

Rearrangement of an Ammonium Ylide: Mechanisms and Kinetic Parameters

Roland Bonneau* and Ingmar Reuter

Université de Bordeaux I
UA 348 du CNRS, F-33405 Talence Cedex, France

Michael T. H. Liu

University of Prince Edward Island
Charlottetown, PE, C1A 4P3 Canada

Received August 9, 1993

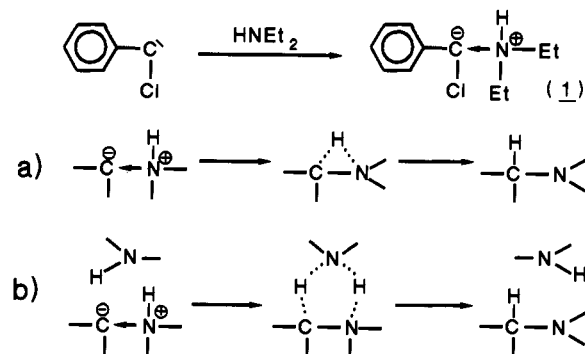
The insertion of singlet carbenes such as arylchlorocarbenes into the N–H bond of amines proceeds via the formation of an ammonium ylide followed by migration of the H atom from the nitrogen to the carbon center. Two mechanisms may be responsible for this H migration: a 1,2-H shift, shown in Scheme 1a, with a rate constant k_{sh} , and an exchange mechanism, where an amine molecule interacts with the ylide as shown in Scheme 1b, with a rate constant k_{ex} .

Theoretical calculations¹ predicted an activation energy equal to 12.5 kcal/mol for the 1,2-H shift, giving CH_3NH_2 from $\text{CH}_2\text{-NH}_3$, so with a preexponential factor in the range 10^{12} – 10^{13} s^{-1} , the rate of the 1,2-H shift at room temperature should be around 10^3 – 10^4 s^{-1} . The ammonium ylide **1** formed from phenylchlorocarbene and diethylamine (DEA) was recently observed by laser flash photolysis;² its lifetime, around 30 ns when $[\text{DEA}] \approx 0.05 \text{ M}$ and decreasing as $[\text{DEA}]$ increases, suggests that the exchange mechanism would be largely predominant. However, the rate for the 1,2-H shift in **1** may be much larger than the value calculated in CH_2NH_3 , due either to an activation energy in **1** lower than that in CH_2NH_3 (substituent effects) or to a tunneling process similar to the one invoked for the rearrangement of methylchlorocarbene.³ We now present a measurement of the kinetic parameters for the 1,2-H shift in ylide **1** which allows the determination of the relative efficiency of these mechanisms for the ylide rearrangement.

The experimental setup uses a mode-locked Nd-YAG laser (200 ps), frequency tripled (355 nm), and the cell holder was put into a clear Dewar flask where it could be cooled down to -90°C by a stream of cold nitrogen gas. The temperature was measured with a thermocouple immersed in the solution. The carbene was produced by laser photolysis of the parent diazine in isooctane in the presence of DEA at various concentrations ranging from 17 to 114 mM, and the absorption of the ylide was monitored at 340 nm. In most cases (high values of $[\text{DEA}]$ and/or low temperature), the rate of formation of the ylide ($\approx 2 \times 10^9 [\text{DEA}]$) is much faster than its decay, so the decay of the transient absorption at 340 nm may be analyzed as a simple first-order process. For the lower values of $[\text{DEA}]$ and temperatures greater than 0°C , the rates for formation and decay of the ylide are of the same order of magnitude, and the kinetic analysis procedure used in these cases allows extraction of the real value of the decay rate constant from the experimental curve.

