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Exchange of Ammonia with Cobalt(II) Ammines in Aqueous Solution[1]

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Received August 16, 1968

Kinetic data obtained by nmr line-broadening techniques are reported for aqueous ammonia solutions of cobalt(II). The rates of ammonia exchange and activation enthalpies are relatively insensitive to ammonia concentration in the range 3–30 *M*. For the rate law $R = k[\mathrm{Co(II)}]$, k_{298} in 14 *M* NH_3 is *ca.* $(3 \pm 0.3) \times 10^7$ sec^{-1} and ΔH^* is 13 ± 1 kcal/mole. The scalar coupling constant A/h for $Co(NH_3)_6^{2+}$ is calculated to be $(8 \pm 0.5) \times 10^6$ cps. Solutions not containing NH_4^+ show slightly different kinetic behavior. The results are similar to those found in anhydrous ammonia.

Introduction

We have previously described the exchange kinetics for NH_3 and $Co(NH_3)_6^{2+}$ in liquid ammonia.[3] In this report we give the results of similar studies in aqueous ammonia solutions of varying concentrations. These studies are of interest for comparisons among the various labile species involved as well as with other labile systems such as those of Ni(II).

Experimental Section

The nmr techniques and equipment used have been previously described.[4] Cobalt reagents used were AR grade $Co(NO_3)_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$ prepared from $CoCO_3$ and $HClO_4$. Nitrate and perchlorate anions gave the same results within experimental error. Samples for nmr analysis were prepared using vacuum-line techniques to ensure the absence of air oxidation of Co(II) and were contained in sealed ampoules of *ca.* 12-mm o.d. The ammonia used was AR grade, or, for the most concentrated solutions, gaseous ammonia was prepared from liquid ammonia and purified in the standard way. The ammonium nitrate used was of AR grade.

Treatment of Data and Results

The line broadening and chemical shifts of the free $^{14}NH_3$ nmr signal (or $^{14}NH_3 + {}^{14}NH_4^+$) produced by addition of Co(II) were measured usually at 2.85 MHz as functions of temperature and solution composition. The broadening results are reported in terms of the quantity $T_{2p}' \equiv 2M_{\mathrm{Co(II)}}/\gamma\Delta'$ where $M_{\mathrm{Co(II)}}$ refers to the total molarity, γ is the magnetogyric ratio for ^{14}N (1934 G^{-1} sec^{-1}), and Δ' is the line broadening (in gauss) produced by Co(II). The line broadening is taken as the difference in full line width at half-maximum intensity in the nmr absorption curve in the presence and absence of Co(II), other conditions being constant. Some results are given in Table I.[5] The quantity W_o is the observed line width of the reference solution containing no Co(II).

TABLE I

LINE-BROADENING DATA FOR $^{14}NH_3$ EXCHANGE[a]

Temp, °C	Δ', G	$10^4T_{2p}'$	W_o, G	$M_{\mathrm{Co(II)}}$
35.0	0.35	0.85	0.49	0.0287
31.0	0.38	0.78	0.57	0.0287
28.8	0.43	0.693	0.66	0.0287
26.3	0.73	0.41	0.67	0.0287
25.0	0.84	0.36	0.66	0.0287
22.7	0.94	0.32	0.72	0.0287
17.0	0.28	0.31	0.72	0.0084
14.5	0.34	0.26	0.75	0.0084
13.0	0.62	0.14	0.75	0.0084
13.0	0.62	0.14	0.68	0.0084
8.1	0.69	0.13	0.76	0.0084
5.7	0.87	0.10	0.86	0.0084
0.5	0.87	0.10	0.86	0.0084
−1.0	0.75	0.12	1.02	0.0084
−5.2	0.72	0.12	1.12	0.0084
−10.0	0.77	0.11	1.17	0.0084
−12.0	0.66	0.13	1.27	0.0084
−15.0	0.66	0.13	1.46	0.0084
−20.5	0.50	0.18	1.48	0.0084

[a] $M_{NH_3} = 7.37$; $M_{NH_4NO_3} = 2.00$.

Chemical shift data were obtained in most cases. The shifts were measured relative to aqueous ammonia or the average signal due to ammonia–ammonium ion exchange depending on the kind of solution involved. The shift results are given in terms of $S = (\omega_o - \omega_{\mathrm{ref}})/\omega_{\mathrm{ref}}$ and $TSM_{NH_3}/M_{\mathrm{Co(II)}}$, where T is the absolute temperature M_{NH_3} is total ^{14}N in NH_3 and NH_4^+, and $M_{\mathrm{Co(II)}}$ refers to total cobalt molarity. These quantities are listed in available tables.[5]

Interpretation of the results follows that described earlier in some detail.[3] For solutions 14 *M* or less in NH_3, most of the line-broadening data refer to conditions under which the chemical-exchange rate is not the controlling factor in line broadening. Consequently plots of T_{2p}'/T^3 *vs.* $10^3\,T$ were used to evaluate these data. The runs at higher ammonia concentration were plotted as TT_{2p}' *vs.* $10^3/T$. Representative graphs are shown in Figures 1 and 2. Figure 1 also shows the relevant shift data. Using fitting procedures described earlier,[3] we have calculated the quantities of interest and list them in Table II. The k values are calculated for the rate law rate $= k[\mathrm{Co(II)}]$ at −23.2°, a temperature in the Arrhenius region of

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[1] This work was supported by USAEC Contract AT(45-1)-2040 and is Report No. RLO-2040-7.

[2] To whom inquiries may be addressed.

[3] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965).

[4] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 206 (1965).

