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A Kinetic Study on the Reactions of OH Radicals with Esters and Alkoxy Esters

A contribution to subproject CMD

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Introduction

Esters and alkoxy esters are the main atmospheric oxidation products of ethers and diethers, both of which are used as solvents and fuel additives. Reaction with the hydroxyl radical is the principal fate of these oxygenated compounds in the troposphere. In this study rate constants were determined for the reactions of the hydroxyl radical with a series of formates and alkoxy formates. Kinetic data was obtained by both absolute and relative methods, and average values were used to calculate the tropospheric lifetimes. The reactivity of esters and alkoxy esters is discussed with reference to the parent ether compounds.

Experimental

Relative rate measurements were carried out at 298 ± 2 K and atmospheric pressure in a 50 L FEP Teflon cylindrical reaction chamber surrounded by 10 Philips TUV 15W germicidal lamps which have an intensity maximum at 254 nm. Measured amounts of substrate and reference compounds were flushed into the chamber with ultra-pure air, and the chamber was then filled to its full volume with air. OH radicals were generated from the photolysis of ozone in the presence of water vapour. Gas chromatography with flame ionisation detection was used to monitor the loss of substrate and reference compounds. The resulting concentration-time profiles provided values of k_{OH} .

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Absolute rate data were obtained using pulsed laser photolysis - laser induced fluorescence. Hydroxyl radicals were generated by the photolysis of H_2O_2 at 248 nm using a KrF excimer laser and their concentration was monitored using laser induced fluorescence. A Nd:YAG pumped frequency doubled dye laser was used to excite the OH radical at 282 nm. Fluorescence from the OH radical was detected by a photomultiplier fitted with a 309 nm narrow bandpass filter. Experiments were carried out under pseudo first-order conditions with $[\text{substrate}] > 100 k[\text{OH}]$. Plots of k' versus $[\text{substrate}]_0$ provided values of k_{OH} . A detailed description of both experimental methods is available in the literature (Porter *et al.*, 1997).

Results and discussion

The rate constant data determined in this study for the reactions of OH radicals with formates and alkoxy formates are presented in Table 1.

Table 1: Rate data for the reaction of OH radicals with formates and alkoxy formates at 298 ± 2 K

Substrate	$10^{12} k^a$	Technique ^b	Reference	Lifetime ^c
HC(O)OCH ₃	0.18 ± 0.01	RR	This work	64 days
	0.17 ± 0.02	PLP-LIF	Le Calvé <i>et al.</i> ^d	
HC(O)OC ₂ H ₅	0.99 ± 0.03	RR	This work	13 days
	0.85 ± 0.08	PLP-LIF	Le Calvé <i>et al.</i> ^d	
HC(O)OCH ₂ OCH ₃	1.99 ± 0.17	RR	This work	144 hours
	1.87 ± 0.10	PLP-LIF	This work	
HC(O)OCH ₂ OC ₂ H ₅	3.71 ± 0.22	RR	This work	66 hours
	4.70 ± 0.18	PLP-LIF	This work	
HC(O)OCH ₂ CH ₂ OCH ₃	6.19 ± 0.33	RR	This work	43 hours
	6.60 ± 0.14	PLP-LIF	This work	
HC(O)OCH ₂ CH ₂ OC ₂ H ₅	11.06 ± 0.69	RR	This work	25 hours
	11.34 ± 0.60	PLP-LIF	This work	

^a in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; ^b RR : relative rate, PLP-LIF : pulsed laser photolysis - laser induced fluorescence; ^c lifetime = $1/k_{\text{OH}}[\text{OH}]$; $[\text{OH}] = 1 \times 10^6 \text{ molecule cm}^{-3}$;

^dLe Calvé *et al.*, 1997.



Data obtained in this work by both the absolute and relative methods are in excellent agreement. For methyl formate and ethyl formate the data from this work agrees well with the values determined by Le Calvé *et al.* (1997).

Rate constants were determined for the OH radical reaction with alkoxy esters over the temperature range 263–372 K. All of these reactions show a slight negative temperature dependence. This is probably due to near-zero activation energies and negative temperature dependent pre-exponential factors.

The reactivity of esters towards hydroxyl radicals can be explained by comparison with the reactivity of the parent ether compounds. k_{OH} for the formates, HC(O)-OR , is lower than that for the parent ethers by at least a factor of ten. For the alkoxy formates, $\text{HC(O)O(CH}_2)_n\text{OR}$, k_{OH} is two to four times lower than k_{OH} for the corresponding ether, $\text{RO(CH}_2)_n\text{OR}$ (Porter *et al.*, 1997). Product studies on these reactions (O'Donnell *et al.*) indicate that H-atom abstraction occurs primarily at the $-\text{OR}$ end of the molecule. This indicates that the lower reactivity exhibited by the formates is due to the strong deactivating effect of the formate group on the alkyl and alkoxy part of the molecules.

The reactivity of the $-\text{CH}_2-$ group in $\text{CH}_3\text{OCH}_2\text{OCH}_3$ resembles that in an alkane, while the reactivity of the $-\text{CH}_2-$ group in $\text{HC(O)OCH}_2\text{OCH}_3$ is significantly lower. The reactivity of the $-\text{C}_2\text{H}_5$ group in $\text{HC(O)OCH}_2\text{OC}_2\text{H}_5$ is much lower than that of the $-\text{C}_2\text{H}_5$ group in the parent ether. The deactivating effect of the formate group therefore extends beyond the ether oxygen and is experienced by the end alkyl group.

The ester derivatives of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ and $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ show similar reduced reactivity compared to that of their parent ether compounds. The extent of the deactivating effect of the formate group is expected to be less due to the presence of a longer alkyl chain between the two functional groups.

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