Absolute Rate Constant for the Reaction of Benzylchlorocarbene with Hydrogen Chloride

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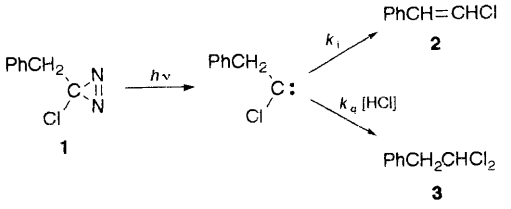
The rate constant for the reaction of benzylchlorocarbene with HCl is 4.7×10^9 dm^3 mol^{-1} s^{-1}

Laser flash photolysis (LFP) of 3-alkyl-3-chlorodiazirines has received a high level of attention recently.[1–5] Since the alkylchlorocarbenes do not absorb above 300 nm, the pyridine probe technique[6] is used to monitor the kinetics of the carbenes. However, in the LFP of 3-chloro-3-benzyldiazirine **1**, the UV absorption spectrum of benzylchlorocarbene[7] has been observed in the 290–330 nm range and therefore the lifetime of the benzylchlorocarbene can be studied directly. We now report the absolute rate constant for the reaction of HCl with benzylchlorocarbene since little is known about the reaction of acids with carbenes.

The UV spectrum of a solution of **1** in isoctane consists of a



structured absorption band in the 310–370 nm region, with low absorption coefficients, and a second band in the 220–290 nm range, broad and intense. Transient absorption measurements are possible in the window, 290–330 nm, between these two bands. LFP of 0.02 mol dm^{-3} **1** in degassed isooctane solution at 25 °C gives a transient absorption in the 305–330 nm region and is assigned to the benzylchlorocarbene. This signal decays to zero with a lifetime of 19 ns which is in excellent agreement with the 18 ns lifetime reported by one of us[7] using a different laser flash apparatus. The lifetime of the carbene is determined by the rate of the 1,2-H migration to produce *Z*- and *E*-β-chlorostyrenes, **2**. The reaction of HCl and benzylchlorocarbene gives 1-phenyl-2,2-dichloroethane **3**.

In the LFP experiments, μl portions of a saturated solution of HCl in isooctane were added to a 2.0 ml sample of 0.02 mol dm^{-3} diazirine in isooctane. The rate constant for the quenching of carbene by HCl was determined from the rate of carbene decay, $k_d = k_i + k_q$ [HCl], measured at 310 nm as a function of HCl concentrations. Least squares analysis of 11 measurements (Fig. 1) with HCl concentrations ranging from 0.1 to 5.2 mmol dm^{-3} gives $k_q = 4.68 \pm 0.46 \times 10^9$ dm^3 mol^{-1} s^{-1} and $k_i = 5.20 \pm 0.12 \times 10^7$ s^{-1}.

It is to be noted that the addition of HCl shortened the lifetime of the carbene. Upon the addition of 5.2 mmol dm^{-3} HCl, the lifetime of the carbene is 13 ns which is approaching the limit of the ns laser apparatus, *i.e.* laser pulse width is 8 ns (FWHM). The reaction of HCl and carbene is diffusion-controlled and a variable temperature study was not attempted. However, efforts were made to search for a new transient due to the absorption of the carbocation, PhCH$_2$C$^+$–HCl, but no significant changes were found in the spectrum. The only evidence for the formation of an ion pair was obtained in the photolysis of **1** in DCl[7] in which a mixture of deuteriated and non deuteriated **2** and **3** were formed. Unfortunately, the k_i/k_q ratio cannot be compared directly with the value from relative rate studies because the reaction was carried out in diethyl ether. Relative rate studies cannot be studied in the present case because of the low solubility of HCl in isooctane (0.1 mol dm^{-3}). Photolysis of **1** in an equimolar mixture of HCl and HOAc in diethyl ether revealed that HCl appears to be approximately three times as effective as acetic acid in the quenching of benzylchlorocarbene.[8] LFP experiments in isooctane lead to the following quenching rate constants: k_q(HCl) = 4.7×10^9 and k_q (HOAC)[9] = 1.0×10^9 dm mol^{-1} s^{-1}.

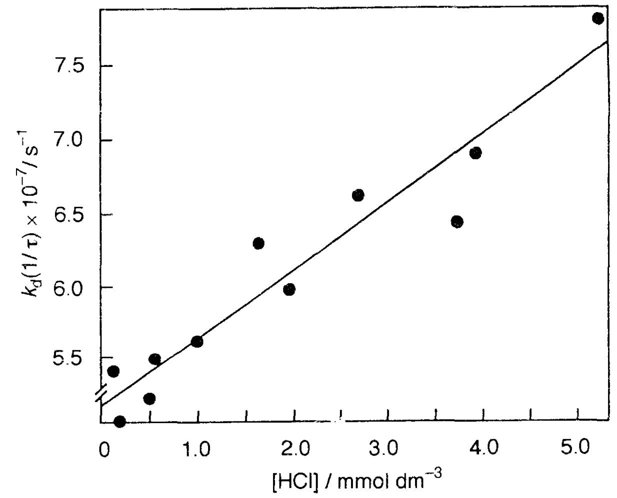


Fig. 1 1/τ *vs.* [HCl]

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