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# The Kinetics of Ammonia Exchange between Nickel Ammine Complexes and Ammonia in Aqueous and Anhydrous Ammonia Solutions Measured by Nuclear Magnetic Resonance of Nitrogen-14. II[1]

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Kinetic data are reported for the $Ni^{II}(NH_3)_6$–$NH_3$ exchange reaction in liquid ammonia. The reaction is homogeneous and unaffected by addition of up to 0.40 *M* $NH_4ClO_4$, 0.85 *M* $NaClO_4$, or 2.5 *M* $H_2O$. The rate law $R = 6k_1[Ni^{II}(NH_3)_6]$ has been used. At 25° $k_1$ is $1.0 \pm 0.1 \times 10^5$ sec.$^{-1}$. Values for $\Delta H^*$ and $\Delta S^*$ (calculated from $k_1$) are found to be 11 ± 1 kcal./mole and +2 ± 3 e.u. Data for the aqueous ammonia system were extended to 24 *M* $NH_3$. The kinetic parameters were found to be the same as in 7 and 14 *M* $NH_3$. Possible mechanisms are discussed and comparisons with related systems are given.

## Introduction

The research reported here represents primarily a more detailed study of the anhydrous ammonia system briefly discussed in an earlier publication.[3]

## Experimental

The n.m.r. data were obtained using the same basic spectrometer and general procedure as in the previous work.[3] The $N^{14}$ resonance in free ammonia was observed at *ca.* 2.85 Mc./sec. and 9300 gauss. Significant improvement of the spectra was obtained by using square wave rather than sine wave magnetic field modulation. In the present case two successive absorption curves (inverted with respect to each other) are obtained rather than a derivative curve. "Half-widths" for the absorption curves were taken as the full width in gauss at half-maximum absorption. Because of the overlapping nature of the observed absorption curves, corrections for obtaining the true widths had to be made. These were made graphically assuming the curves to be Lorentzian in shape. The corrections were usually of the order of 10% or less. Saturation curves were run in order to be certain that the radiofrequency power level was not too high. An improved method for matching the signal phase with that of the phase-sensitive detector was employed. A 30 c.p.s. modulation frequency was used with variable amplitude depending on the line half-width. Other features of the n.m.r. measurements remained as previously described.[3]

The salt $Ni(NH_3)_6(ClO_4)_2$ was prepared[3] from a nickel carbonate obtained by reaction of A.R. $Ni(NO_3)_2 \cdot 6H_2O$ and primary standard grade $Na_2CO_3$. Erratic behavior with respect to the formation of precipitates after dissolution of the hexaammine salt in ammonia was observed unless some ammonium salt was also present. In the absence of added ammonium salt it was usually found that a gray solid formed which slowly became brown-red in color, probably due to ammonolysis to $Ni(NH_2)_2$. Anhydrous $NaClO_4$ was prepared by the method of Willard and Smith.[4] The $NH_4ClO_4$ was prepared from A.R. $HClO_4$ and $NH_4OH$. The product was washed with ice water, absolute ethanol, and diethyl ether. It was dried further by pumping on a vacuum line. Ammonia was purified in the standard way. Solutions were prepared by condensing $NH_3$ from the gaseous state onto the appropriate dry solids using a vacuum system. Thick-walled Pyrex ampoules (*ca.* 12 mm. o.d.) were used to contain the solutions. These were selected to have constant inside dimensions so that, using a fixed amount of solution, the n.m.r. probe coil was always filled to the same extent. Temperatures were controlled using a thermostated $N_2$ gas flow device. These were constant to ±0.5° near room temperature but gradients of 1° might have been present near 0°. Samples were pre-equilibrated at the desired temperature before being placed in the sample coil. The apparent half-width for the $N^{14}$ resonance line in liquid $NH_3$ was found to be 0.29 ± 0.03 gauss essentially independent of temperature from 30 to −30°. This value is similar to that of Schmidt, *et al.*[5] (0.20 gauss); both values include some contribution from instrumental broadening. Our results depend on differences in half-widths and we have assumed that instrumental broadening (*e.g.*, due to field inhomogeneity) will cancel out.

