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The 1,2-Hydrogen Rearrangement of Methylchlorocarbene: Contribution of Quantum Mechanical Tunneling

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The 1,2-hydrogen and carbon rearrangements of singlet alkylcarbenes to alkenes is a reaction of current theoretical and experimental interest.[1,2] Several recent experiments have focused on the temperature dependence of the rate constants for these rearrangements.[3] Interestingly, the obtained activation parameters are quite different from those predicted by theory. In particular, the energies are smaller and the entropies significantly more negative than the values obtained from *ab initio* molecular orbital calculations. Although several explanations for this discrepancy have been presented, none has been adequately tested.[2,3] In this regard, we have reinvestigated the 1,2-hydrogen shift of methylchlorocarbene,[4] and we believe that quantum mechanical tunneling may provide an answer. We have determined the rate constants for this reaction as a function of temperature and isotopic substitution. Our results suggest that the reaction proceeds classically at high temperatures, as suggested by theory, but proceeds primarily by quantum mechanical tunneling at low temperatures.

Irradiation of methylchlorodiazirine (**1**) yields methylchlorocarbene (**2**), which subsequently undergoes a 1,2-hydrogen rearrangement to vinyl chloride (**3**) (Scheme I).[4] The rate of this rearrangement as a function of temperature (11.5 to 61.0 °C) has been previously determined by photoacoustic calorimetry (PAC).[4] The obtained Eyring parameters, $\Delta H^{\ddagger} = 4.3$ kcal/mol and $\Delta S^{\ddagger} = -16.1$ eu, differ significantly from the calculated values, $\Delta H^{\ddagger} = 10.6$ kcal/mol and $\Delta S^{\ddagger} = -3.2$ eu.[2a,5b]

Scheme I

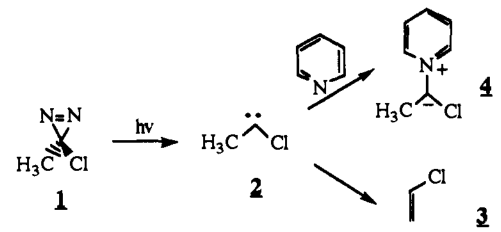

Table I. Rates of Disappearance of **2** (k_H) and **2**-d_3 (k_D) in 1,2-Dichloroethane at Various Temperatures[7]

T (K)	k_H (10^5 s^{-1})	k_D (10^5 s^{-1})	k_H/k_D
248	8.4 (2.2)[a]	9.5 (1.5)	0.9
273	9.2 (0.8)	8.7 (0.4)	1.1
294	12.1 (1.0)	8.4 (1.0)	1.4
313	14.9 (1.4)	9.5 (1.0)	1.6
343	30.8 (6.0)	17.3 (2.5)	1.8

[a] The values in parentheses are 1σ from at least five determinations.

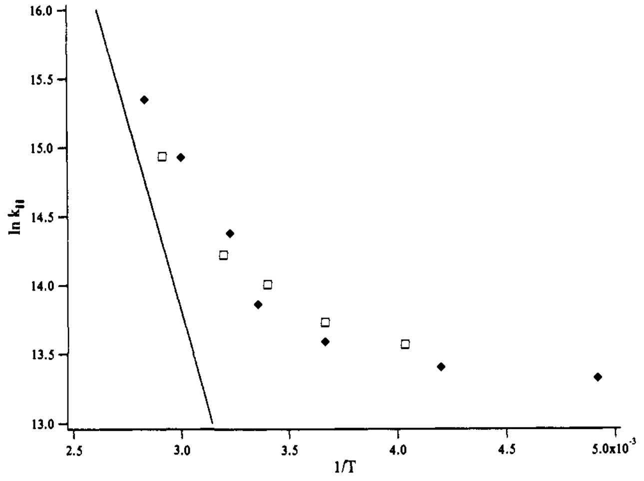

Figure 1. Plot of ln k_H vs $1/T$ for **2** in heptane (◆) and 1,2-dichloroethane (□). The solid line indicates the theoretical values for the classical pathway.

