Transactions on Ecology and the Environment vol 28, © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

Kinetic Studies on the Reaction of OH Radicals with Aromatic Compounds

A contribution to subproject CMD

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Introduction

Aromatic compounds when released into the atmosphere can have a direct effect on health as well as contributing to the formation of secondary air pollutants including ozone. The major loss process for aromatics in the troposphere is by reaction with the OH radical and the rate constants with several aromatics have been established (Atkinson, 1989). The degradation of aromatics by the OH radical proceeds via two pathways: addition to the benzene ring or abstraction of a H atom from an alkyl side chain. All investigations have shown that the ratio of addition over abstraction is temperature dependant and at room temperature the addition pathway for toluene predominates with a ~ 90 % contribution to the overall rate constant.

Structure activity trends from previous studies have shown that increasing the degree of alkyl substitution leads to increased reactivity towards the electrophilic OH radical. However, there has been no systematic study carried out on the effect of increasing the length of the alkyl side chain. Fluorinated aromatics are widely used as intermediates in the chemical industry however there have been relatively few studies to date on the reactions of OH with these compounds (Atkinson, 1989 and references therein).

The main focus of this work was to determine room temperature rate constants for the reaction of OH radicals with a series of (i) alkyl benzenes and (ii) fluorinated aromatics using a relative rate technique. The results are compared with previous literature values and discussed in terms of structure activity relationships.

Proceedings of EUROTRAC Symposium '98
Editors: P.M. Borrell and P. Borrell

Experimental and results

All experiments were carried out in a 50 L Teflon reaction chamber housed in a constant temperature(298 ± 2K) cabinet and surrounded by 10 germicidal lamps ($\lambda = 254$ nm).

OH radicals were produced by the photolysis of ozone in the presence of water vapour. Quantitative analyses were carried out by monitoring the decays of the organics by GC-FID on a DB-5MS 30 m × 0.53 mm column. The kinetic investigation was carried out using a relative rate technique (Atkinson *et al*,1981) and Fig. 1 shows a typical plot for a series of alkyl substituted aromatics. Relative rate constants for all aromatics studied were placed on an absolute basis using k(OH + cyclohexane) = 7.5×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson, 1989) and are shown in Table 1 together with the available literature data.

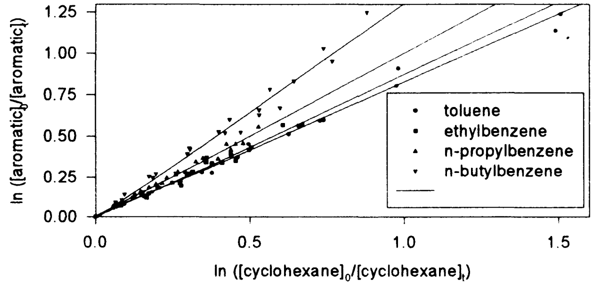


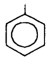
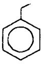
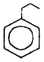
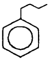
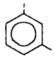
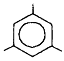
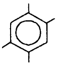
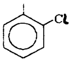
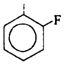
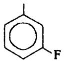
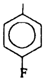
Fig. 1: Relative rate plots for the alkylbenzene series at 298 K and 1 atm.

Discussion

Alkylbenzenes

In general, the room temperature rate constants determined in this work are in agreement with previous literature values. Rate constants for the straight chain alkyl benzenes show a slight but definite increase along the series: toluene < ethylbenzene < *n*–propylbenzene < *n*–butylbenzene. This may be due to one or a combination of two factors: a) the rate of addition is enhanced due to the increased inductive effect of the larger alkyl group; b) the relative importance of the abstraction pathway increases with alkyl chain length.

Table 1: Rate constants for reaction of OH radicals with a series of aromatic compounds at 298K and 1 atm.

