The Reactivity of Chlorine Atoms in Aqueous Solution

A contribution to subproject CMD

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Introduction

The Cl· atom is an extremely reactive species which may be produced in cloud water by the reaction of $SO_4^{\cdot -}$ with chloride (McElroy, 1990). In the presence of chloride, the equilibrium

$$Cl\cdot + Cl^- \leftrightarrow Cl_2^{\cdot -} \quad (1)$$

is formed with $K_1 = 1.4 \times 10^5$ dm^3 mol^{-1} (Buxton, *et al.*, 1998). Taking [Cl^-] to be 10^{-4} mol dm^{-3} in cloud water, it may be seen that $Cl_2^{\cdot -}$ is the predominant form of radical chlorine in the atmospheric aqueous phase. Perhaps for this reason, many studies have been made of the reactions of $Cl_2^{\cdot -}$ (Hasegawa, *et al.*, 1978) whilst there has been little done on the Cl· atom. However, previous work (Gilbert, *et al.*, 1988, and Buxton, *et al.*, 1998) has shown that Cl· reacts rapidly with many species and even at high [Cl^-] contributes to the decay of $Cl_2^{\cdot -}$ through equilibrium (1). This study aims to provide data on the reactions of Cl· independently of equilibrium (1) by using the photolysis of chloroacetone as a source of the Cl· atom.

Experimental

Laser flash photolysis was carried out using an Excimer Mulitiplex Laser operating at 248 nm. Photolysis of chloroacetone in aqueous solution has been reported to produce chlorine atoms, reaction (2) (Treinin and Hayon, 1975, Strachan and Blacet, 1955). The Cl· atoms were monitored by kinetic spectroscopy at 320 nm.

$$CH_3COCH_2Cl + h\nu \rightarrow \cdot CH_2COCH_3 + Cl\cdot \quad (2)$$

Pulse radiolysis was carried out as described in Buxton *et al.* (1998).

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

Reactions of Cl· with solutes.

The decays were analysed for the reactions of Cl· with a number of organic species. The absorption profile fitted a first-order decay down to a plateau, which was due to $\cdot CH_2COCH_3$ and products from reactions of the Cl· atom (see Fig. 1). Gradients from the plots of k_{obs} *vs* solute concentration, [S], were used to determine the bimolecular rate constants at 10 °C intervals from 5 to 35 °C.

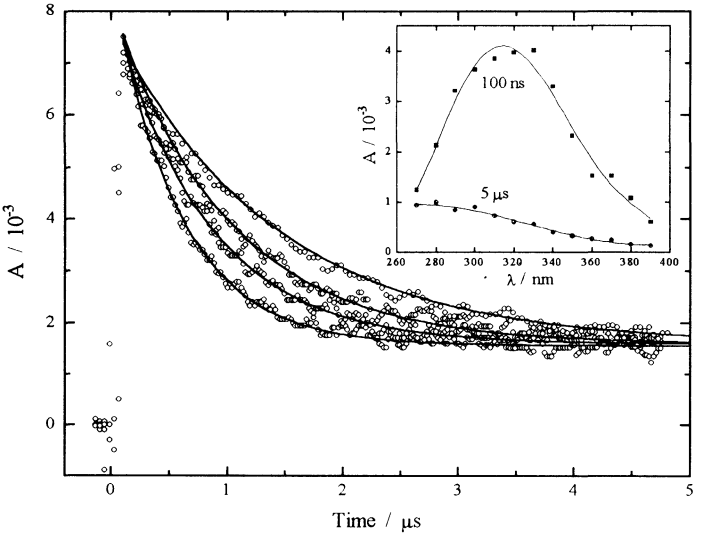

Fig. 1: Absorption at 320 nm following LFP of chloroacetone with various [*t*-BuOH], see Table 1.

The intercepts of k_{obs} *vs* [S] correspond to the reactions of Cl· with water and chloroacetone and were in the range (3.0 to 5.0) × 10^5 s^{-1}. There was a slight increasing trend with temperature, but the typical error of ± 0.5 × 10^5 s^{-1} meant that the effect was barely noticeable. Subtracting the contribution from the reaction with chloroacetone (see below) gave an estimate for the rate of reaction with water of *ca.* 2 × 10^5 s^{-1} at 25 °C.