## Treatment of Data and Results

We have followed the treatment of Swift and Connick[6] in obtaining kinetic information from the n.m.r. line-broadening data. The basic relationships are that $(1/T_2 - 1/T_{2A}) \equiv 1/T_{2p} = \gamma\Delta'/2$ where $T_2$ is the observed transverse relaxation time for the $N^{14}$ nucleus in free $NH_3$ in the presence of the paramagnetic nickel ions, $T_{2A}$ is the same quantity in the absence of paramagnetic ions, $\gamma$ is the magnetogyric ratio for $N^{14}$ (1934 gauss$^{-1}$ sec.$^{-1}$), and $\Delta'$ is the line broadening measured from the full line widths at half-maximum in the absorption curves. Because the concentrations of our solutions are most accurately known on a molal basis and since $\Delta'$ is proportional to total nickel molality we have referred the measurements to 1 *m* nickel concentration, thus

$$\gamma\Delta'/2m(\mathrm{Ni}) = 1/T_{2p}m(\mathrm{Ni}) \equiv 1/T_{2p}''$$

$$\text{or } T_{2p}'' \equiv 2m(\mathrm{Ni})/\gamma\Delta'$$

where $m(\mathrm{Ni})$ refers to the molality of nickel. When the line broadening is controlled by the chemical exchange rate ($R$) of ammonia between the ammine complex and free ammonia, $1/T_{2p}'' = 1/\tau_A m(\mathrm{Ni})$ where $\tau_A$ is the mean life of a free $NH_3$ molecule in the solution ($[NH_3]/R$). The rate is then given by $R = [NH_3] \cdot m(\mathrm{Ni})/T_{2p}''$, where the bracket refers to molar concentration units and $R$ is in moles/l. sec.

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[1] This work supported by the U. S. Atomic Energy Commission, contract No. AT(45-1)-1031.

[2] To whom inquiries may be addressed.

[3] J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963).

[4] H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **44**, 2817 (1922).

[5] B. M. Schmidt, L. C. Brown, and D. Williams, *J. Mol. Spectry.*, **2**, 539 (1958).

[6] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

No chemical shifts in the $NH_3$ resonance (>30 p.p.m.) were observed in these studies. The molar concentrations of salts were calculated from the known weights of salts and ammonia assuming that the densities of the solutions were the same as for pure ammonia[7] at a given temperature. This assumption should be valid within the precision of the measurements of the line broadenings (±5 to 10%).

The concentration of added $NH_4ClO_4$ was varied from 0 to *ca.* 0.4 *M* at several temperatures, and no significant effects on the line broadenings were observed.

The concentration of added $NaClO_4$ was varied from 0 to 0.85 *M* in four separate runs at 30° and again no effects on the line broadenings were observed.

Finely divided silica gel and "activated" charcoal were added in two separate experiments at 30°. In both cases the solids settled out quite rapidly. In neither case were changes in line broadenings produced by the added material.

The effects of varying nickel concentrations and temperature were studied in some detail. Since, as will be seen shortly, the line broadenings are controlled by the exchange rate, we proceed to treat the data in the following way. We assume that all the Ni(II) is present as $Ni^{II}(NH_3)_6$. The concentration of $NH_3$ does not vary significantly, and we use the rate law $R = 6k_1 \cdot [Ni^{II}]$ where $k_1$ refers to the specific rate constant for *a particular* ammonia ligand. With these assumptions, $k_1$ can be obtained from the relation $k_1 = 58.9/6T_{2p}''$ where 58.9 is the number of moles of $NH_3$ per 1000 g. of ammonia and no assumptions regarding calculations of molarities are involved. The $T_{2p}''$ results are given in Table I. A plot of log $k_1$ *vs.* $10^3/T$ is given in Figure 1.

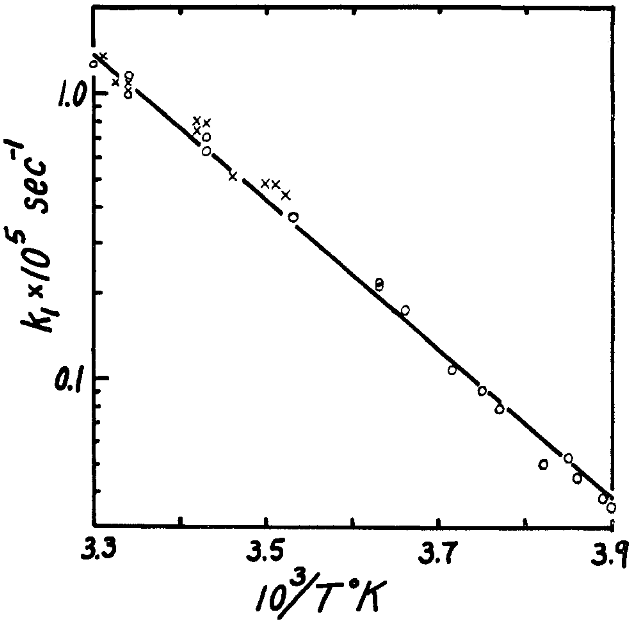

Figure 1.—Arrhenius plot for anhydrous $NH_3$ exchange data: ×, no $NH_4ClO_4$ added.

