M acid, the principal deeply colored species exhibits a maximum at 466 mμ ($\epsilon > 600$), which, unlike the 473-mμ species formed in 1.2 M acid, persists well beyond the 5.0-equiv region and is therefore assigned to one or more azo intermediates.

During Cr^{2+} reduction of the 4-nitro-3-methylbenzoato complex in 1.2 F $HClO_4$, a species strongly absorbing at 513 mμ is formed. The development and disappearances of this pigment as successive portions of reductant are added (Figure 4) parallel the behavior of the 504-mμ complex derived from the p-nitrobenzoato derivative; hence it may be likewise ascribed to a Cr(III)-bound, one-electron reduction product. With the m-nitrobenzoato complex, on the other hand, transient absorption (λ_{max} 420 mμ) develops more gradually, reaches a maximum at about 3.5 equiv, then virtually disappears at 4.0–4.5 equiv (Figure 4), suggesting that the principal absorbing species is the three-electron reduction product, that is, a nitroso radical cation analogous to XLV.[27] In this case, the possibility that this radical ion is an intermediate in the principal reduction sequence cannot be excluded.

In summary, the present study of nitro complexes, despite the tentative nature of some of the conclusions drawn, reemphasizes the lesson that acceptance of a reducing electron by a group in conjugation with COOCo(III) in the ligand is not at all tantamount to reduction of the coordinated Co(III). Although structural features favoring one process often favor the other, the detailed requirements for the two are generally different.

Acknowledgments. The author is grateful to Mr. F. Nordmeyer, Mr. E. Deutsch, and Mr. D. LaFollette for making known the results of their experiments prior to publication. He is also indebted to Professor Henry Taube for a number of valuable discussions.

The 473-mμ absorption is most prominent in the 2.5–4.5 (nitroso) region and appears to be formed in a one-electron oxidation which also regenerates XLI; it is therefore assigned to the three-electron reduction product, here represented as radical cation XLV. The intense absorption of this species indicates coordination to Cr(III), both here and in its presumed precurser, XLIII.

The conversion of the 504- to the 473-mμ species in the absence of added Cr(II) is fastest in the 2–3-equiv region, that is, when the concentration of the nitroso complex is presumably greatest. This points to conversion of the nitroso complex to its radical cation XLV, but here the electron donor appears to be XLI, rather than its Cr(II) counterpart XLIV, which accomplishes the same reduction more rapidly.

Since the rate of formation of XLI should not be pH dependent, its nonappearance at higher pH values indicates that it is being consumed rapidly, not by reduction (which should proceed no more rapidly at the higher pH), but rather by heterolysis to the more faintly colored and more reactive radical cation XLII.

(27) The alternate three-electron reduction product, an azoxy derivative, is ruled out here by the position of the maximum. Aromatic azoxy compounds generally exhibit peaks near 320 mμ, but not, in the absence of other chromophoric groups, near 420 mμ: see, for example, M. J. Kamlet, "Organic Electronic Spectral Data," Interscience Publishers, Inc., New York, N. Y., 1960, p 442.

The Relaxation of Protons in Liquid Ammonia by Nickel(II) and the Kinetics of Ammonia Exchange

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Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio. *Received February 16, 1966*

Abstract: Anhydrous solutions of $Ni(NH_3)_6(ClO_4)_2$ in liquid ammonia were prepared, and the proton nmr spectra were recorded as a function of temperature. The line shapes were shown to be the result of spin–spin relaxation of protons with no detectable contribution from spin–lattice relaxation of ^{14}N. Moreover, the temperature dependence of the proton T_2 revealed that the relaxation process is chemical exchange controlled below about 0° and that the relaxation mechanism is the "chemical shift" mechanism. With these facts established, quantitative kinetic studies were performed with solutions of $Ni(NH_3)_6(ClO_4)_2$ in ammonia to which a small amount of $HClO_4$ had been added to produce the collapse of the ^{14}N triplet. The first-order rate constant for the ammonia exchange was found to be $1.9 \pm 0.1 \times 10^5$ sec^{-1} at 25°; ΔH^* is 10.1 ± 0.5 kcal/mole and ΔS^* is -0.5 ± 1 eu. The coupling constant, A/h, is $3 \pm 1 \times 10^6$ cps.

