Kinetic Studies on the Reactions of Hydroxyl Radicals with Cyclic Ethers

A contribution to subproject CMD

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Introduction

Ethers are widely used as fuel additives and solvents, and some short chain ethers are being considered as alternatives to conventional automobile fuels. The effect of these species on tropospheric ozone and the formation of other secondary pollutants following release into the atmosphere is therefore of some concern (Porter *et al.*, 1997). The major fate of oxygenated organic compounds released into the atmosphere is reaction with hydroxyl radicals (Atkinson, 1989) and the rate at which compounds react with OH radicals can provide estimates of their atmospheric lifetimes.

The purpose of this work is to determine rate coefficients for the reaction of OH radicals with a series of cyclic ethers using a photolytic relative rate method. The rate coefficients for the reaction of OH radicals with cyclic ethers appear to show significant deviations from simple structure-activity relationships (Kwok and Atkinson, 1995). The results also yield estimates of the atmospheric lifetimes and hence indicate the potential impact these compounds will have on the environment.

Experimental

Relative rate experiments were carried out at 298 ± 2 K and atmospheric pressure in an FEP Teflon cylindrical vessel (volume ~ 50 L). The chamber was surrounded by ten Philips TUV 15 W germicidal lamps which have an intensity maximum at 254 nm. Measured amounts of both substrate and reference compounds were flushed from calibrated Pyrex bulbs into the reaction vessel containing ozone and water, by a stream of ultra-pure air, and the chamber was then filled to its full volume with air. Hydroxyl radicals were generated from the photolysis of O_3 in the presence of water vapour.

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

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

Reaction mixtures were allowed to mix for at least 30 minutes prior to the start of photolysis. The loss of reagents was monitored by flame ionisation gas chromatography and the resulting linear concentration-time profiles were used to provide values of k_{OH}.

Results

The hydroxyl radicals formed will react with the substrate and reference compounds

$$OH + \text{substrate} \rightarrow \text{products} \qquad (3)$$

$$OH + \text{reference} \rightarrow \text{products} \qquad (4)$$

Table 1: Experimental rate coefficients for the reaction of OH radicals with cyclic ethers at 298 ± 2 K

Substrate	$10^{12}\,k_{expt}$ [a, b]	Technique [c]	Reference
tetrahydrofuran	19.6 ± 1.5	RR	This work
	17.8 ± 1.6	FP-RF	Wallington *et al.*, 1988
1,3-dioxolane	11.8 ± 0.5	RR	This work
	11.1 ± 0.3	PLP-LIF	Le Calvé *et al.*
tetrahydropyran	11.5 ± 0.6	RR	This work
	13.8 ± 0.7	FP-RF	Dagaut *et al.*, 1990
1,3-dioxane	11.4 ± 0.5	RR	This work
	9.2 ± 0.4	FP-RF	Dagaut *et al.*, 1990
1,4-dioxane	9.7 ± 0.8	RR	This work
	9.7 ± 0.7	RR	Porter *et al.*, 1988
1,3,5-trioxane	5.3 ± 0.5	RR	This work
	5.9 ± 0.2	LP-LIF	Zabarnick *et al.*, 1988
oxepane	18.6 ± 1.4	RR	This work
	15.4 ± 1.3	FP-RF	Dagaut *et al.*, 1990
1,3-dioxepane	12.3 ± 0.9	RR	This work

[a] In units of $cm^3\ molecule^{-1}\ s^{-1}$. [b] Errors are twice the standard deviation and represent precision only. [c] RR, relative rate; PLP-LIF, pulsed laser photolysis–laser-induced fluorescence; FP-RF, flash photolysis-resonance fluorescence; LP-RF, laser photolysis–resonance fluorescence.

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

$$\ln \{[\text{substrate}]_0 / [\text{substrate}]_t\} = k_3 / k_4 \ln \{[\text{reference}]_0 / [\text{reference}]_t\}$$

where the subscripts 0 and t indicate concentrations before irradiation and at time t respectively.

Under reaction conditions employed, the substrate and reference compound were found to decay by approximately 50 % during the experiments and concentration-time data plotted according to this equation showed the expected linear relationship. The experimental rate coefficients are shown in Table 1. There is good agreement between results obtained in this study and previously reported data. A comparison of the experimental rate coefficients and those calculated by the methods of structure-activity relationships (SAR) and group reactivities (GR) are shown in Table 2.

Table 2: Experimental and calculated rate coefficients for the reaction of OH radicals with cyclic ethers at 298 ± 2 K and the corresponding tropospheric lifetimes.

Substrate	$10^{12} k_{\text{expt}}$[a, b]	$10^{12} k_{\text{SAR}}$[a, c]	$10^{12} k_{\text{GR}}$[a, d]	lifetime [e]/hours
Tetrahydrofuran	19.6	15	20	14
1,3-Dioxolane	11.8	19	27	24
Tetrahydropyran	11.5	24	27	24
1,3-Dioxane	11.4	29	31	24
1,4-Dioxane	9.7	39	32	29
1,3,5-Trioxane	5.3	24	32	53
Oxepane	18.6	25	30	15
1,3-Dioxepane	12.3	30	35	23

[a] In units of cm^3 $molecule^{-1}$ s^{-1}. [b] Rate data from this work. [c] Kwok and Atkinson (1995) [d] Dagaut *et al.*, (1989).
[e] Lifetime = $1/k_{OH}[OH]$; $[OH] = 1 \times 10^6$ molecule cm^{-3}.

Discussion

The kinetic data for the reactions with cyclic ethers can be used to test the structure-activity relationships (SAR) developed by Kwok and Atkinson (1995) to estimate OH radical rate coefficients for hydrogen atom abstraction reactions from organic compounds. Calculation of H-atom abstraction rate coefficients for C-H bonds is based on the estimation of —CH_3, —CH_2— and >CH— group rate coefficients, assuming that the rate coefficients are dependent on the identity of the substituents attached to the group. Agreement between the experimental data and the SAR calculated values for the cyclic ethers is, in general, rather poor. The cyclic ethers themselves do not appear to be as reactive as the corresponding aliphatic ethers and their reactivity depends on the number and position of the oxygen atoms in the ring. The most obvious trend seen is that, for ethers of the same ring size, the order of reactivity is monofunctional > difunctional > cyclic alkane, thus showing the enhancement of the rate coefficient by addition of an O atom and deactivation if two or more O atoms are present. There appears to be no correlation between strain energies and reactivity and therefore it is likely that steric effects strongly influence k_{OH}.

The atmospheric lifetime of a compound with respect to reaction with OH radicals is a function of the bimolecular rate coefficient and the OH concentration in the troposphere, (lifetime = $1/k_{OH}[OH]$). Assuming a tropospheric concentration of 1×10^6 molecule cm^{-3} for OH radicals in a moderately polluted atmosphere, the lifetime of the cyclic ethers are found to vary between 14 and 53 hours, Table 2. Because the rate coefficients are relatively fast compared to unsubstituted alkanes cyclic ethers have shorter lifetimes in the atmosphere. These compounds will be fairly rapidly removed *via* reaction with OH radicals and the products of the OH initiated oxidation of cyclic ethers will be important in local ozone formation.

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