The decay of ylide **1**, $-\text{d}[1]/\text{d}t = k_{sh}[1] + k_{ex}[\text{DEA}][1]$, is a pseudo-first-order process since the value of $[\text{DEA}]$ is several orders of magnitude larger than the concentration of carbene produced by a laser pulse. Therefore, the observed decay rate

Scheme 1



constant is $k_{obs} = (k_{sh} + k_{ex}[\text{DEA}])$ or:

$$k_{obs} = A_{sh} \exp(-E_{sh}/RT) + A_{ex}[\text{DEA}] \exp(-E_{ex}/RT) \quad (1)$$

The plots of $\log(k_{obs})$ vs $1/T$, shown on Figure 1, are not straight lines, indicating that both the 1,2-H shift and the exchange mechanisms are efficient in the considered range of temperature and that their activation energies are different. When the exchange mechanism is predominant, $k_{obs} \approx A_{ex}[\text{DEA}] \exp(-E_{ex}/RT)$, so that, for a given temperature:

$$\log(k_{obs}) = C + \log([\text{DEA}]) \quad (2)$$

with $C = \log(A_{ex}) - E_{ex}/(2.303RT)$. The spacing of the curves obtained with various values of $[\text{DEA}]$ should be equal to $\log([\text{DEA}])$. This appears to be the case for the "low-temperature" region (right side of Figure 1), whereas the value of k_{obs} depends only slightly on $[\text{DEA}]$ when $T > 0^\circ\text{C}$. Therefore, the 1,2-H shift mechanism must be associated with the large activation energy.

Values of A_{sh} , A_{ex} , E_{sh} , and E_{ex} have been estimated by computer fitting of the sets of experimental data with theoretical curves drawn from eq 1. Several methods have been used:

(a) The five sets of data obtained with the five values of $[\text{DEA}]$ were fitted by using the nonlinear least-squares analysis module of GraphPad InPlot, 4 (GraphPad Software Inc.). This program does not optimize the values entered for A_{sh} and A_{ex} , but, for any couple of values given to these parameters in the ranges $(0.4\text{--}8) \times 10^{12} \text{ s}^{-1}$ ($0.4\text{--}5$) $\times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively, the four sets of points corresponding to the four higher values of $[\text{DEA}]$ are fitted with the same (within 5% or less) values of E_{sh} and E_{ex} .

(b) Each set of data points was then fitted by using a program taken from *Data Reduction and Error Analysis for the Physical Sciences*.⁴ This program adjust all four parameters and gives five sets of values in the following ranges: $(1.2 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for A_{ex} ; $0.41 \pm 0.07 \text{ kcal/mol}$ for E_{ex} ; $(1.95 \pm 0.75) \times 10^{12} \text{ s}^{-1}$ for A_{sh} ; and $6.0 \pm 0.2 \text{ kcal/mol}$ for E_{sh} .

(c) The plot of $\log(k_{obs} - A_{ex}[\text{DEA}] \exp(-E_{ex}/RT))$ vs $(1/T)$ (see Figure 2) should give a single line for all the points obtained with the various $[\text{DEA}]$ values, with an intercept of $\log(A_{sh})$ and a slope of E_{sh}/R . A good fit between the 84 data points recorded with the four higher $[\text{DEA}]$ values and a single line is obtained for A_{ex} in $(4.2\text{--}13) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and E_{ex} in $0\text{--}0.4 \text{ kcal/mol}$, yielding $A_{sh} = (1.5 \pm 1) \times 10^{12} \text{ s}^{-1}$ and $E_{sh} = 5.8 \pm 0.5 \text{ kcal/mol}$.

From these analyses, one can define only rather large confidence intervals such as:

$$A_{sh} (2 \pm 1.5) \times 10^{12} \text{ s}^{-1} \quad A_{ex} = (1.3 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

$$E_{sh} = 5.9 \pm 0.7 \text{ kcal/mol} \quad E_{ex} = 0.2 \pm 0.2 \text{ kcal/mol}$$

(1) Pople, J. A.; Raghavarachi, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1983, 105, 6389.

(2) Bonneau, R.; Liu, M. T. H. *J. Am. Chem. Soc.* 1991, 113, 9872.

(3) Dix, E. J.; Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* 1993, 115, 10425.

(4) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill, Inc.: New York, 1969.

