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Berkeley, California

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The Structure and Kinetics of Metal-Ammonia Solutions

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ABSTRACT

Physical chemical studies of dilute metal-ammonia solutions indicate that the principal species in these solutions are the ammoniated metal cation M^+, the ammoniated electron e^-, the "monomer" M, the "dimer" M_2, and the "metal anion" M^-. The species e^- and M are paramagnetic, whereas M_2 and M^- are diamagnetic. Most data suggest that M, M_2, and M^- are simple electrostatic assemblies of ammoniated cations and ammoniated electrons - that is, that they are an ion pair, an ion tetramer, and an ion trimer, respectively.

The reaction $e^- + NH_3 \longrightarrow \frac{1}{2}H_2 + NH_2^-$ has been shown to be reversible, and the directly measured equilibrium constant agrees fairly well with that estimated from other thermodynamic data. Kinetic data for the reaction of ethanol with sodium and for various metal-ammonia-alcohol reductions of aromatic compounds suggest that steady-state concentrations of ammonium ion are established in these reactions. Mechanisms are proposed which account for the unusual features of these reactions. The data for the ethanol-sodium reaction permit the estimation of an upper limit for the rate constant of the reaction $e^- + NH_4^+ \longrightarrow \frac{1}{2}H_2 + NH_3$.

The Structure of Metal-Ammonia Solutions

A wide variety of physical chemical techniques have been applied to the study of metal-ammonia solutions (23, 32). Some techniques have been useful as analytical methods for the identification of dissolved species and for studying equilibria involving these species. These techniques include, in the approximate order of decreasing usefulness, (a) conductivity measurements (concentration dependence and transference studies), (b) magnetic susceptibility measurements (both static and e.s.r.), (c) nuclear magnetic resonance (Knight shifts), (d) vapor pressure measurements, and (e) optical spectroscopy. Another group of physical chemical techniques, including some of those already mentioned, have been useful for determining the structures of the dissolved species. These include, again in the approximate order of decreasing usefulness, (a) optical spectroscopy, (b) density measurements, (c) nuclear magnetic resonance (Knight shifts), (d) conductivity measurements (mobilities and temperature coefficients), (e) electron spin resonance, and (f) thermochemistry. There is every reason to believe that, in the future, other techniques will be applied to these studies, and that a number of subtle features of the solutions will be uncovered.

First let us consider the empirical formulas of the species which have been postulated to exist in alkali metal-ammonia solutions and which have received the serious consideration of more than a few investigators. In this connection it is important to realize that the identification of a species in terms of its empirical formula is not the same thing as the determination of its structure. In 1908 Kraus (30)

proposed, on the basis of conductivity measurements and electrolytic experiments, that alkali metals exist in ammonia as monatomic species, M, in equilibrium with the corresponding cations, M^+, and ammoniated electrons, e^-. In 1938 Huster (21) proposed, in order to account for the decrease in molar magnetic susceptibility with increasing concentration, that the cations and electrons are in equilibrium with the diamagnetic diatomic species M_2. In order to explain similar magnetic data, Freed and Sugarman (14) and Ogg (33, 34) proposed the species e_2^{2-} (which generally has not been considered seriously since then) and Bingel (3) proposed the species M^-.

In order to account for both the conductivity data and the magnetic susceptibility data, Becker, Lindquist and Alder (2) proposed that the following two equilibria be considered:

$$M = M^+ + e^-$$

$$M_2 = 2M^+ + 2e^-$$

Arnold and Patterson (1) found that a better fit of the data could be obtained by considering three equilibria:

$$M = M^+ + e^-$$

$$M^- = M^+ + 2e^-$$

$$M_2 = 2M^+ + 2e^-$$

Let us consider the various structures which have been proposed for the species involved in the latter three equilibria. The only uncontroversial species is the metal cation, M^+, which has always been assumed to be solvated by a shell of ammonia molecules, with the

negative ends of the ammonia dipoles (the nitrogen atoms) pointing toward the central cation.

The ammoniated electron, e^-, has been described by Ogg (35) and various other authors as an electron-in-a-cavity. In this model, the electron is stabilized in a large cavity by polarization and orientation of the peripheral ammonia molecules. A "polaron" model due to Davydov (9) and Deigen (10), in which the electron is assumed to be stabilized by polarization of a continuous dielectric medium, is ruled out by density measurements which show that the electron occupies a very large volume.

