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Equilibrium constants for Triphenylmethyl bromide and 3-Bromo-3-phenyldiazirine in Acetonitrile

by

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Summary: The equilibrium constants at 25°C are 7.6×10^{-3} and 2.0×10^{-5} for triphenylmethyl bromide and bromodiazirine respectively.

Moss and co-workers[1,2] demonstrated the existence of tight ion pairs from the exchange reactions of 3-halo-3-aryldiazirines. Particularly, they found 3-bromo-3-phenyldiazirine to be more effective than the corresponding 3-chloro-3-phenyldiazirine in carrying out exchange reactions with tetra-n-butyl ammonium fluoride at ambient temperature. This study will observe the solution properties of triphenylmethyl bromide and 3-phenyl-3-bromodiazirine in order to obtain the equilibrium constants for these compounds.

The equivalent conductances, Λ, of varying concentrations of triphenylmethyl bromide, 1, and 3-bromo-3-phenyldiazirine, 2, in acetonitrile were measured.[3] The results are given in the following Table.

Table: Equivalent conductance (Λ') of 1 and 2 in CH_3CN at 25°C in ohms^{-1}cm^2 mol^{-1}.

1		2	
conc. x 10^4 (M)	Λ'	conc x 10^4 (M)	Λ'
99.9	76.43	9.98	20.13
49.9	85.76	4.99	22.07
39.9	92.30	0.998	55.42
29.9	101.2	0.499	62.31
19.9	108.6	0.0998	98.79
9.98	117.3		
4.99	123.3		

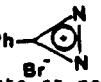
The equivalent conductances after solvent correction, Λ', were obtained by using the following equation:

$$\Lambda' = \frac{\Lambda + A\sqrt{c}}{1 - B\sqrt{c}}$$

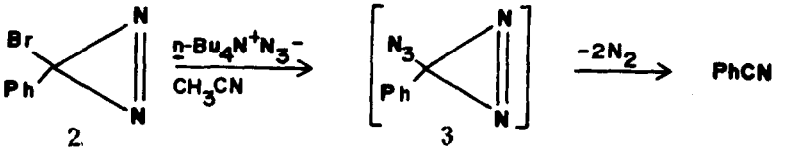
where A and B are Onsager constants for uni-univalent electrolyte which are equal to 229 and 0.716 for acetonitrile[4]. Information on the equilibrium constant, K, and conductance at infinite dilution, Λ_0, can be derived from

$$\Lambda' c = K\left[\frac{\Lambda_0^2}{\Lambda'} - \Lambda_0\right]$$

Least-squares analysis of $\Lambda' c$ vs $1/\Lambda'$ yields Λ_0 = 130 ± 12 ohm^{-1} cm^2 mol^{-1} and K_1 = 7.6 ± 0.6 x 10^{-3} for 1 and Λ_0 = 140 ± 27 ohms^{-1} cm^2 mol^{-1} and K_2 = 2.0 ± 0.3 x 10^{-5} for 2. This result agrees with the equilibrium constant reported for triphenylmethyl bromide in nitromethane[5], 2.39 x 10^{-3} at 25°C. Since the equivalent conductance at infinite dilution in acetonitrile for Br^- can be calculated to be 99 ohms^{-1}cm^2 mol^{-1} at 25°C[6], the estimated equivalent conductance at infinite dilution is 31 ohm^{-1} cm^2 mol^{-1} and 41 ohm^{-1} cm^2 mol^{-1} for the triphenylmethyl cation and the diazirinium cation respectively. Hence, the degree of dissociation ($\alpha = \Lambda'/\Lambda_0$) for 1 and 2 can be calculated to be 0.90 and 0.14 at a concentration of 1 x 10^{-3} M solution.

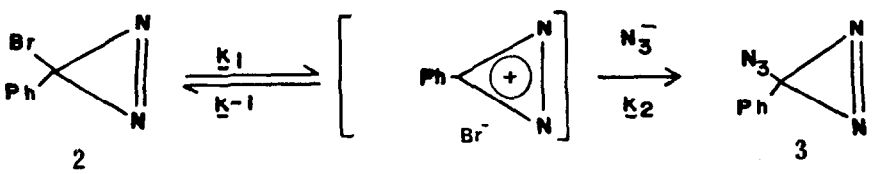
The results indicate that in acetonitrile, 3-bromo-3-phenyldiazirine is less ionized than triphenylmethyl bromide. This agrees with our recent observation that the tight ion pairs of $Ph_3C^+Br^-$ and  have been found to catalyze the isomerization of diethyl maleate to diethyl fumarate at room temperature[7]. The rate of isomerization was approximately an order of magnitude greater in the case of $Ph_3C^+Br^-$ than in the bromodiazirine.