Pulse radiolysis study

The rate of decay of $Cl_2^{\cdot -}$ was measured in Ar-saturated solution over a range of [Cl^-] and [chloroacetone] (see *t*-BuOH from Buxton *et al.*, 1998). The results are shown in Fig. 2 and give a rate constant for Cl· with chloroacetone of (9.7 ± 1.5) × 10^6 dm^3 mol^{-1} s^{-1} at 25 °C.

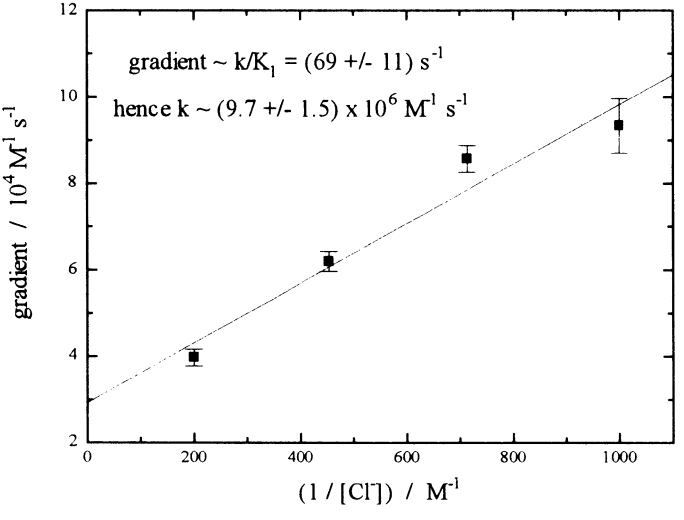

Fig. 2: Gradients of (k_{obs} *vs* [chloroacetone]) *vs* $[Cl^-]^{-1}$ from pulse radiolysis.

Discussion

The rate constants measured in this study are listed in Table 1. The values for Cl· with *t*–BuOH and water are in agreement with our previous work in chloride solution (Buxton *et al.*, 1998).

Activation energies are of similar magnitude for all the organic species at around 10 to 20 kJ mol^{-1}. For alcohols, the trend in E_a is opposite to that of the ·OH radical, for which a decrease with decreasing C–H bond strength is reported, (Elliot and Simsons, 1984) as expected for an H-abstraction reaction. This suggests that Cl· may react by a different mechanism. Gilbert *et al.*, reported that Cl· reacts with alcohols by both H-abstraction and electron transfer (from the OH group), based on ESR spectra of the products. However,

the reaction with water was not considered by Gilbert and it is possible that the formation of ·OH by this route, and hence H-abstraction products, were attributed to the Cl· reaction. Further work is being undertaken to make clearer the mechanisms and pattern of reactivity of the Cl· atom.

Table 1: The rate constants determined in this study.

Reaction /Cl·+ S	[S] range /10^{-3} M	k at 25 °C /M^{-1} s^{-1}	E_a /kJ mol^{-1}
H_2O	–	*ca.* 2×10^5 [a]	–[b]
CH_3COCH_2Cl[c]	0 to 30	$(9.7 \pm 1.5) \times 10^6$	–[b]
CH_3OH	0.2 to 1.0	$(1.0 \pm 0.1) \times 10^9$	12 ± 2
CH_3CH_2OH	0.1 to 0.7	$(1.7 \pm 0.1) \times 10^9$	15 ± 2
$(CH_3)_3COH$	0.2 to 1.4	$(6.2 \pm 0.5) \times 10^8$	21 ± 2
HCHO	0.2 to 0.8	$(1.4 \pm 0.1) \times 10^9$	–[b]
$HCOO^-$ (pH 6)	0.1 to 0.4	$(4.2 \pm 0.3) \times 10^9$	16 ± 2
HCOOH (pH 1)	2.5 to 10.0	$(1.3 \pm 0.1) \times 10^8$	9 ± 1
CH_3COO^- (pH 6)	0.1 to 0.4	$(3.7 \pm 0.5) \times 10^9$	13 ± 2
CH_3COOH (pH 1)	10 to 40	$(3.2 \pm 0.1) \times 10^7$	8 ± 1

[a] Units s^{-1} [b] Not determined [c] Obtained by pulse radiolysis

Acknowledgements

This work is supported by NERC research grant GST/02/1258.

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