The monomer species, M, has been described by Kraus (31) as an ion-pair. Although he did not elaborate on its possible structure, it may be assumed that he pictured this species as two ammoniated ions held together by electrostatic forces. Douthit and Dye (12) pointed out that such a picture is consistent with the absorption spectra of sodium-ammonia solutions. Becker, Lindquist and Alder (2) proposed an "expanded metal" model in which an electron was assumed to circulate in an expanded orbital on the protons of the coordinated ammonia molecules of an M^+ ion. The latter model is ruled out by optical, volumetric, and n.m.r. data.

The dimer species, M_2, was described by Huster (21) as a simple dissolved diatomic molecule. Such a species would be very unstable with respect to the ammoniated species, M^+ and e^-, and may be ruled out by thermochemical data. The "expanded metal dimer" model of Becker, Lindquist and Alder, in which two ammoniated metal ions are held together by a pair of electrons in a molecular orbital located principally between the two ions, may be ruled out for the same reasons

that the expanded metal monomer was ruled out. In order to account for the similar absorption spectra of e^-, M, M_2 (and any other species such as M^- or M_4 that might exist at moderate concentrations of metal), Gold, Jolly and Pitzer (16) assumed that species such as M and M_2 consist of ionic aggregates in which the ammoniated electrons remain essentially unchanged from their state at infinite dilution.

Recently Golden, Guttman and Tuttle (17) proposed that the M^- species is an ammoniated metal anion and that the M_2 species is an ion-pair of this anion with the ammoniated metal cation. By using reasonable estimates of ionic ammoniation energies, it is possible to show that an ammoniated metal anion is thermodynamically plausible. However the only experimental data which were specifically used to support the existence of this species were optical extinction coefficient data of Gold and Jolly (15). These data were obtained at 24,000 Å, which happens to be the longest wavelength investigated by Gold and Jolly because of limitations of the spectrophotometer and strong absorption by the solvent; hence the data may be spurious.

Blandamer <u>et al</u> (4) have recently made a half-hearted effort to resurrect the e_2^{2-} species. They state that if a species such as M_2 or M^- contains two ammoniated electrons with sufficient overlap of the electronic wave functions to cause the species to exist in a singlet state, then only by a coincidence could the absorption spectrum be similar to that of the far-separated ammoniated electrons. They suggest that a comparable coincidence could just as well occur in the case of the e_2^{2-} species. Some clarification of the ionic cluster model is therefore called for. It should be recognized that the energy difference between the singlet and triplet states of the electron

pair is only required by the data to be of the order of magnitude of kT (0.5 kcal. or 170 cm^{-1} at -33°). The equilibrium constants have generally been calculated assuming that M^- and M_2 are completely diamagnetic (corresponding to a singlet-triplet separation of several kT), but this is probably an unnecessary restriction. However, even if we assume that spin coupling in the ionic clusters causes the relative energies of the ground and excited states of the optical transition to change by three times kT, the calculated shift in absorption frequency is less than the 600 cm^{-1} shift observed on going from very dilute solutions to 0.03 M (15). It should also be recognized that the magnetic coupling between the electrons may be enhanced by spin polarization of the intervening atoms, in much the same way that magnetic coupling occurs in antiferromagnetic compounds such as MnO and FeO (5).

Thermodynamic and Mechanistic Studies of Reactions

The reactivity of metal-ammonia solutions is a topic at least equal in importance to the structure of metal-ammonia solutions. The solutions have been used as reagents in an enormous number of syntheses, but very little quantitative systematization of the reactions has been achieved. However, in recent years significant progress has been made in the thermodynamics and kinetics of a few reactions of metal-ammonia solutions, and in the remainder of this paper I shall discuss some of these reactions.

Thermodynamics. - By correlation of thermochemical and electrochemical data for liquid ammonia, it has been possible to estimate thermodynamic functions for a wide variety of ionic species in liquid ammonia at 25° (22, 24). The heats and free energies of formation and

entropies (relative to H^+) for a few species are given in Table 1. These values have been calculated from the data of references 6, 19, 20 and 24.

Table 1.

Thermodynamic Functions for Species in Liquid Ammonia at 25°

Species	ΔH°_f kcal./mole	ΔF°_f kcal./mole	S° cal./deg. mole
H^+	0	0	0
NH_4^+	-16.1	-2.7	24.7
Na^+	-38.0	-43.6	15
K^+	-39.3	-47.0	25
NH_3	-16.1	-2.7	24.7
e^-	37.4	46	-13
NH_2^-	9.8	35.0	-15

Using the data from Table 1, one calculates an equilibrium constant of 10^6 for the reaction

$$e^- + NH_3 = NH_2^- + \tfrac{1}{2}H_2$$

Thus one predicts that a 1 M solution of potassium amide which is in equilibrium with one atmosphere pressure of hydrogen will contain 10^{-6} M ammoniated electron. By using electron spin resonance for determining the concentration of ammoniated electrons, we have recently shown that this equilibrium can indeed be attained and that the above equilibrium constant is correct within an order of magnitude (28).

