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SHORT COMMUNICATION

DIRECT MEASUREMENT OF THE ENERGY BARRIER FOR 1,2-CHLORINE ATOM MIGRATION IN α-METHYL-α-CHLOROBENZYL(CHLORO)CARBENE

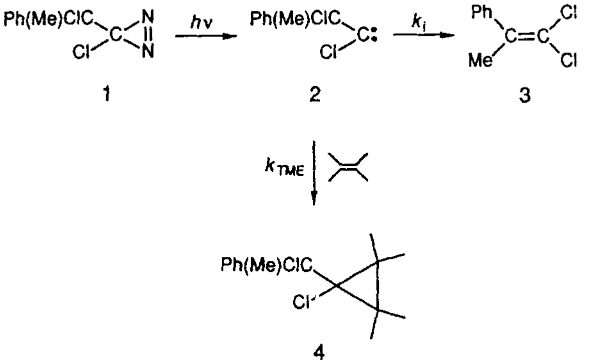
MICHAEL T. H. LIU
Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, C1A 4P3 Canada

AND

JOHN E. CHATEAUNEUF
Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, USA

The first direct determination of a 1,2-chlorine atom shift in a chlorobenzylcarbene was achieved by nanosecond laser flash photolysis. Arrhenius activation parameters of $E_{act} = 3.39 \pm 0.14$ kcal mol^{-1} and log $[A(s^{-1})] = 10.98 \pm 0.14$ were obtained for 1,2-chlorine migration in α-methyl-α-chlorobenzyl(chloro)carbene. The lifetime of this carbene is considerably longer than previously estimated and the measured E_{act} is in excellent agreement with that determined by product analysis.

Recently, the activation energy for 1,2-chlorine migration in α-methyl-α-chlorobenzyl(chloro)carbene (**2**) was accurately measured by classical methods.[1] The energy barrier was determined by the temperature dependence on product distribution between intramolecular rearrangement of carbene **2** to α-methyl-β,β-dichlorostyrene (**3**) and competitive cyclopropanation with tetramethylethylene (TME) to form cycloadduct **4** (Scheme 1). In order to place the competitive reactivity of carbene **2** on an absolute scale, a comparison of the activation parameters for the cyclopropanation of *p*-chlorobenzyl(chloro)carbene with TME was required. This comparison resulted in an estimate of the room temperature lifetime of carbene **2** to be <1 ns and therefore beyond direct spectroscopic detection in the nanosecond regime. In this paper we report the lifetime of carbene **2** to have been underestimated and describe the measurement of the Arrhenius activation parameters for chlorine atom migration in carbene **2** and the absolute rate constant for reaction of **2** with TME by nanosecond laser flash photolysis (LFP).



Scheme 1.

The LFP apparatus has been described previously.[2] A Quanta Ray DCR-1 Nd : YAG (*ca* 8 mJ, pulse width *ca* 6 ns) provided laser excitation at 355 nm with a pulsed 1000 W xenon lamp as the monitoring source. Temperatures were stabilized to ±0·2 °C prior to each kinetic experiment. 3-α-Methyl-α-chlorobenzyl-3-chlorodiazirine (**1**) was prepared by the method of Graham[3] and purified by column chromatography (silica gel; hexanes) prior to use.

It has been demonstrated[1] that photolysis of diazirine **1** in isooctane generates ground-state singlet carbene **2** which primarily yields the chlorine migration product **3** in the absence of quenching substrates. LFP at 355 nm of a 0.8 OD (optical density) solution of **1** in isooctane at room temperature (21 °C) resulted in a transient absorption signal observed within the excitation pulse that closely followed the time profile of the laser pulse (Figure 1). The absorption signal ranged from 290 to

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340 nm (Figure 1, inset) with $\lambda_{max} = 320$ nm. The spectral characteristics and subsequently observed reactivity of this species were found to be nearly identical with those of the parent benzylchlorocarbene,[4] and therefore this transient is assigned to carbene **2**.