In a recent investigation Swift and Sayre[1] have shown that certain rapid reactions directly involving water molecules in aqueous solution may be used to obtain information concerning the hydration of cations. The authors employed manganous ion as their "probe" reagent and list the following requirements for a probe in order that the probe may be suitable for the study of ion hydration. (1) It must react directly with water molecules. (2) The rate constant for the direct reaction between the probe and primary hydration sphere waters must differ considerably from the rate for all other types of water molecules. (3) The lifetime of the probe must be obtainable from a precisely measurable experimental quantity.

In the interpretation of their results concerning the hydration numbers of several doubly changed ions, the authors have introduced the possibly sizable role of the solvent structure in the determination of the solvation numbers of ions in solution.

As a consequence of these results, a series of investi-

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[1] T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, **44**, 3567 (1966).

gations was begun in this laboratory toward the eventual determination of solvation numbers of cations in liquid ammonia, and the first major study in this direction was the search for a suitable probe reagent for liquid ammonia.

The first reagent chosen for investigation was nickelous ion. The kinetics of exchange of ammonia between the first coordination sphere of Ni^{2+} and the solution bulk had been studied in detail[2,3] through the use of ^{14}N nuclear magnetic resonance data. These kinetic studies had shown that the ^{14}N spin–spin relaxation time in solutions of Ni^{2+} in liquid ammonia at the temperatures employed is determined by the rate of the exchange mentioned above.

There is a strong possibility that nickelous ion would fulfill the first two requirements outlined above for a suitable probe reagent, but it certainly would not meet the third requirement if the physical observable were to be a ^{14}N resonance signal width. The required degree of precision in the measurement of the observed physical property has been shown to be a few parts per thousand as an average deviation. The average deviation in the measurement of ^{14}N signal widths in liquid ammonia is no better than ±10%.[2]

A comparison of nuclear relaxation data for protons[4] with that of ^{17}O in aqueous solutions containing Ni^{2+} has revealed that the spin–spin relaxation of both nuclei is controlled by the rate of exchange of water molecules between the first coordination sphere of Ni^{2+} and the bulk at temperatures near 0°. Chemical exchange control is observable with proton resonance because the rate of water molecule exchange involving Ni^{2+} is relatively slow at these temperatures.[5]

The rate constant for the ammonia exchange involving Ni^{2+} in liquid ammonia is quite comparable in magnitude[3] to the rate constant for water molecule exchange[5] in the temperature range for which a comparison can be made.

As a consequence of these considerations it was considered quite possible that the spin–spin relaxation of protons in liquid ammonia produced by Ni^{2+} is also controlled by the rate of ammonia molecule exchange over a significantly large temperature range. If this can be established, proton line widths can be used as the physical observable in the study of ion solvation in ammonia, and the third requirement for a suitable probe reagent would be fulfilled by Ni^{2+}.

Theory

The proton resonance spectrum of highly purified liquid ammonia has been given by Ogg and Ray[6] and more recently by Swift, Marks, and Sayre.[7]

The spectrum consists of a relatively broad triplet due to the rather rapid quadrupolar spin–lattice relaxation of ^{14}N in liquid ammonia, and the shapes of the spectra at various temperatures have been used[7] to obtain values for the quadrupolar transition probability.

A thorough investigation of the role of Ni^{2+} in liquid ammonia would demand the preparation of a scrupulously dry solution of a suitable nickel salt in liquid ammonia and the recording of the proton spectrum as a function of temperature. It will be shown in a subsequent section of this paper that this rather tedious procedure proved to be unnecessary, and a greatly simplified approach is equally valid. Nevertheless this could only be established through a study of the anhydrous solutions.