TABLE I

LINE-BROADENING DATA FOR $Ni^{II}(NH_3)_6$–$NH_3$ EXCHANGE IN LIQUID $NH_3$

| *t*, °C. | Δ′, gauss | $T_{2p}'' \times 10^4$, *m* sec. |
|---|---|---|
| (A) Ni = 0.090 *m*, *ca.* 0.054 *M* | | |
| 11.0 | 0.42 | 22.1[c] |
| 13.1 | 0.47 | 19.8[c] |
| 16.3 | 0.49 | 19.0[c] |
| 18.5 | 0.60 | 15.5[a] |
| 18.8 | 0.75 | 12.4[c] |
| 19.0 | 0.77 | 12.1[c] |
| 25.8 | 0.98 | 9.5[c] |
| 26.0 | 1.13 | 8.2[a] |
| 26.0 | 1.05 | 8.9[c] |
| 26.1 | 0.96 | 9.7[a] |
| 27.3 | 1.02 | 9.1[b] |
| 27.6 | 1.05 | 8.9[c] |
| 29.0 | 1.29 | 7.2[c] |
| 29.5 | 1.21 | 7.7[a] |
| (B) Ni = 0.120 *m*, *ca.* 0.062 *M* | | |
| 11.8 | 0.61 | 20.3[c] |
| 19.4 | 0.95 | 13.1[c] |
| (C) Ni = 0.269 *m*, *ca.* 0.15 *M* | | |
| 2.8 | 0.61 | 45.6[a] |
| 9.9 | 1.05 | 26.4[a] |
| 18.6 | 2.01 | 13.8[a] |
| (D) Ni = 0.82 *m*, *ca.* 0.40 *M* | | |
| −16.6 | 0.30 | 283[a] |
| −15.8 | 0.33 | 257[a] |
| −14.1 | 0.39 | 217[a] |
| −13.1 | 0.46 | 185[a] |
| −11.5 | 0.43 | 197[a] |
| −8.2 | 0.67 | 127[a] |
| −6.4 | 0.78 | 109[a] |
| −3.4 | 0.94 | 90[a] |
| 0.0 | 1.51 | 56[a] |
| +2.4 | 1.83 | 46[a] |

[a] $NH_4ClO_4$ = 0.163 *m*, *ca.* 0.096 *M*. [b] $NH_4ClO_4$ = 0.66 *m*, *ca.* 0.39 *M*. [c] No added $NH_4ClO_4$.

The straight line is drawn for the data obtained from solutions containing $NH_4ClO_4$ as some precipitation may have been involved in the others. At 25° $k_1$ is $1.0 \pm 0.1 \times 10^5$ sec.$^{-1}$. From the temperature coefficient and $k_1$ at 25° we calculate $\Delta H^* = 11 \pm 1$ kcal./mole and $\Delta S^* = +2 \pm 3$ e.u.

The previously reported values[3] were $k_1 = 5 \times 10^4$ sec.$^{-1}$ at 25° and $\Delta H^* = 10 \pm 1$ kcal./mole, $\Delta S^* = -3 \pm 4$ e.u. It now seems likely that some saturation of the $N^{14}$ resonance in liquid $NH_3$ was occurring in the earlier experiments affecting the absolute values of $k_1$.

As a check on and extension of the aqueous $NH_3$ data some further experiments were performed in aqueous $NH_3$. In 14 *M* $NH_3$ at 0.05 and 0.10 *M* $Ni(NH_3)_6(NO_3)_2$ and at 30 and 0°, good agreement was found with the previously reported results.[3] At 30° we find $k_1 = 7.7 \times 10^4$ compared to $7.1 \times 10^4$ previously found and at 0° $k_1 = 1.4 \times 10^4$ compared to $1.2 \times 10^4$ (the new value fits the Arrhenius plot better than the older one).

A 24 *M* aqueous $NH_3$ solution was prepared (sealed tube) containing 0.10 *M* $Ni(NH_3)_6(NO_3)_2$ and measured at 30 and 16°. The $k_1$ and $\Delta H^*$ were the same as found in the range 7–14 *M* aqueous $NH_3$.[3] The solubility of the nitrate salt decreases as ammonia concentration increases, making further extension of the

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(7) C. S. Cragoe and D. R. Harper 3rd, National Bureau of Standards, Scientific Paper No. 420, U. S. Government Printing Office, Washington, D. C., 1921, p. 313.

data difficult. The perchlorate salt is soluble enough only in much more highly concentrated ammonia solutions.