Kinetics and Mechanisms. - Ammonium ions react very rapidly with electrons in ammonia:

$$NH_4^+ + e^- \longrightarrow NH_3 + \tfrac{1}{2}H_2$$

Although nobody has succeeded in directly measuring the rate constant of this reaction, Kelly et al (27) have reported some kinetic data which permit us to estimate an upper limit for the rate constant. These investigators followed the reaction of sodium with ethanol in liquid ammonia at -33.4° by measuring the evolved hydrogen as a function of time.

$$e^- + EtOH \longrightarrow EtO^- + \tfrac{1}{2}H_2$$

They noted that, during the first 25% of reaction, the reaction was first-order in alcohol and essentially zero-order in sodium. During the second 25% of reaction, the reaction did not appear to be of definite kinetic order, but during the last half of reaction, the reaction was much slower and was first-order in both alcohol and sodium, or second-order overall. These results are at least in qualitative agreement with the rate law

$$-\frac{d(EtOH)}{dt} = \frac{k_1(EtOH)(e^-)}{(k_2/k_3)(EtO^-) + (e^-)}$$

which corresponds to a mechanism involving a low steady-state concentration of ammonium ion:

$$EtOH + NH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4^+ + EtO^-$$

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

In order to account quantitatively for the rate data over the entire extent of reaction, it is necessary to consider the fact that sodium ethoxide is only slightly soluble in ammonia and that its solubility is markedly increased by the addition of ethanol. It happens that, for the purpose of accounting for the kinetics, the following arbitrarily chosen equilibrium is satisfactory.

$$EtOH + EtO^- = EtOHOEt^-$$

Probably other equilibria would serve just as well. Using an equilibrium constant of 10^3 for this reaction and a solubility product of 1.73×10^{-3} for sodium ethoxide, the constants $k_1 = 8 \times 10^{-3}$ sec^{-1} and $(k_2/k_3) = 6 \times 10^3$ were evaluated. The value for k_1 is fairly firm (and is in agreement with NMR data which indicate that the rate constant is less than 10 sec^{-1}), but the value of (k_2/k_3) is dependent on an arbitrary choice, within limits, of the $EtOHOEt^-$ equilibrium constant and the sodium ethoxide solubility product. In fact, the kinetic data are consistent with any value for (k_2/k_3) greater than 10^3. The experimental data of Kelly et al are presented in Fig. 1 in the form of a plot of the fraction reaction vs. the logarithm of time. The curve through the experimental points corresponds to the rate constants and equilibrium constants given above.*

If the ionization constant for ethanol in liquid ammonia, k_1/k_2, were known, it would be possible to calculate a value for k_3, the $NH_4^+ + e^-$ rate constant. At present, the best we can do is to estimate

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* A similar, less rigorous interpretation of the data has been published elsewhere (25).

this ionization constant. Several types of evidence indicate that the pK values of normal acids are about 8 units less in ammonia than in water.* Thus, since the aqueous pK of ethanol (7) is 17, we might estimate a pK of 9 for ethanol in liquid ammonia. However, the ethoxide ion is probably strongly hydrogen-bonded in aqueous solution and is probably abnormally stable in aqueous solution relative to ammonia solution. The analogous ion, hydroxide, is stabilized in water to such an extent that the pK value for water in ammonia (ca 18) is greater than that in water (ca 16)(22). The relative stabilization in water of the ethoxide ion is probably not as marked as that of the hydroxide ion, and so we estimate a very approximate pK value of 13 for ethanol in liquid ammonia. (A pK value greater than 13 would correspond to the unlikely situation in which k_2 had a value greater than 10^{11} $\underline{M}^{-1}$ sec^{-1}, i.e., greater than that for a diffusion-controlled reaction.) This pK value, together with the data $k_1 = 8 \times 10^{-3}$ and $(k_2/k_3) > 10^3$, yields $k_3 < 10^8$ $\underline{M}^{-1}$ sec^{-1}. This result indicates that the $NH_4^+ + e^-$ reaction is not an ultra-fast, diffusion-controlled reaction like the $H_3O^+ + e^-$ reaction (18) and that the $NH_4^+ + e^-$ reaction has an appreciable activation energy. If we assume that the mechanism involves the formation of atomic hydrogen, then a lower limit for the activation energy should be obtained from the heat of the reaction

