Reaction of the Solvated Electron with Water in Liquid Ammonia

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SOLUTIONS of sodium in liquid ammonia react readily with water[1] and Pleskov[2] reported that these metal solutions may be employed as a rapid method for the determination of small quantities of water. The observed reaction which is due almost certainly to solvated electrons, e^-_{am}, can be written:[1]

$$e^-_{am} + H_2O \rightarrow \tfrac{1}{2} H_2 + OH^- \qquad (1)$$

in which NaOH precipitates readily.[3] The mechanism of this reaction is of considerable interest and is at present incompletely understood.[4,5]

We have been studying the reaction of t-butyl alcohol with sodium in liquid ammonia and have confirmed earlier reports that alcohols do not react completely with sodium.[6,7] Our preliminary kinetic data are in agreement with the following mechanism for the ethanol–sodium–ammonia system suggested by Jolly:[8]

$$ROH + NH_3 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NH_4^+ + RO^- \qquad (2)$$

$$NH_4^+ + e^-_{am} \xrightarrow{k_3} NH_3 + \tfrac{1}{2} H_2 \qquad (3)$$

so that

$$-\frac{d[e^-]}{dt} = \frac{k_3k_1[e^-][NH_3][ROH]}{k_2[RO^-] + k_3[e^-]}$$

is readily obtained. As the reaction proceeds, the alkoxide ion concentration increases which in turn reduces the ammonium ion concentration until the overall rate falls off to a negligible value. For example, the reaction rate as followed by conductivity measurements became negligible when the concentrations were $1{\cdot}0 \times 10^{-5}$, $5{\cdot}7 \times 10^{-2}$, and $9{\cdot}4 \times 10^{-3}$ mole/l. for sodium, t-butyl alcohol, and t-butoxide ion respectively. We also found that the remaining blue colour characteristic of the sodium could not readily be bleached by the addition of water.

The extent of the hydrolytic reaction (4) in wet ammonia:

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^- \qquad (4)$$

is unknown. Addition of t-butoxide ion will, however, reduce the ammonium ion concentration as is evident from equation (2). In a typical experiment, t-butyl alcohol ($3{\cdot}02 \times 10^{-2}$M) was treated with sodium ($1{\cdot}26 \times 10^{-2}$M) in liquid ammonia until the reaction rate became negligibly small. When water ($4{\cdot}55 \times 10^{-2}$M) was added to the mixture, fading required 24 hr. and no precipitate was observed. Precipitation was observed in another run using a higher water concentration. This fact, coupled with solubility data[3] for NaOH in wet liquid ammonia, implies that reaction (5)

$$RO^- + H_2O \rightleftarrows ROH + OH^- \qquad (5)$$

does not proceed far to the right for R = Bu^t.

Since in the absence of a soluble base, such as sodium t-butoxide, solutions of sodium in liquid ammonia are essentially bleached upon mixing with water, we conclude that the mechanism is (4) and (3), *i.e.*,

$$H_2O + NH_3 \rightleftarrows NH_4^+ + OH^- \qquad (4)$$

$$NH_4^+ + e^-_{am} \rightarrow NH_3 + \tfrac{1}{2} H_2 \qquad (3)$$

and the overall reaction rate can be decreased by reduction of the ammonium ion concentration.

A similar reaction which involves the conversion of hydrated electrons, e^-_{aq}, into hydrogen atoms by water, *i.e.*,

$$e^-_{aq} + H_2O \rightarrow H + OH^- \qquad (6)$$

has been the subject of many investigations.[9,10] The use of extreme precautions in solvent purification has permitted a value of 16 ± 1 mole^{-1} sec.$^{-1}$ to be deduced as an upper limit for the rate constant of the $e^-_{aq} + H_2O$ reaction.[10] Anbar[11] has suggested that the best value of the activation energy for reaction (6) in water should be greater than 4·6 kcal./mole. If we assume that a comparable value for reaction

$$e^-_{am} + H_2O \rightarrow H + OH^- \qquad (7)$$

in liquid ammonia applies and further that the relative rate constants are comparable in liquid ammonia and water we can calculate an approximate value for the rate constant of reaction (6) at $-34°$. Using 16 mole^{-1} sec.$^{-1}$ as the rate constant for reaction (6) at $+20°$[10] and an activation energy of about 6 kcal./mole, a rate constant of reaction (6) of 1·6 mole^{-1} sec.$^{-1}$ at $-34°$ is calculated. Our results, however, imply that if reaction (7) occurs in the water–sodium–liquid ammonia system, the rate constant should be less than 5×10^{-3} mole^{-1} sec.$^{-1}$ at $-34°$.

The reverse of reaction (7), reported for the hydrated electron–water system,[12] probably does not occur to any appreciable extent in the sodium–water–liquid ammonia system. This can be deduced from the reported limited solubility of sodium hydroxide in wet ammonia[3] and published rate data[13] for hydrogen atom reactions in aqueous systems, assuming comparable rates at $-34°$ in liquid ammonia.

The relatively high stability of the solvated electron in liquid ammonia toward reaction with water suggested in this work is consistent with the conclusion of Magee and Burton[14] and Platzman[15] that the reaction

$$e^- + H_2O \rightarrow H + OH^- \qquad (8)$$

can occur only in liquid water where the solvation energy of the hydroxyl ion is available.

All work reported in this study 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 in this study.

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