The Bloch equations for anhydrous ammonia which contains an added paramagnetic ion are

$$\begin{gathered}
-G_{+1}[1/T_2 + (3/\tau) - 2\pi iJ(X - 1)] + \\
\hfill G_0(1/\tau) + G_{-1}(2/\tau) = i\omega_1 M_0{}^{+1} \\[2ex]
G_{+1}(1/\tau) - G_0[1/T_2 + (2/\tau) - 2\pi iJX] + \\
\hfill G_{-1}(1/\tau) = i\omega_1 M_0{}^{0} \quad (1) \\[2ex]
G_{+1}(2/\tau) + G_0(1/\tau) - G_{-1}[1/T_2 + \\
\hfill (3/\tau) - 2\pi iJ(X + 1)] = i\omega_1 M_0{}^{-1}
\end{gathered}$$

where the G's are complex magnetizations appropriate to the ^{14}N spin states, $1/\tau$ is the quadrupolar transition probability, p, defined by Pople,[8] J is the ^{14}N–H coupling constant, X is the dimensionless variable defined by Pople,[8] and T_2 is the proton spin–spin relaxation time.

Equations 1 were solved for $G = G_{+1} + G_0 + G_{-1}$, and from G the absorption signal, v, was obtained and $v \propto A/B$ where

$$\begin{aligned}
A = {} & \eta'^5[\eta^3(10X^2 + 2) + 90\eta] + \\
& \eta'^4[\eta^4(3X^4 + 1) + \eta^2(102X^2 + 108) + \\
& 675] + \eta'^3[\eta^3(48X^2 + 38) + 720\eta] + \\
& \eta'^2[\eta^4(6X^2 + 4) + 282\eta^2] + 48\eta'\eta^3 + 3\eta^4 \\
B = {} & n'^6[\eta^4(X^6 - 2X^4 + X^2) + \\
& \eta^2(34X^4 - 2X^2 + 4) + 225X^2] + \\
& \eta'^5[\eta^3(16X^4 + 4X^2 + 4) + \eta(240X^2 + 60)] + \\
& \eta'^4[\eta^4(3X^4 + 1) + \eta^2(128X^2 + 62) + 225] + \\
& \eta'^3[\eta^3(32X^2 + 20) + 240\eta] + \\
& \eta'^2[\eta^4(3X^2 + 2) + 94\eta^2] + 16\eta'\eta^3 + \eta^4
\end{aligned} \qquad (2)$$

and the terms η and η' are $2\pi J\tau$ and $2\pi JT_2$, respectively.

The value of η' for any given nickel(II)–ammonia solution can be obtained by the procedure mentioned in the Results section.

Experimental Section

A. Preparation of Anhydrous Nickel(II)–Ammonia Solutions. The apparatus used in the preparation of anhydrous nickel(II)–ammonia solutions was identical with that described by Swift,

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

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

(4) T. J. Swift and T. A. Stephenson, *ibid.*, **5**, 1100 (1966).

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

(6) R. A. Ogg and J. D. Ray, *ibid.*, **26**, 1515 (1957).

(7) T. J. Swift, S. B. Marks, and W. G. Sayre, *ibid.*, **44**, 2797 (1966).

(8) J. Pople, *Mol. Phys.*, **1**, 168 (1958).

Marks, and Sayre for the preparation of ammonia-amide solutions. In the following description, several of the symbols used are taken from the authors' Figure 1.[7]

A weighed amount of dried $Ni(NH_3)_6(ClO_4)_2$ was added to bulb B and the access tube was sealed. The apparatus was then attached to a high-vacuum line. A heating mantle was placed around bulb B and the bulb was heated at a temperature of 180–200° for several hours until the violet-blue solid turned pale green.

Doubly distilled potassium was distilled into the bulb at the left of Figure 1 in ref 7, and *ca.* 20 cc of NH_3 was distilled into the bulb from a container in which the ammonia had been stored over potassium for several days.