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

If we assume no solvation energy for atomic hydrogen in ammonia (and thus probably overestimate the heat) we calculate $\Delta H° = 15$ kcal./mole

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* For example, para-nitroacetanilide has a pK of 5.1 in ammonia (8) and a pK of about 13.2 in water.

for the latter reaction. It is hoped that the rate constant for the $NH_4^+ + e^-$ reaction soon will be evaluated by the same techniques of pulse radiolysis (18) or photolysis (36) which have been used to study the $H_3O^+ + e^-$ reaction.

Keenan et al (26) carried out experiments designed to compare the rate of the $NH_4^+ + e^-$ reaction with that of the reaction

$$NH_3 + NH_4^+ \longrightarrow NH_4^+ + NH_3$$

They observed that, when a solution of lithium in tritiated ammonia was mixed with a solution of ammonium bromide in ordinary ammonia, the evolved hydrogen contained much less tritium than when a solution of lithium in ordinary ammonia was mixed with a solution of ammonium bromide in tritiated ammonia. These results were taken as evidence that the $NH_4^+ + e^-$ reaction is an order of magnitude faster than the $NH_4^+ + NH_3$ reaction. However when one considers that electrons in ammonia have an abnormally high mobility and that they probably migrate without carrying ammonia molecules with them (11, 23), this interpretation seems doubtful. It is possible that the electrons diffused into the ammonium bromide solutions much more rapidly than the ammonium ions diffused into the lithium solutions, and that consequently the evolved hydrogen was always characteristic of the ammonium bromide solutions. Thus these experiments yield little information about the relative rates of the $NH_4^+ + e^-$ reaction and $NH_4^+ + NH_3$ reaction.

In view of the mechanism suggested above for the ethanol-sodium reaction, it seems likely that reduction of aromatic compounds by solutions of alcohols and alkali metals in liquid ammonia proceeds by a general mechanism involving a steady-state concentration of ammonium ion.

Krapcho and Bothner-By (29) observed that the reduction of benzene and several substituted benzenes in lithium-alcohol-ammonia solutions,

$$ArH + 2e^- + 2ROH \longrightarrow ArH_3 + 2RO^-,$$

proceeds by the third-order rate law

$$-\frac{d(ArH)}{dt} = k(ArH)(ROH)(e^-)$$

It can be shown that this rate law is consistent with the mechanism

$$ROH + NH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4^+ + RO^-$$

$$ArH + e^- \overset{fast}{\rightleftharpoons} ArH^- \qquad K = \frac{(ArH^-)}{(ArH)(e^-)}$$

$$NH_4^+ + ArH^- \xrightarrow{k_3} NH_3 + ArH_2$$

$$ArH_2 + e^- + NH_4^+ \xrightarrow{fast} ArH_3 + NH_3$$

By applying the steady-state approximation to the ammonium ion concentration, we calculate the rate law

$$-\frac{d(ArH)}{dt} = \frac{k_1 k_3 K(ROH)(ArH)(e^-)}{k_2(RO^-) + k_3 K(ArH)(e^-)}$$

which reduces to that found by Krapcho and Bothner-By when K is small and when the metal alkoxide is only slightly soluble. Their observation that the reduction rates with lithium, sodium and potassium decrease in that order is predictable from the expected increase in solubility of the alkoxides in the same order. Eastham and Larkin (13)

studied the reduction of the 1-naphthoxide ion with alcohol and potassium in ammonia. One would expect K to be relatively large for this substrate, and consequently one would predict that the rate law would reduce to

$$-\frac{d(ArH)}{dt} = k_1(ROH)$$

In agreement with this rate law, Eastham and Larkin observed that addition of alkoxide had no effect on the reduction, but greatly retarded hydrogen evolution.

Many of these aromatic reductions proceed with almost quantitative yield, indicating that the reaction

$$NH_4^+ + ArH^- \longrightarrow NH_3 + ArH_2$$

proceeds much more rapidly than the reaction

$$NH_4^+ + e^- \longrightarrow NH_3 + \tfrac{1}{2}H_2$$

However, when ammonium salts are added to solutions of aromatic compounds and alkali metals in ammonia, relatively poor yields of the reduced hydrocarbon are obtained. This result is probably due to the fact that the rate constants of the reactions

$$ArH + e^- \longrightarrow ArH^-$$

$$NH_4^+ + e^- \longrightarrow NH_3 + \tfrac{1}{2}H_2$$

are of comparable magnitude. When the ammonium ion concentration is low, hydrogen production does not compete seriously with the reduction.

