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Kinetics for the OH Reaction with Oxygenated VOCs

A contribution to subproject CMD

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Introduction

Oxygenated Volatile Organic Compounds (OVOCs) have a wide range of application (solvents, fuels additives, ...); they are also formed as intermediates in the atmospheric degradation of a variety of volatile organic compounds. These OVOCs are introduced to the atmosphere where they undergo complex chemical transformations which result in the production of ozone and other secondary pollutants in urban and rural areas. The main tropospheric degradation process for the OVOCs is the reaction with OH radicals. To assess their impact on the air quality, accurate kinetic and mechanistic data for their oxidation initiated by the OH radical are required.

We have determined rate constant data for the reaction of OH radicals with a series of 18 esters using the laser photolysis-laser induced fluorescence method (Boudali *et al.*, 1996; Le Calvé *et al.*, 1997a; 1997b; 1997c). The results yield estimates of the atmospheric lifetimes of these OVOCs. In addition, the results complement the existing database used for the calculation of the rate constants for the gas phase reactions of the OH radical with organic compounds using structure-reactivity relationships, specially the SAR developed by Atkinson (1995).

Results and discussion

The rate constants obtained at room temperature are given in Table 1 for the series of OVOCs studied in this work. From the results obtained, the following conclusions can be drawn.

Atmospheric lifetimes

With a typical tropospheric OH concentration of 10^6 molecule cm^{-3} , the estimated tropospheric lifetimes for the studied OVOCs are in the range 1.6 day (*n*-propyl acetate and methyl caproate) to more than 2 months (methyl

formate). Since the primary reaction of OH with OVOCs is likely to be the rate limiting step in the overall oxidation mechanism, these lifetimes together with transport data are essential parameters in defining the location of ozone and photo-oxidant formation. For the compounds with short lifetimes, the generation of ozone and photo-oxidants will be close to the emission sources.

Table 1: Comparison between experimental and calculated values and the calculated lifetimes for the studied esters.

compound	$10^{12} \times k_{\text{exp}}^{\text{a,b}}$	$10^{12} \times k_{\text{exp}}^{\text{a,c}}$	$10^{12} \times k_{\text{calc}}^{\text{a,d}}$	$10^{12} \times k_{\text{calc}}^{\text{a,e}}$	lifetime(days)
methyl formate	0.173±0.021	0.227±0.034	0.218	0.172	66.9
ethyl formate	0.852±0.075	1.02 ± 0.14	1.66	0.818	13.6
<i>n</i> -propyl formate	1.80 ± 0.17	2.38 ± 0.27	3.15	2.10	6.4
<i>n</i> -butyl formate	3.54 ± 0.52	3.12 ± 0.33	4.57	3.42	3.3
<i>tert</i> -butyl formate	0.746±0.091		0.502	0.593	15.5
methyl acetate	0.322±0.026	0.341±0.029	0.319	no change	36
ethyl acetate	1.67 ± 0.22	1.51 ± 0.14	1.76	no change	7
<i>n</i> -propyl acetate	3.42 ± 0.26	3.45 ± 0.34	3.26	no change	3.4
<i>n</i> -butyl acetate	5.52 ± 0.51	4.15 ± 0.30	4.67	no change	2.1
<i>n</i> -pentyl acetate	7.34 ± 0.91		6.08	no change	1.6
iso-propyl acetate	3.77 ± 0.29	3.72 ± 0.29	3.55	no change	3.1
iso-butyl acetate	6.33 ± 0.52		4.67	no change	1.8
<i>sec</i> -butyl acetate	6.04 ± 0.58	5.65 ± 0.59	5.41	no change	1.9
<i>tert</i> -butyl acetate	0.56 ± 0.05		0.604	no change	21
methyl propionate	0.831±0.087	1.03 ± 0.04	1.08	1.21	14
ethyl propionate		2.14 ± 0.30	2.52	2.65	5.4
<i>n</i> -propyl-propionate		4.02 ± 0.32	4.01	4.14	2.9
methyl butyrate	3.30 ± 0.25	3.04 ± 0.33	2.38	3.29	3.5
ethyl butyrate		4.94 ± 0.38	3.83	4.73	2.3
<i>n</i> -propyl butyrate		7.41 ± 0.32	5.32	6.23	1.6
<i>n</i> -butyl butyrate		10.6 ± 1.3	6.73	7.64	1.1
methyl valerate	4.83 ± 0.55		3.80	4.91	2.4
methyl caproate	7.15 ± 0.70		5.21	6.32	1.6

