The Reaction of Sodium with Urea in Liquid Ammonia: the Rate Constant of the Reaction of the Ammonium Ion with the Ammoniated Electron

By WILLIAM L. JOLLY* and LEONARDO PRIZANT

(*Department of Chemistry, University of California, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, California,* 94720)

KINETIC STUDIES of the reactions of alcohols[1,2] and water[2] with sodium in liquid ammonia have been interpreted[2,3] in terms of the following mechanism

$$\mathrm{HA} + \mathrm{NH_3} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{NH_4^+} + \mathrm{A^-}$$

$$\mathrm{NH_4^+} + e^- \xrightarrow{k_3} \mathrm{NH_3} + \tfrac{1}{2}\mathrm{H_2}$$

where HA represents an alcohol or water molecule. The kinetic data are consistent with a low steady-state concentration of ammonium ion and the corresponding rate law

$$-d[e^-]/dt = k_1[\mathrm{HA}][e^-]/\{(k_2/k_3)[\mathrm{A^-}] + [e^-]\}$$

Evaluation of the rate constants from the data is difficult because of the strong complexing of the alkoxide ion by dissolved alcohol[3] [probably to form species of the type $\mathrm{OR(HOR)}_n{}^-$] and of the hydroxide ion by dissolved water[4] [probably to form species of the type $\mathrm{OH(H_2O)}_n{}^-$]. However, we have found that the same type of rate law (and presumably the same mechanism) applies to the reaction of sodium with urea, in which complex-formation of this type is absent. In this case the rate constants may be evaluated relatively unambiguously. It seems possible that the above mechanism, characterized by the lack of a direct reaction between the electron and the species HA, is fairly general for the reaction of metal–ammonia solutions with protic acids.

We followed the course of the urea–sodium reaction by measuring the electrical conductivity of the solution as a function of time at −45°. The measured conductivity at any given time was assumed to be the sum of the conductivity of a sodium solution† of concentration $[e^-]$ and the conductivity of an $\mathrm{NaHN{\cdot}CONH_2}$ solution‡ of concentration $[e^-]_0 - [e^-]$, where $[e^-]_0$ is the initial concentration of sodium metal. A least-square fitting of the experimental data for a given run to the rate law was accomplished with the aid of a computer, which calculated values of k_1 and k_2/k_3 and plotted the theoretical curve (based on these values of k_1 and k_2/k_3) of conductivity against time along with the experimental points. Several runs, with initial urea–sodium ratios ranging from 1·5 : 1 to 10 : 1, yielded the values $k_1 = 3{\cdot}6 \times 10^{-4}$ sec.$^{-1}$ and $k_2/k_3 = 0{\cdot}30$. The computer plot of conductivity against time for a run with an initial urea–sodium ratio of 5–1 is given in the Figure.

Urea is one of the few acids whose ionization constants in ammonia are known. Herlem[5] has determined that $K_a = 1{\cdot}25 \times 10^{-13}$ for urea at −60°. By neglecting the difference in K_a between −60° and −45°, we may take $K_a = k_1/k_2 \approx 1{\cdot}25 \times 10^{-13}$ at −45°, the temperature of our kinetic runs. By combining this value with our value for k_1, we obtain $k_2 \approx 3 \times 10^9\mathrm{M}^{-1}$ sec.$^{-1}$. The magnitude of this rate constant appears reasonable when compared with the rate constants for the reactions of the ammonium ion with the hydroxide ion and ammonia in aqueous solution

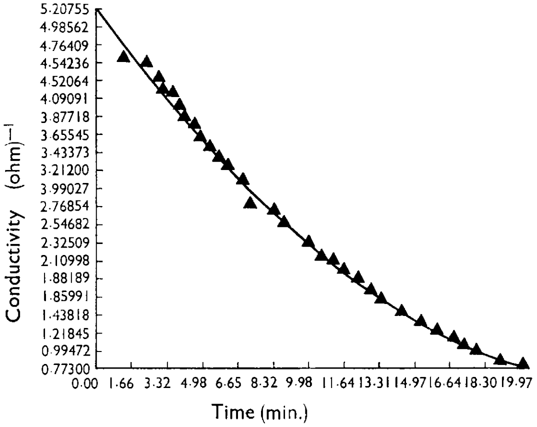

FIGURE. *Plot of conductivity against time for the reaction of urea with sodium in liquid ammonia at* − 45°. *The points represent the experimental data; the curve is computer-calculated.*

---

† In a separate set of experiments, the conductivity of a series of sodium solutions was determined. The data were expressed as a polynomial which was used in the computer calculations.