However, when the ammonium concentration is high, the hydrogen-producing reaction seriously competes with the rate of formation of ArH^-.

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Figure 1. Fraction Reaction vs Logarithm of Time for the Reaction of Ethanol with Sodium in Liquid Ammonia.

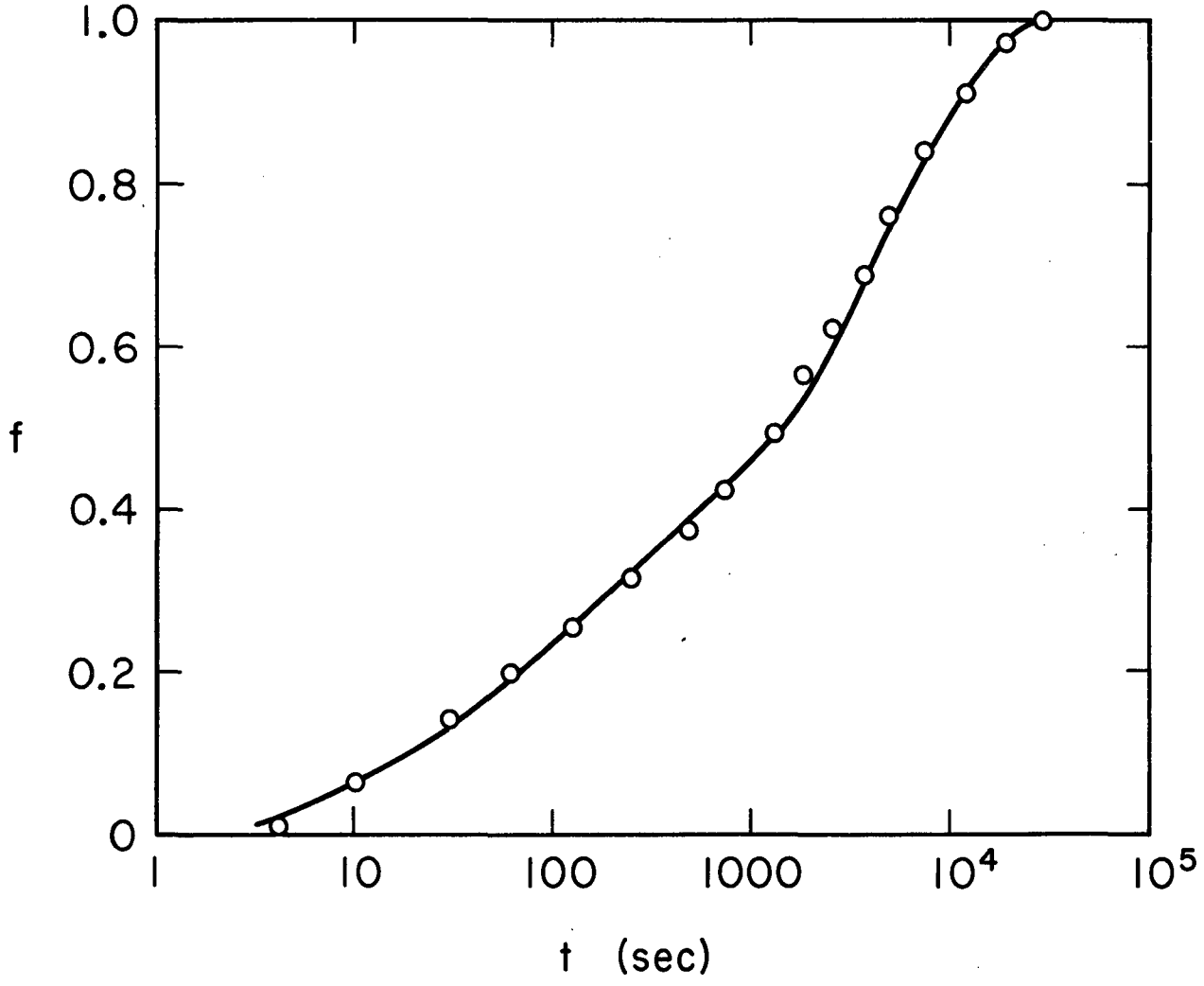

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Fig. 1

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