^a: units of molecule cm^{-3} ; ^b: our values; ^c: values from Wallington *et al.*, (1988);
^d: SAR from Kwoka and Atkinson (1995); ^e: modified SAR: $F(-\text{CH}_2\text{C}(\text{O})\text{OR}) = 2.2$;
 $F(-\text{OC}(\text{O})\text{H}) = 0.6$; $k(\text{HC}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work)

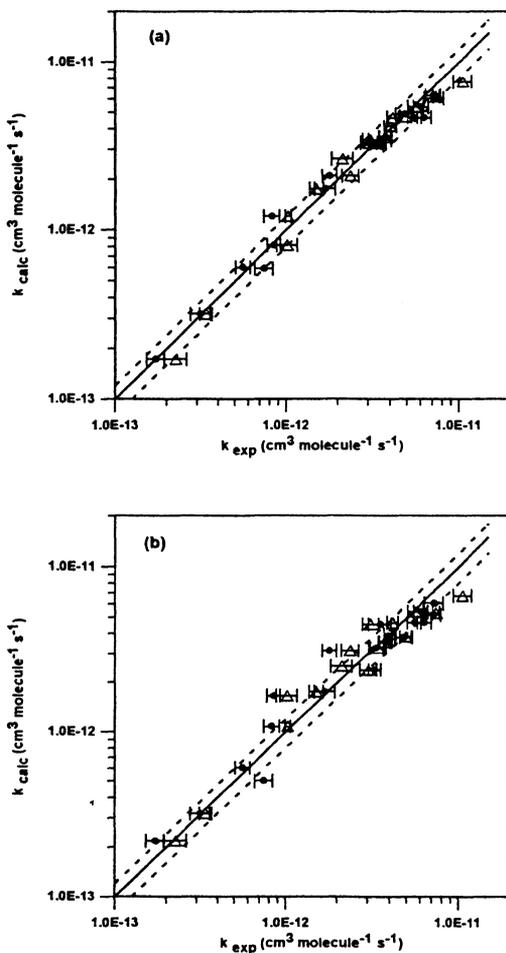


Fig. 1: Comparison of the experimental, k_{exp} , and calculated, k_{calc} , rate constants at 298 K for OH reaction with 23 esters. The experimental data are from this work and Wallington *et al.*, (1988). The dashed lines correspond to a departure of 20 % from the best fit (solid line).

(a) The substituent factors are: $F(-\text{CH}_2\text{C}(\text{O})\text{OR}) = 2.2$; $F(-\text{OC}(\text{O})\text{H}) = 0.6$;
 $k(\text{H}-\text{C}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work), $F(-\text{C}(\text{O})\text{OR}) = 0.74$
and $F(-\text{OC}(\text{O})\text{R}) = 1.6$ (Kwok and Atkinson, 1995).

(b) $F(-\text{C}(\text{O})\text{OR}) = 0.74$;

$F(-\text{OC}(\text{O})\text{R}) = 1.6$, and $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 1.23$ (Kwok and Atkinson, 1995).

**Trends in the OH + ester reaction rate constants**

The present rate constant values can be compared with those calculated from the updated structure-activity relationship (SAR) of Atkinson based on group reactivity (Kwok and Atkinson, 1995). By fitting the calculated and experimental rate constant values, the following new substituent factors were derived:

$$F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 2.2, \quad F(-\text{O}-\text{C}(\text{O})\text{H}) = 0.6$$

and $k(\text{H}-\text{C}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

These values, together with the existing values $F(-\text{C}(\text{O})\text{OR}) = 0.74$ and $F(-\text{OC}(\text{O})\text{R}) = 1.6$ [SAR], have been used to calculate the rate constants at 298K for a series of 23 esters, for which experimental rate constants are available for comparison. The experimental rate constants are from the present work and from the work of Wallington *et al.*, (1988). The experimental and calculated rate constants are reported in Table 1. The calculated values using the substituent factors from Kwok and Atkinson (1995) are also reported :

$$F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 1.23, \quad F(-\text{O}-\text{C}(\text{O})\text{H}) = 1.6$$

and $k(\text{H}-\text{C}(\text{O})\text{OR})$ is considered as negligible.

The plots of the present calculated values against experimental ones, $\log k_{\text{calc}}$ vs $\log k_{\text{exp}}$ are shown in Fig. 1a. Fig. 1b gives similar plots where k_{calc} are calculated using the substituent factors from Kwok and Atkinson (1995). A comparison of both figures show a slightly better correlation in Fig. 1a.

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