[5] For detailed tables, order Document No. NAPS-00183 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

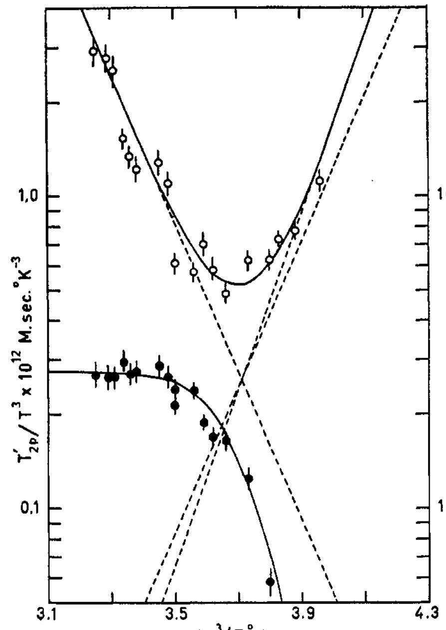

Figure 1.—Plot of T_{2p}'/T^3 and $TSM_{NH_3+NH_4^+}/M_{Co(II)}$ vs. $10^3/T$ for $^{14}NH_3$: open circles for line broadening; solid circles for shift data; the dashed lines are those used in the curve-fitting procedure (7.32 M NH_3 + 2.00 M NH_4NO_3).

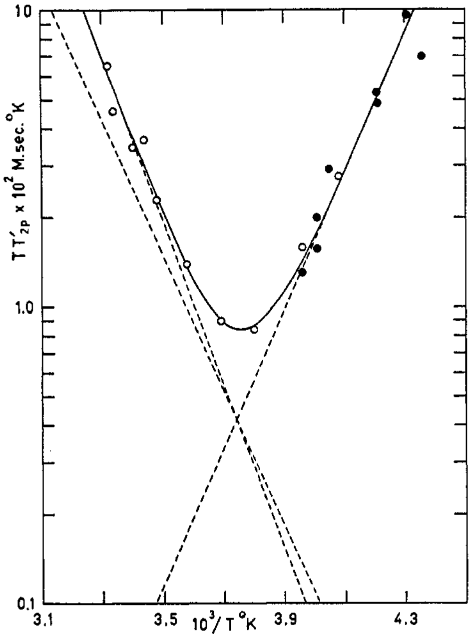

Figure 2.—Plot of TT_{2p}' vs. $10^3/T$ for $^{14}NH_3$: open symbols, 27.4 M NH_3; solid symbols, 31.4 M NH_3; the dashed lines are those used in the curve-fitting procedure.

the T_{2p}' plots and not involving a large and rather uncertain extrapolation to 25°. The extrapolated values for 25° are also listed for convenience. The A/h values are calculated assuming $NH_3:Co = 6$ and $S = {}^3/_2$ and are averages of those calculated from the shift function limit and the intersection point of the T_{2p}' plots. These generally agree to ±10% or better. The line-broadening and shift data suggest that a $\Delta\omega$ mechanism[6] is responsible for the observed broadenings. Some runs were made at the higher temperatures using 7.56 MHz rather than the usual 2.85 MHz. For a $\Delta\omega$ mechanism, one expects T_{2p}' to be lowered by a factor of 7 at the highest temperatures. This was found to be true within ±10% for the 7 M NH_3 + 2 M NH_4^+ and 13.8 M NH_3 solutions. The k values listed in Table II for 13.8 M NH_3 were calculated from the experiments at 7.56 MHz because of the better precision obtained at the higher field.

TABLE II

RESULTS OF NMR STUDY ON Co(II)–NH$_3$ SOLUTIONS

M_{NH_3}	$M_{NH_4^+}$	10^5k_{250}, sec^{-1}	10^6k_{298}, sec^{-1}	ΔH^*, kcal mol^{-1}	$10^6A/h$, cps
3.14	1.95	3.8	7	9	7.7
6.90	....	3.7	25	13	6.9
7.37	2.00	3.6	13	11	8.5
10.4	1.95	5.0	9	9	7.7
11.6	2.00	5.1	9	9	7.7
13.8	....	4.2	28	13	7.6
Ca. 29	....	*Ca.* 4.3	15	11	8.0
36[a]	....	10.5	43	11	7.5

[a] Reference 3; anhydrous ammonia.

Discussion

The data obtained are not precise owing to experimental problems with the ^{14}N resonance measurements. The k values are reliable to ±10% at best and errors in ΔH^* are estimated to be 1–2 kcal mol^{-1}. The data cover a fair range of species. In *ca.* 2 M NH_4NO_3 one can use Bjerrum's[7] results to calculate species concentrations. The quantity $\bar{n}$ varies from 5.3 to 6 over the range studied. At the lowest ammonia concentration the tetraammine is present to *ca.* 9.7%, the pentaammine to *ca.* 49.6%, and the hexaammine to *ca.* 40.2%. Solution compositions are only slightly dependent on temperature. The small variation in exchange rate at 250°K with ammonia concentration suggests that the hexa- and pentaammines are contributing about equally. The ΔH^* values appear to be similar. Calculated A/h values based on $NH_3:Co = 6$ also vary only slightly. This fact requires that both species be involved in exchange with similar rate behavior. The apparent faster exchange rate in anhydrous ammonia (*ca.* a factor of 2) was also noted in the analogous Ni(II) system.[4]

Equilibrium studies on solutions not containing NH_4^+ are not available. Presumably some hydrolysis can occur in these solutions. There is some suggestion at least that ΔH^* is higher for these cases.

Comparisons have been made earlier between Ni(II) and Co(II) systems[4] and these are not changed by the additional data reported here. It would be of interest to try to study exchange at low ammonia concentration to see where exchange rates slow down.

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

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1957.