Aromatic	$k_{298} \times 10^{12} cm^3 molec^{-1} s^{-1}$	Reference
Benzene 	1.23	Atkinson, 1989
	1.3 ± 0.1	Wallington *et al.*, 1987
	1.24 ± 0.12	Hansen *et al.*, 1975
	1.4 ± 0.1	This work
Toluene 	5.96	Atkinson, 1989
	6.37 ± 0.08	Ohta *et al.*, 1985
	5.78 ± 0.58	Hansen *et al.*, 1975
	6.18 ± 0.22	This work
Ethylbenzene 	7.1	Atkinson, 1989
	6.84 ± 0.30	Ohta *et al.*, 1985
	7.95 ± 0.50	Ravishankara *et al.*, 1978
	7.0 ± 1.4	Lloyd *et al.*, 1976
	6.58 ± 0.32	This work
n–propylbenzene 	6.0	Atkinson, 1989
	6.94 ± 0.24	Ohta *et al.*, 1985
	5.86 ± 0.50	Ravishankara *et al.*, 1978
	5.4 ±1.1	Lloyd *et al.*, 1976
	7.51 ± 0.28	This work
n–butylbenzene 	9.90 ± 0.52	This work
m–xylene 	23.6	Atkinson *et al.*, 1989
	23.6 ± 2.4	Hansen *et al.*, 1975
	24.0 ± 2.5	Perry *et al.*, 1977
	23.1 ± 2.2	This work
1,3,5–trimethylbenzene 	57.5	Atkinson *et al.*, 1989
	47.2 ± 4.8	Hansen *et al.*, 1975
	62.4 ± 7.5	Perry *et al.*, 1977
	69.7 ± 4.3	This work
1,2,4,5-tetramethylbenzene 	62.47 ± 4.4	This work
2-chlorotoluene 	2.58 ± 0.19	This work
2-fluorotoluene 	2.20 ± 0.09	This work
3-fluorotoluene 	4.60 ± 0.10	This work
4-fluorotoluene 	3.18 ± 0.17	This work

The rate constants obtained allow for calculation of an average $-CH_2-$ group rate constant for reaction with OH radicals of ~ 1.24×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This value is similar to the group rate constant previously estimated (Atkinson, 1987) for hydrogen atom abstraction by OH radicals from $-CH_2-$ groups in alkanes ($k_{-CH2-} = 1.29 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) which would strongly suggest that the enhanced reactivity is due mainly to an increase in the importance of the abstraction pathway.

The correlation between the rate constant for OH radical addition to aromatic rings and the sum of the electrophilic substituent constants $\Sigma\sigma+$(Brown and Okamata, 1958), provides a means of estimating the rate constant for OH radical addition to the aromatic ring. Using this correlation it has been reported for a series of aromatic compounds (Atkinson *et al* 1987) that:

$$\log k_{add}\ (cm^3\ molecule^{-1}\ s^{-1}) = -\ 1.35\ \Sigma\sigma+ -\ 11.69$$

This may be used to predict the room temperature rate constants for the addition of OH radicals to the aromatic ring for the methyl substituted benzenes and halotoluenes studied. The calculated rate constant for 1,2,4,5-tetramethylbenzene(38×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) and 2–chlorotoluene (4×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) are in broad agreement with those determined in this work, however, the calculated rate constant for 2-fluorotoluene (7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) is considerably greater than the experimental value.

Halotoluenes

As with previous studies on halogenated aromatics (Atkinson, 1989 and references therein), the results of this study show that the presence of a halogen on the aromatic ring decreases the reactivity towards OH radicals relative to the parent aromatic. Furthermore, consistent with previous work (Wallington *et al.*, 1987), a systematic decrease in reactivity was observed with increasing degree of electronegativity of the halogen substituent (*e.g.* 2-fluorotoluene is less reactive than 2-chlorotoluene).

From the observed rate constants it appears that the relative positioning of the halogen on the ring has a significant effect on reactivity towards the OH radical. The stability of the addition adduct is central to rationalising these differences in reactivity. As with carbocations, the stability order of alkyl radicals is tertiary > secondary > primary. This is due to delocalisation of electrons through overlap between the half-filled *p* orbital and the σ orbital of the alkyl group known as hyperconjugation stabilisation. It can be shown that the 3-fluorotoluene adduct has three of a possible twelve resonance structures stabilised by hyperconjugation whereas the adducts of both 2-fluorotoluene and 4-fluorotoluene have only two such resonance stabilised structures each. Using

Transactions on Ecology and the Environment vol 28, © 1999 WIT Press, www.witpress.com, ISSN 1743-3541

this rationale it is expected that 3-fluorotoluene would be more reactive than either 2-fluorotoluene or 4-fluorotoluene.

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