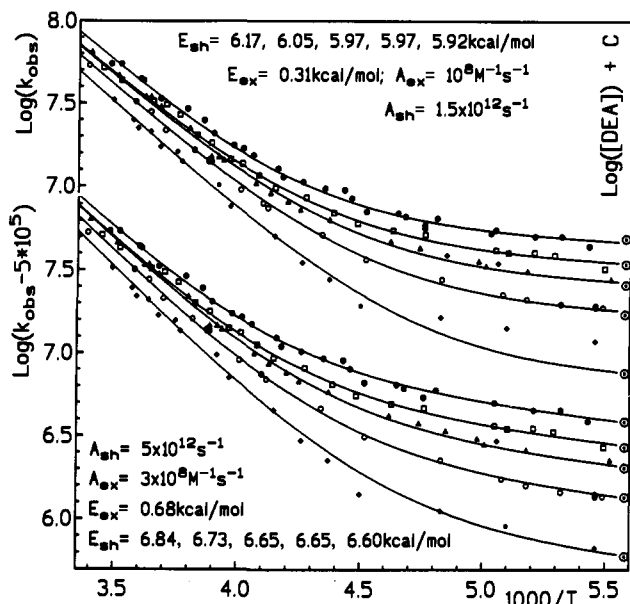


Figure 1. Arrhenius plots, $\log(k_{\text{obs}})$ and $\log(k_{\text{obs}} - 5 \times 10^5)$ vs $1/T$, for [DEA] = 17 (\blacklozenge), 39.5 (\circ), 59 (\blacktriangle), 80 (\square), and 114 mM (\bullet). Curves are drawn from eq 1 with A_{sh} , A_{ex} , E_{sh} , and E_{ex} given in the figure. Notice the overlap of the two y axis scales. On the righthand border, the circles represent $\log([\text{DEA}]) + c$ (see eq 2).

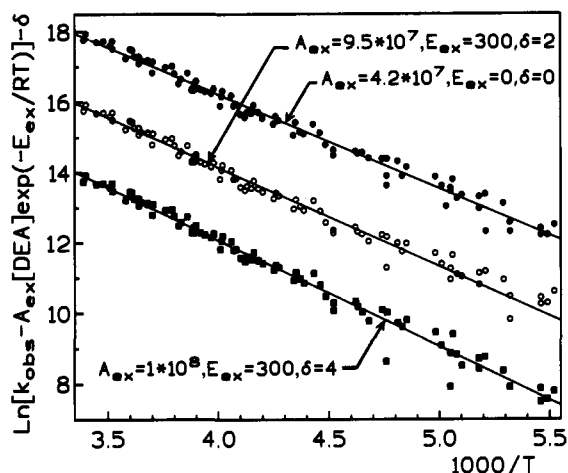


Figure 2. Plots of $\log[k_{\text{obs}} - A_{\text{ex}}[\text{DEA}] \exp(-E_{\text{ex}}/RT)]$ vs $(1/T)$ for three couples of A_{ex} ($\text{M}^{-1} \text{ s}^{-1}$) and E_{ex} (cal/mol) values. Least-squares analysis of the 84 points (four higher values of [DEA]) yields $A_{\text{sh}} = (4.8, 8.3, \text{ or } 16.7) \times 10^{11} \text{ s}^{-1}$ and $E_{\text{sh}} = 5.34, 5.64, \text{ or } 6.03 \text{ kcal/mol}$, respectively. Notice the change by a factor 2 in the value of A_{sh} due to a small change (5%) in the value of A_{ex} . Similar plots may be obtained for all 104 points when k_{obs} is changed to $(k_{\text{obs}} - 5 \times 10^5)$.