‡ At the end of each run, the conductivity of the solution was that of an $\mathrm{NaHN{\cdot}CO{\cdot}NH_2}$ solution of concentration $[e^-]_0$.

($3{\cdot}4 \times 10^{10}$ and $1{\cdot}06 \times 10^{9}$ M^{-1} sec.$^{-1}$, respectively)[6] and with the rate constant for the transfer of a proton from the ammonium ion to ammonia in liquid ammonia (2×10^{8} M^{-1} sec.$^{-1}$ at 25°).[7] Apparently the transfer of a proton from an ammonium ion to the anion of urea is essentially a diffusion-controlled reaction.

From the values for k_2 and k_2/k_3 we calculate $k_3 \approx 10^{10}$ M^{-1} sec.$^{-1}$. This value again corresponds to a diffusion-controlled reaction having a low activation energy, and it is interesting to note that the value is considerably greater than that of the rate constant for the reaction of the aqueous ammonium ion with the aqueous electron,[8] $1{\cdot}5 \times 10^{6}$ M^{-1} sec.$^{-1}$. There is reason to question whether the rate-determining step for the liquid ammonia reaction can be formulated as it has been for the aqueous reaction:

$$NH_4^+ + e^- \longrightarrow NH_3 + H$$

The heats of formation in liquid ammonia for the first three species in this equation are known,[3] and that for atomic hydrogen may be estimated (probably with an accuracy of ±3 kcal./mole) by assuming zero heat of solution. Thus we calculate $\Delta H^\circ = 15 \pm 3$ kcal./mole for the liquid ammonia reaction. Now if this process is the rate-determining step, then $\Delta H^\ddagger$ must be at least 15 ± 3 kcal./mole, corresponding to a slow reaction. Thus the formation of atomic hydrogen is inconsistent with the rate constant in liquid ammonia. Perhaps the rate-determining process is better represented by the equation

$$NH_4^+ + e^- \longrightarrow NH_4$$

The ammonium radical might be expected to react further, as in either of the following sequences.

$$\begin{aligned} &NH_4 + e^- \longrightarrow NH_2^- + H_2 \\ &NH_4^+ + NH_2^- \longrightarrow 2NH_3 \\ &NH_4 \longrightarrow NH_2 + H_2 \\ &NH_2 + e^- \longrightarrow NH_2^- \\ &NH_4^+ + NH_2^- \longrightarrow 2NH_3 \end{aligned}$$

It should be pointed out that if, as expected for a variety of weak acids, k_2 always has a value near 10^{9} M^{-1} sec.$^{-1}$, then the kinetic determination of k_1 is in effect a determination of k_1/k_2 or K_a. In some cases the kinetic measurement may be more easily accomplished than the equilibrium measurement.

This work was supported by the U.S. Atomic Energy Commission.

(*Received, August 2nd,* 1968; *Com.* 1053.)

---

[1] E. J. Kelly, H. V. Secor, C. W. Keenan, and J. F. Eastham, *J. Amer. Chem. Soc.*, 1962, **84**, 3611.

[2] R. R. Dewald and R. V. Tsina, *Chem. Comm.*, 1967, 647; R. R. Dewald and R. V. Tsina, paper presented before the Division of Physical Chemistry at the National A.C.S. Meeting in Chicago, September, 1967.

[3] (a) W. L. Jolly, "Advances in Chemistry Series", American Chemical Society, Washington, 1965, No. 50, p. 27; (b) W. L. Jolly and C. J. Hallada, "Non-Aqueous Solvent Systems", ed. T. C. Waddington, Academic Press, London, 1965, p. 1.

[4] W. L. Jolly, *J. Chem. Educ.*, 1967, **44**, 304; *J. Phys. Chem.*, 1954, **58**, 250.

[5] M. Herlem, *Bull. Soc. chim. France*, 1967, 1687.

[6] H. Strehlow, "Technique of Organic Chemistry", ed. S. L. Friess, E. S. Lewis and A. Weissberger, Interscience, VIII, Pt. II, p. 865; M. Eigen and L. deMaeyer, *ibid.*, p. 895.

[7] D. R. Clutter and T. J. Swift, *J. Amer. Chem. Soc.*, 1968, **90**, 601.

[8] J. Rabani, ref. 3a, p. 242.