Kinetics of the Reaction of the Solvated Electron with Tri-n-butyl-n-propylammonium Iodide in Liquid Ammonia

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For the cleavage of tetra-alkylammonium halides by alkali metals in liquid ammonia,[1] Birch[2] has postulated a general scheme for the reductive cleavage that involves N–C bond fission.

We have studied the reaction of tri-n-butyl-n-propylammonium iodide with sodium in liquid ammonia conductometrically.[3] The work was carried out in a closed system capable of evacuation to pressures less than 5×10^{-6} torr. Also, extreme precautions were taken to ensure purity of materials and cleanliness of vessels used. All experiments were carried out with an excess of tri-n-butyl-n-propylammonium iodide such that its concentration could be considered constant. The reaction was found to be pseudo-first-order in the solvated electron concentration so that the rate constant could be obtained from the half-time of the reaction. The half-times of the reaction were determined from logarithmic plots of $R_\infty(R - R_0)/R(R_\infty - R_0)$ against time. Also a control experiment was performed in which no sodium was added. In this case, the tri-n-butyl-n-propylammonium iodide was dissolved in liquid ammonia and the resistance of the solution did not vary with time (18 hr.). The volatile materials were then pumped out of the reaction vessel, and 99% of the original quaternary ammonium salt was recovered, as shown by elemental analysis.

Within the concentration range studied, the kinetic data was found to be in agreement with the rate expression:

$$\frac{-\mathrm{d}[\mathrm{e}^-_{\mathrm{am}}]}{\mathrm{d}t} = k\ [\mathrm{e}^-_{\mathrm{am}}]\ [\mathrm{NBu^n{}_3Pr^{n+}}] \tag{1}$$

The data are shown in the Figure. The second-order rate constant was obtained from the pseudo-first-order rate constants by assuming an ion-pairing dissociation constant of $1{\cdot}2 \times 10^{-2}$ for the quaternary ammonium salt in liquid ammonia at $-65°$. The ion-pairing dissociation was estimated from the theory by Fuoss[4] by using a distance of closest approach of 7 Å. The second-order rate constant was found to decrease with increasing tri-n-butyl-n-propylammonium iodide concentration. We attribute this to a kinetic salt effect.

The Brønsted–Bjerrum theory of ionic reactions combined with the extended Debye–Hückel theory leads to equation (2),

$$\log_{10} k = \text{constant} + \alpha\sqrt{\mu}\,\frac{(Z_\mathrm{A} + Z_\mathrm{B})^2}{1 + a^\ddagger\beta\,\sqrt{\mu}} - \frac{Z_\mathrm{A}{}^2}{1 + a_\mathrm{A}\beta\sqrt{\mu}} - \frac{Z_\mathrm{B}{}^2}{1 + a_\mathrm{B}\beta\sqrt{\mu}} \tag{2}$$

where the symbols have their usual meaning.[5]

By assuming a mean value for the distance of closest approach, equation (2) becomes:

$$\log_{10} k = \text{constant} + \frac{2\alpha Z_A Z_B \sqrt{\mu}}{1 + \beta a \sqrt{\mu}} \qquad (3)$$

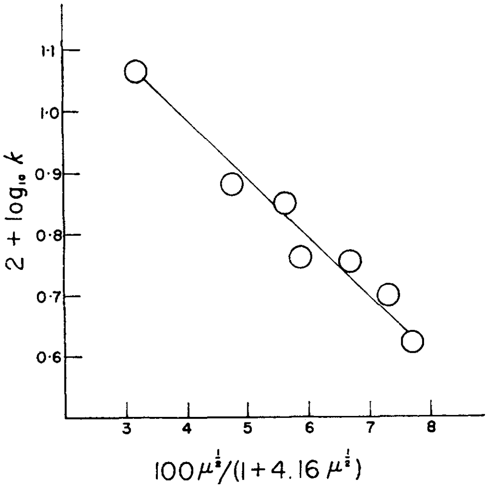

FIGURE. *Variation of* 2 + $\log_{10}$ *k with* $\mu^{\frac{1}{2}}/(1 + 4{\cdot}16\ \mu^{\frac{1}{2}})$. *The line is predicted by equation* (4).

For liquid ammonia at −65° and by making the approximation that *a* in equation (3) is 6 Å, the corresponding equation is

$$\log_{10} k = \text{constant} + \frac{9{\cdot}66\, Z_A Z_B \sqrt{\mu}}{1 + 4{\cdot}16 \sqrt{\mu}} \qquad (4)$$

In the Figure, $\log_{10} k$ is plotted against $\sqrt{\mu}/(1 + 4{\cdot}16\sqrt{\mu})$. Within the experimental error, the slope of the Brønsted–Bjerrum plot is in agreement with the expected value. The method of least-squares yields a slope of −9·04 for the experimental points shown. Also, by using equation (2) and values of 3·2 and 8 Å for the distances of closest approach for e^-_{am} and $Bu^n_3NPr^{n+}$, respectively, we obtained a good agreement with the experimental results. This provides experimental evidence for the existence of a unit negative charge on the solvated electron produced by the dissolution of alkali metals in liquid ammonia.

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