In their pioneering work, Moss and co-workers[1] discovered that the reaction of 3-aryl-3-bromodiazirines with molten tetrabutylammonium fluoride at 25°C yielded the corresponding 3-aryl-3-fluorodiazirines. They suggested that "the most reasonable mechanism for halodiazirine exchange reaction requires the centrality of an intimate ion pair intermediate".[2] When diazirine 2 reacted with tetrabutylammonium azide (TBAAZ) in dry acetonitrile, 89% of benzonitrile was isolated.



2 3

Kinetic measurement by N_2 evolution for the reaction of 2 with TBAAZ yielded an activation energy of 18.6 kcal mol^{-1} and an A factor of $4.42 \times 10^9 s^{-1}$. This analysis assumes that the conversion of diazirine 2 to azidodiazirine 3 is rate determining and the decomposition of 3 to PhCN and N_2 is rapid. Thus, the rate of nitrogen formation may be equated to the rate of formation of 3. The assumption for the rate determining formation of 3 can further be corroborated by the negative $\Delta S^{\neq}$ (-16.3 e.u.). According to Moss[1,2], the results are consistent with significant dipolar solvent orientation accompanying the rate-determining ionization of 2 to an ion pair which is subsequently intercepted by azide ion.



2 3

Steady state treatment of the above equation leads to the rate of formation of 3 as

$$\frac{d[3]}{dt} = k_1[2] \quad \frac{k_2[N_3^-]}{k_{-1}[Br^-] + k_2[N_3^-]}$$

Taking $k_1 = 4.4 \times 10^9 \exp(-18{,}600/RT)\ s^{-1}$ ($k_1 = 10^{-4} s^{-1}$ at 25°C) and $k_1/k_{-1} = 10^{-5}$, the value for k_{-1} is ~ 10 at 25°C. If $k_{-1}[Br^-] > k_2[N_3^-]$, then the rate of formation of 3 will be first-order in both diazirine 2 and N_3^-. This is exactly what Moss and co-workers[1,2] observed experimentally. The exercise above supports the view that our estimate on the equilibrium constant for 3-phenyl-3-bromodiazirine is in the right order of magnitude.

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References:

1. Moss, R.A., Terpinski, J., Cox, D.P., Denney, D.Z., and Krogh-Jespersen, K., J. Am. Chem. Soc., 107, 2743 (1985).
2. Moss, R.A. Exchange Reactions of Halodiazirines, in Chemistry of Diazirines, Vol. 1, Liu, M.T.H., Ed. CRC Press, Boca Raton, Fla., 1987, Chap. 3.
3. 3-bromo-3-phenyldiazirine was synthesized according to Graham's method (Graham, W.H., J. Am. Chem. Soc. 87, 4396 (1965). The diazirines were purified by column chromatography followed by Kugelrohr distillation. GLC analysis indicated that the diazirines are >99.5% pure. Triphenylmethyl bromide was purchased from Aldrich and was recrystallized before use. Acetonitrile was purified by distillation over P_2O_5 in an all glass apparatus. The distillate was further distilled over anhydrous potassium carbonate. The YSI conductivity bridge Model 31 with Freas-type conductance cell was used for conductance measurements. The temperature was controlled to 25 ± 0.1°C.
4. Glasstone, S. "An Introduction to Electrochemistry", 7th printing, van Nostrand Co. Inc., New York, 1956.
5. Heublein, G. and Bauerfeind, D. J. Prakt. Chemie, 324, 882 (1982); Heublein, G. and Spange, S. Z. Chem., 21, 368 (1981).
6. Coplan, M.A., and Fuoss, R.M. J. Phy. Chem., 68, 1181 (1964); Evans, D.F., Zawoyski, C. and Kay, R.L. J. Phy. Chem., 69, 3878 (1965); Kay, R.L., Hales, B.J., and Cunningham, G.P. J. Phy. Chem. 71, 3925 (1967).
7. Liu, M.T.H., Doyle, M.P., Loh, K-L and Anand, S. J. Org. Chem., 52, 323 (1987).

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