It was found that at temperatures below $-20\,^{\circ}$C the lifetime of **2** became significantly longer than the excitation pulse (Figure 1), and therefore the absolute decay kinetics of **2** could be obtained. Monitoring at 310 nm, the first-order rate constants (k_i) for decay of **2** were measured from $-20\cdot1$ to $-71\,^{\circ}$C. The temperature dependence on k_i (Figure 2) resulted in an Arrhenius activation energy of $E_{act} = 3\cdot39 \pm 0\cdot14$ kcal mol^{-1} (1 kcal = $4\cdot184$ kJ) and log $[A(\mathrm{s}^{-1})] = 10\cdot98 \pm 0\cdot14$.

The activation energy measured is identical with that predicted by the relative rate study,[1] but the A factor is considerably smaller than the value of 12.1 previously estimated. Using the activation parameters for the reaction of *p*-chlorobenzyl(chloro)carbene with TME as equivalent to those for **2** with TME resulted in the erroneous lifetime predicted. The current results predict $k = A\exp(-E_{act}/RT)$, $1/k = 3\cdot5$ ns at 21 °C, as opposed to $0\cdot3$ ns (estimated). The longer lifetime is consistent with the observation of **2** within the laser pulse, since the time for full decay of the carbene would be comparable to the pulse profile.

The differences in activation parameters for k_i and k_{TME} obtained in the previous study[1] now allow for the prediction of $E_{TME} = -4\cdot69 \pm 0\cdot26$ kcal mol^{-1} and log $A_{TME} = 4\cdot16$. Unfortunately these values have not been corroborated by direct measurement since the determination of k_{TME} over a substantial temperature range was not obtainable. A reliable k_{TME} of $(9\cdot49 \pm 1\cdot16) \times 10^{7}$ l mol^{-1} s^{-1} was determined, however, at $-60\,^{\circ}$C (Figure 2, inset). Calculation of k_{TME} at $-60\,^{\circ}$C yields a rate constant of $9\cdot34 \times 10^{8}$ l mol^{-1} s^{-1}. This discrepancy is not unexpected, however, considering the severe and well publicized non-linearity of Arrhenius plots below $-20\,^{\circ}$C for the reaction of other halocarbenes with TME.[5]

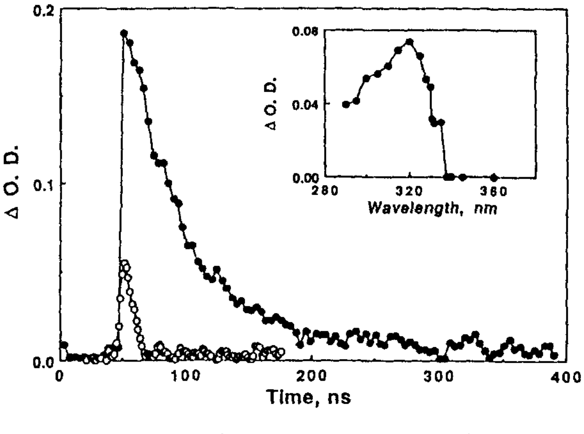

Figure 1. Time-resolved absorption signals observed at 310 nm following 355 nm LFP of **1** in isooctane at (○) 21 °C and (●) −70 °C. Inset, absorption spectrum observed at 21 °C

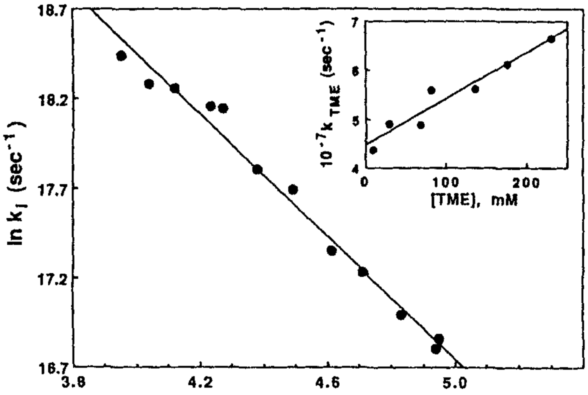

Figure 2. Arrhennius plot for the 1,2-chlorine atom migration of carbene **2**. Inset, quenching plot for the reaction of **2** with TME at −60 °C

In conclusion, the first direct determination of a 1,2-chlorine atom migration in a chlorobenzylcarbene has been reported. Even though the A factor presented appears low for an intramolecular reaction, the value obtained is similar to those reported[6,7] for 1,2-hydrogen migration in other halocarbenes, and is most likely a ramification of a highly ordered transition state.[8]

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