When $T < 60$ °C and [DEA] = 17 mM, the value of k_{obs} is larger than the sum of the rates for the exchange reaction and the 1,2-H shift over the barrier (see upper part of Figure 1). It seems that, in these conditions, another process contributes significantly to the ylide decay. The plots of $\log(k_{\text{obs}} - 5 \times 10^5)$ vs $1/T$ (see lower part of Figure 1) can be nicely fitted with values of E_{sh} and E_{ex} which are (nearly) the same for the five

values of [DEA] as long as A_{sh} and A_{ex} are in the ranges $(1-10) \times 10^{12} \text{ s}^{-1}$ and $(1-8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In a type c analysis (of the three types discussed above) and by using $(k_{\text{obs}} - 5 \times 10^5)$ instead of k_{obs} , a good fit between the 104 data points recorded with the five values of [DEA] and a single line is obtained for $A_{\text{ex}} = (2 \pm 1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $E_{\text{ex}} = 0.63 \pm 0.1 \text{ kcal/mol}$, yielding $A_{\text{sh}} = (3 \pm 2) \times 10^{12} \text{ s}^{-1}$ and $E_{\text{sh}} = 6.2 \pm 0.2 \text{ kcal/mol}$.

The "correction" of k_{obs} by $5 \times 10^5 \text{ s}^{-1}$ modifies significantly the above confidence intervals, which become:

$$A_{\text{sh}} = (4 \pm 3) \times 10^{12} \text{ s}^{-1} \quad A_{\text{ex}} = (3 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

$$E_{\text{sh}} = 6.3 \pm 0.5 \text{ kcal/mol} \quad E_{\text{ex}} = 0.7 \pm 0.3 \text{ kcal/mol}$$

The third process with a rate constant close to $5 \times 10^5 \text{ s}^{-1}$, (nearly) temperature independent, at least from -90 °C to -50 °C, could be the 1,2-H shift by tunneling since: (i) the ylide, which is not a very reactive species, cannot react with any component of the solution (solvent, diazirine, impurity, etc.) with a negligible activation energy and (ii) the rate of this process is very similar to that for the 1,2-H shift in methylchlorocarbene at -70 °C ($6 \times 10^5 \text{ s}^{-1}$) which, according to Goodman,³ occurs exclusively by tunneling at this temperature.

The preexponential factor for the 1,2-H shift, around 1×10^{12} or $5 \times 10^{12} \text{ s}^{-1}$, is larger than that reported for the rearrangement of benzylchlorocarbene⁵ ($\approx 10^{11} \text{ s}^{-1}$), methylchlorocarbene,⁶ or ethyldenes⁷ ($\approx 10^9-10^{10} \text{ s}^{-1}$) and is close to the limit of the values expected for an intramolecular rearrangement. The measured activation energy is about one-half of the value calculated for the system CH_2NH_3 , but the agreement between theory and experiment is quite satisfactory when the large differences between 1 and the model used for calculations are considered.

The very small but steady decrease of E_{sh} upon increasing [DEA] (see values in Figure 1), if not due to some systematic error, may be tentatively related to an increase of the polarity of the solvent cage surrounding the ylide: according to Platz,^{7a} a polar environment would decrease the energy barrier for the 1,2-H shift.

The value of E_{ex} is surprisingly low: even if the exchange reaction has no real activation energy, one should find an apparent activation energy around 2 kcal/mol due to the effect of temperature on the diffusion rate constant. As the temperature decreases, the DEA may have some propensity to dimerization and/or aggregation. The value of A_{ex} , 10^2 or 10^3 times smaller than that expected for a diffusion-controlled process, most probably indicates a strictly defined geometry for the transition state shown on Scheme 1b. Finally, at room temperature, the rearrangement of ammonium ylide 1 is mainly due to an intramolecular 1,2-H shift.

(5) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915. Recent measurements on an extended temperature range, to be published, indicate that several processes contribute to the decay of benzylchlorocarbene in isoctane, so the preexponential factor for the 1,2-H shift in this carbene would be around $10^{11.9} \text{ s}^{-1}$.

(6) (a) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877. (b) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (c) Recent measurements³ indicate that several processes contribute to the decay of methylchlorocarbene, so the preexponential factor for the 1,2-H shift in this carbene may be around 10^{13} s^{-1} .

(7) (a) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966. (b) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 470.