The temperature range employed for these previous studies was limited by our experimental PAC apparatus. However, we have now measured the rate of this rearrangement over a wider temperature range in both 1,2-dichloroethane (−25 to 70 °C) and heptane (−70 to 80 °C) by nanosecond absorption spectroscopy, using the pyridinium ylide method.[6] In the presence of pyridine, methylchlorocarbene (**2**) forms the pyridinium ylide **4** ($\lambda_{max} = 368$ nm), whose rate of appearance and yield can be determined. Extrapolation of the observed rate constant to [pyridine] = 0 at each temperature yields the rate constant for disappearance of **2** (k_H), presumably due to the 1,2-hydrogen rearrangement, Table I.[7] The Arrhenius plot, ln k_H vs $1/T$, clearly shows pronounced curvature over the wider temperature range employed in this study, Figure 1. The rate of rearrangement of methylchlorocarbene-d_3 (**2**-d_3, k_D), prepared from photolysis of methylchlorodiazirine-d$_3$ (**1**-d_3) in $C_2H_4Cl_2$,[9] as a function of temperature was also measured, Table I. The obtained values of k_H/k_D show a rather surprising trend over the temperature range; they increase with *increasing* temperature.

Several different constructs can potentially explain these two experimental observations, the curved Arrhenius plot and the increasing k_H/k_D with temperature. One possibility is that this

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(7) This extrapolated rate constant is equal to the sum of *all* the rate constants which destroy **2**. An intermolecular reaction between carbene **2** and **1**, which presumably yields azine, does compete with rearrangement to **3**. A double extrapolation which involves varying [**1**] removes this contribution to k_H.[8] The rate constant is also independent of O_2 concentration. The dimerization of **2** at low temperatures is also a possible reaction. However, the extrapolated rate constant is independent of laser power, and no 2,3-dichloro-2-butene is found when **1** is decomposed under laser conditions. In addition, the yield of heptane C–H insertion products are <5% at all the temperatures employed in this study.

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rearrangement may have a variable transition state because of its small activation energy and large negative activation entropy.[11] A reaction as such should indeed show a curved Arrhenius plot and have k_H/k_D either increase or decrease with temperature. Although variational transition-state theory (VTS) has been previously applied to carbene cycloaddition reactions,[12] theoretical studies by Houk and co-workers have indicated that this reaction is adequately described by conventional transition-state theory.[5] In addition, VTS theory alone does not explain why this reaction should be so entropically disfavored.

A second possibility is that methylchlorocarbene disappears by two (or more) competing pathways to yield vinyl chloride and an additional product (or products). The relative contribution of these two pathways would potentially change with temperature: the corresponding Arrhenius plot would be curved if the two competing pathways have different apparent activation energies, and k_H/k_D could increase with temperature if the two pathways have different isotope effects. Although vinyl chloride **3** is formed in high yield (>80%), several other minor products (mostly azine) are formed, presumably from carbene **2**. However, the rate constants for disappearance of **2** have been corrected at each temperature to account for the formation of these products.[7] Consequently, other reactions of carbene **2** which compete with the 1,2-rearrangement do not appear to satisfactorily explain the experimental observations.

A third possibility involves a contribution from quantum mechanical tunneling: the reaction proceeds classically at high temperatures, as suggested by theory, but proceeds primarily by quantum mechanical tunneling at low temperatures. Although tunneling has not been observed experimentally for a 1,2-hydrogen rearrangement of a carbene, theory, in fact, suggests that it can be extremely important.[2i,5a] Given the mass and the small requisite bending movement of the migrating hydrogen, tunneling can contribute significantly even when the classical barrier is quite small.

The calculated rate constants for the classical pathway are shown by the solid line in Figure 1.[2a,5b] As the temperature increases, the observed rate constant approaches that predicted by theory.[14] Deviation from classical behavior occurs at lower temperatures, as tunneling dominates. At 298 °C, tunneling accounts for >85% of the total reaction. In fact, the surprisingly large rate constants for tunneling can perhaps explain several unsuccessful attempts to matrix isolate and characterize **2** at low temperatures (10–77 K).[15] The increase in k_H/k_D with increasing temperature can be explained by assuming that the classical pathway has an appreciable isotope effect over the temperature range of these studies and that the tunneling correction reduces it.[5,16]

In conclusion, consideration of quantum mechanical tunneling in the reaction $\mathbf{2} \rightarrow \mathbf{3}$ can explain (i) the observed curved Arrhenius plot, (ii) the increase in k_H/k_D with increasing temperature, and (iii) the previously observed unusual Eyring parameters. In fact, other carbene rearrangements involving both hydrogen and carbon might also involve tunneling, as perhaps indicated by their large negative activation entropies.[3] Further experiments will be necessary to determine if tunneling is indeed important in 1,2-rearrangements of other carbenes.

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