Small amounts of water could be added to the $Ni(NH_3)_6(ClO_4)_2$ solutions in liquid ammonia without precipitating the nickel salt. No effects on $k_1$ at 30° were found upon addition of up to *ca.* 2.5 $M$ $H_2O$.

## Discussion

The kinetic data lead to the conclusion that neutral $NH_3$ is being exchanged homogeneously with the $Ni^{II}(NH_3)_6$ species since effects due to $NH_4ClO_4$, ionic strength, and increased surface are small, if any exist. The order with respect to $NH_3$ is not given by the present experiments. The data in aqueous ammonia in which both $H_2O$ and $NH_3$ have been significantly varied suggest that neither $H_2O$ nor $NH_3$ is directly involved in the mechanism of exchange and that a dissociation type process is involved in the rate-determining step. The activation parameters for the aqueous and anhydrous systems are quite similar ($\Delta H^* = ca.$ 10 kcal./mole and $\Delta S^* = -5$ e.u. for the aqueous system). At 25°, however, the rate in liquid $NH_3$ is *ca.* double the rate in aqueous $NH_3$. Among the more obvious differences in the two systems are found the dielectric constant, solvent structure, and anionic species present. The low dielectric constant of $NH_3$ is expected to lead to extensive ion association so that the reacting species might well be different in the two media. The results in the $Cr^{II}(NH_3)_6$–$N^{15}H_3$ exchange system[8,9] in liquid $NH_3$ are rather different from those for Ni(II). Not only is exchange very much slower for Cr(III), but both ammonium salts and anions inhibit the exchange. To be consistent with the interpretation of the Cr(III) data, we would have to postulate only relatively slight ammonolysis for Ni(II) and essentially complete formation of $Ni(NH_3)_6(ClO_4)_2$ ion triplets (not unreasonable postulates). Because of the differences in species in the aqueous and anhydrous media one might have expected somewhat more different activation parameters. Naïvely it might appear that charge reduction by ion association would facilitate a dissociation process by lowering the $\Delta H^*$ value contrary to what is observed. Such a conclusion should, however, be modified by including solvation effects.

The change in kinetic behavior from an aqueous to a nonaqueous system appears to occur in the range 24–2.5 $M$ $H_2O$. It does not appear convenient to study this range using $NO_3^-$ or $ClO_4^-$ salts.

It is interesting to note that the aqueous systems $Ni(H_2O)_6^{2+}$, $Ni(NH_3)_6^{2+}$, and $Ni(H_2O)_2(NCS)_4^{2-}$ and the present one all have $\Delta H^*$ values near 10 kcal./mole with rates of about the same order of magnitude ($k_1$ *ca.* $10^4$–$10^5$ sec.$^{-1}$).

Some comparisons with analogous exchange reactions in liquid ammonia can be made. The Cu(II)–$NH_3$(l) system has been studied by n.m.r. in some detail.[10] The data over a very wide range of temperature give only lower limits to the exchange rates. These limits do show, however, that the Cu(II)–$NH_3$ exchange is faster than for Ni(II)–$NH_3$ (>8 times) as seems to be a general result in comparing Cu(II) and Ni(II). Data on the $Co^{II}(NH_3)_6^{2+}$ exchange[10] give a value for $k_1$ of *ca.* $1 \times 10^7$ sec.$^{-1}$ at 25°, *ca.* 100-fold faster than for Ni(II). The Co(II) results will be presented in a later publication and compared with the Ni(II) data in more detail.

Extrapolation of the present data to $-50°$ gives a rate constant of *ca.* 120 sec.$^{-1}$, which can be compared with the rough tracer result[11] of 28 sec.$^{-1}$.

We are looking for nickel salts to bridge the remaining gap between aqueous and anhydrous ammonia. In addition to the studies on Cu(II), Ni(II), and Co(II) systems we are hopeful of extending the series to include Cr(II), V(II), and V(III) in aqueous and nonaqueous ammonia where possible.

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[8] T. W. Swaddle, L. F. Coleman, and J. P. Hunt, *Inorg. Chem.*, **2**, 950 (1963).

[9] H. H. Glaeser and J. P. Hunt, *ibid.*, **3**, 1245 (1964).

[10] H. H. Glaeser, F. Klanberg, H. W. Dodgen, and J. P. Hunt, unpublished results.

[11] J. R. Sutter and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 6420 (1960).