative temperature dependence observed for rate coefficients determined for the reaction of OH with ethers.[11,12]

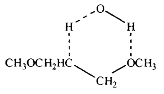
Although Smith and Ravishankara[28] limit their discussion to carboxylic acids, aldehydes, and ketones, we propose that the reactivity of aliphatic ethers and diethers with hydroxyl radicals can be rationalized in a similar manner. The initial step in the reaction involves the formation of a complex in which a hydrogen bond exists between the H atom of the attacking OH radical and the O atom of the ether. A second hydrogen bond could then be formed in the complex between the O atom of the OH radical and the H atoms in the hydrocarbon chain. Interaction of OH with a H atom at the α-carbon of an ether would involve a five-membered-ring system while interaction with H atoms at the β- and γ-carbon atoms would give rise to six- and seven-membered-ring structures, respectively. The reaction then proceeds via intramolecular H atom transfer to produce H_2O and the oxygenated alkyl radical. As discussed by Porter et al.,[8] product studies show that the rate coefficient for H atom abstraction from an α $-CH_2-$ group in an ether is about a factor of 2 higher than those for β and γ $-CH_2-$ groups. This is mainly attributed to a lower C−H bond energy in the α $-CH_2-$ group while the enhanced reactivity of the β and γ $-CH_2-$ groups in ethers compared to those in alkanes can be explained by the formation of strain-free six- and seven-membered-ring structures with the OH radical. In contrast, H atom abstraction from the α $-CH_2-$ group results in the formation of a strained five-membered-ring structure. As the ring size increases beyond six, ring strain is unlikely to increase significantly; however, the entropy for ring formation will be less favorable. Hence, as abstraction takes place at sites increasingly remote from the ether group in the OH−ether adduct, the probability of H atom transfer will become progressively smaller.

The rate coefficients for the diethers $CH_3O(CH_2)_nOCH_3$ (n = 1−4) are shown in Table 4. As discussed by Porter et al.,[8] the rate coefficient for the reaction of hydroxyl radicals with dimethoxymethane, $CH_3OCH_2OCH_3$, of 4.9×10^{-12} cm^3 molecule^{-1} s^{-1} is somewhat lower than might be expected on the basis of the reactivity of the $-CH_2-$ groups in diethyl ether. Both molecules could form a five-membered-ring transition state with the attacking OH radical.[29] However, it seems likely that the relatively low reactivity of the $-CH_2-$ group in dimethoxymethane, which is α to two oxygen atoms, is largely related to strengthening of the C−H bond compared to the α $-CH_2-$ group in monoethers. Bond dissociation energy data for C−H bonds in which the carbon atom is bound to two oxygen atoms have not been reported. However, Huie et al.[30] have previously suggested that the lower reactivity shown by SO_4^- radicals in aqueous solution toward cyclic ethers containing $-CH_2-$ groups α to two oxygen atoms compared to cyclic monoethers is related to an increase in C−H bond strength of the $-CH_2-$ groups situated between two ether groups. It was proposed that the $-OCHO-$ radical generated by H atom abstraction has an odd electron delocalized close to the two lone-pair electrons of the oxygen atoms leading to throughspace electron−electron repulsions. Such repulsions would be expected to destabilize a nascent $-OCHO-$ radical and hence reduce the reactivity of a $-CH_2-$ group α to two oxygen atoms.

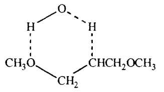
The rate coefficient for reaction of OH radicals with 1,2-dimethoxyethane, $CH_3OCH_2CH_2OCH_3$, is significantly higher than that for dimethoxymethane, $CH_3OCH_2OCH_3$. Product yield studies[31,32] indicate that abstraction at the $-CH_2-$ groups account for approximately 80% of the observed products, suggesting that the methyl groups have reactivity similar to those in dimethyl ether, and the rate coefficient per $-CH_2-$ group is around 12 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. It is reasonable to assume that the carbon−hydrogen bond strength in the $-CH_2-$ groups in $CH_3OCH_2CH_2OCH_3$ is similar to that in an α $-CH_2-$ group in monoethers. Hence the enhancement in the reactivity of the $-CH_2-$ groups in $CH_3OCH_2CH_2OCH_3$ compared to α $-CH_2-$ groups in *n*-alkyl ethers is suggested to arise largely as a result of the initial formation of a hydrogen-bonded adduct followed by formation of a six-membered-ring structure as described above.

The experimental value of the rate coefficient for the reaction of OH radicals with $CH_3OCH_2CH_2CH_2OCH_3$ as determined in this work is 51.0 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Presumably the ether groups in $CH_3OCH_2CH_2CH_2OCH_3$ are sufficiently remote from each other that the bond strengths of the α $-CH_2-$ groups are similar to those in *n*-alkyl ethers. Abstraction at the α $-CH_2-$ sites in $CH_3O(CH_2)_3OCH_3$ will thus be facile and possibly enhanced by the formation of a seven-membered-ring structure involving the H atom of the OH radical with the O atom of the ether group in the γ-position. The central $-CH_2-$ site can be activated by both ether groups due to the possibility of six-membered-ring formation in the complexes for the reaction involving either of the $-O-$ groups:

$$OH + CH_3OCH_2CH_2CH_2OCH_3 \rightarrow$$



$$OH + CH_3OCH_2CH_2CH_2OCH_3 \rightarrow$$



The net result of the activation of the α $-CH_2-$ groups and the central $-CH_2-$ group appears to give rise to the observed high reactivity of the $CH_3O(CH_2)_3OCH_3$ molecule.

Upon increasing the chain length on going from $CH_3O(CH_2)_3$-OCH_3 to $CH_3O(CH_2)_4OCH_3$, the value of the overall rate coefficient would be expected to increase due to the presence of an additional $-CH_2-$ group. However, the possibility that transfer of a H atom from the α $-CH_2-$ groups may occur by ring formation involving a hydrogen bond to the other ether group is less likely as the ring size increases, due to entropy restrictions. This may explain why the rate coefficient for reaction of OH radicals with $CH_3O(CH_2)_4OCH_3$ is lower than expected.

Trends in the Rate Coefficients for Cyclic Ethers. In an attempt to rationalize the experimental results for the cyclic ethers, it is useful to compare their reactivity with the cyclic alkanes. The rate coefficients for the reaction of OH radicals with cyclopentane, cyclohexane, and cycloheptane at 298 ± 2 K are 5.0 × 10^{-12}, 7.2 × 10^{-12}, and 13 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively.[11,12] It is evident from the present work that cyclic ethers are more reactive toward OH radicals than the analogous cycloalkanes, Table 4. A similar increase in reactivity is also shown by aliphatic ethers relative to the corresponding linear alkanes. However, calculation of the rate coefficients for cyclic ethers using the ether α-substituent factor derived by Kwok and Atkinson[22] from the kinetic data for aliphatic ethers generally overestimates the rate coefficients, whereas for linear ethers the calculated values are very much less than the experimental data. Thus, cyclic ethers appear to be considerably less reactive than their linear analogues suggesting that the long-range activating effects, which are apparent in the reactions of OH with linear ethers, are minimal in the reactions with cyclic ethers.

The long-range activating effect of the ether functional group has been rationalized in terms of the initial formation of a hydrogen-bonded adduct followed by intramolecular H atom transfer by ring formation in the adduct. Ring formation in the HO−cyclic ether adducts is likely to be sterically restricted, leading to a much lower reactivity compared with the corresponding aliphatic ethers. It is proposed that the reaction of OH radicals with cyclic ethers occurs by a direct H atom transfer process in which the hydrogen-bonded adduct that almost certainly exists between the OH radical and cyclic ether is of little importance in the reaction. The slightly negative temperature dependence observed for the rate coefficients for the reaction of OH with cyclic ethers, Table 3, are consistent with facile direct H atom transfer reactions involving OH and reactive hydrocarbons.[11,12] The *A* factors are also in the range expected for reactions of this type.

It is of interest to compare the reactivity of the $-CH_2-$ groups α to the ether functionality in tetrahydrofuran, tetrahydropyran, and oxepane. The experimental data can be used to estimate the partial rate coefficients for H atom abstraction from α-CH_2- groups in these compounds of approximately 7 × 10^{-12}, 4 × 10^{-12}, and 6 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively, assuming that the $-CH_2-$ groups remote from the ether group have reactivity similar to those in the parent cycloalkane molecules. Thus, it appears that α-CH_2- groups in cyclic ethers show a somewhat reduced reactivity compared to those in linear chain ethers.[22] The variation in reactivity with ring size is probably a consequence of slight differences in the C−H bond strengths in the cyclic ethers.

The effects of more than one ether group in cyclic ethers are well illustrated by consideration of the kinetic data for reaction of OH radicals with six-membered-ring systems. The rate coefficient for reaction of OH with 1,3,5-trioxane indicates that the rate coefficient for H atom abstraction from the $-OCH_2O-$ group is similar to that found for this group in the linear chain analogue $CH_3OCH_2OCH_3$. The relatively low reactivity of the $-OCH_2O-$ group compared to an α-CH_2- group in monoethers appears to be mainly related to a higher C−H bond energy in the diether.[30] The rate coefficient for reaction of OH with 1,4-dioxane shows that the $-O(CH_2)_2O-$ group in the compound is around a factor of 4 less reactive than in $CH_3O(CH_2)_2OCH_3$. 1,3-Dioxane contains $-OCH_2O-$ and $-O(CH_2)_3O-$ groups. Assuming the reactivity of the $-OCH_2O-$ group is similar to that in 1,3,5-trioxane, then the $-O(CH_2)_3O-$ group is some 5 times less reactive than in the corresponding linear chain ether. As previously discussed, this low reactivity of the $-CH_2-$ groups in six-membered cyclic diethers is probably related to the steric restrictions on ring formation of HO−cyclic ether adducts. In a similar manner, the rate coefficients for reaction of OH with 1,3-dioxolane and 1,3-dioxepane indicate that the respective $-O(CH_2)_2O-$ and $-O(CH_2)_4O-$ groups in these cyclic ethers are considerably less reactive than in linear chain diethers.

Atmospheric Implications. Reactions of OH radicals with all of the ethers studied in this work are relatively facile, and hence gas-phase reaction with OH radicals is expected to be the major atmospheric sink for these compounds. The atmospheric lifetime of a compound with respect to reaction with OH radicals can be calculated by lifetime = $1/k_{OH}[OH]$, where k_{OH} is the bimolecular rate coefficient and [OH] is the tropospheric concentration of OH radicals. In a relatively polluted atmosphere [OH] is generally taken as 1×10^6 molecules cm^{-3}.[33] The calculated lifetimes for the ethers studied in this work are shown in Table 4. The relatively short lifetimes for these compounds indicate that, if released into the atmosphere, they will undergo degradation in the free troposphere and contribute to regional ozone formation and possibly the long-range transport of NO_y.

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