The solvent and all the interior glass surface to the left of the fritted glass filter were made completely free of water through the procedure outlined by Swift, Marks, and Sayre.[7]

Ammonia was then distilled from the potassium-ammonia solution into bulb B and then from bulb B back to the potassium solution. This procedure was repeated several times over the course of a few days.

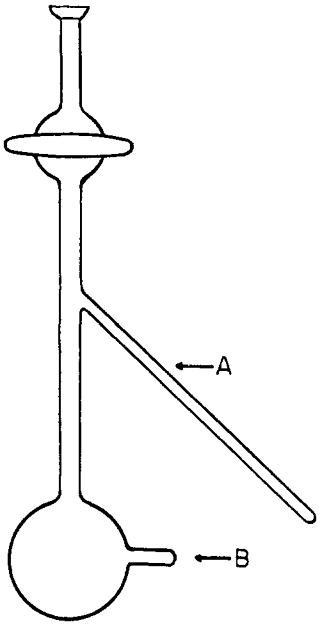

Figure 1. Apparatus used in the preparation of acidified solutions of $Ni(NH_3)_6(ClO_4)_2$ in liquid ammonia: (A) sample tube, (B) access for titration and solution preparation.

Finally the interior glass surface to the left of the filter was again cleansed by the procedure mentioned above and all the ammonia was distilled into bulb B. The bulb containing the potassium was then removed by sealing off the tube above the spiral.

The nickel(II)-ammonia solution was passed through the filter to bulb A, and a small amount of ammonia was distilled from it to one of the sample tubes. This sample tube was sealed off and removed and used as a check on the amount of water remaining in the system. The proton resonance spectra of these test samples of NH_3 were found to be identical with those for pure NH_3 recorded by Swift, Marks, and Sayre.[7]

Some of the nickel(II)-ammonia solution was then poured into the second sample tube, and the tube was sealed and removed. Spectra were recorded on a Varian A-60 spectrometer.

In the analysis of the nickel(II)-ammonia solutions, the apparatus was replaced on the vacuum line and the ammonia was distilled from bulb A to a container holding concentrated H_2SO_4, and the amount of ammonia absorbed was determined by the gain in weight of the container.

Bulb A was then opened and the solid $Ni(NH_3)_6(ClO_4)_2$ was dissolved in a known volume of standardized HCl. The ammonia content of the solid was then obtained by back titration with standardized NaOH. As a check on this analysis, the Ni content was then determined through the standard gravimetric procedure with dimethylglyoxime. In all cases the two analytical procedures yielded agreement within ±1%.

B. Preparation of Nickel(II)-Ammonia Solutions with Added Perchloric Acid. It will be shown in a subsequent section that the preparation of anhydrous nickel(II)-ammonia solutions proved to be unnecessary and even disadvantageous in the present study. As a consequence, several solutions of Ni^{2+} in ammonia were prepared to which a small volume of concentrated $HClO_4$ solution was added.

The apparatus for the preparation of these solutions was quite simple and is shown in Figure 1.

A weighed amount of dried $Ni(NH_3)_6(ClO_4)_2$ was added to the bulb through the access tube, and then from a calibrated micropipet 0.314 ml of 2.36 *M* aqueous $HClO_4$ was added. The access tube was sealed and the apparatus was placed on the high-vacuum line. Dried ammonia was then distilled into the bulb and the solution was prepared. Part of the solution was poured into the sample tube and the sample tube was sealed and removed.

The analysis of the solution was performed in the identical manner as that described above for the anhydrous solutions. The volumetric and gravimetric determinations of the nickel content were again in excellent agreement.

In addition to these solutions, a "blank" solution was also prepared which contained only the aqueous perchloric acid and the ammonia.

Results

Figure 2 shows the proton spectrum of pure NH_3 at −38.5° and that of an anhydrous nickel(II)-ammonia solution for which $[Ni^{2+}]/[NH_3]$ is equal to 5.7×10^{-3}. Spectra such as these tended to indicate that the most important relaxation effect produced by the nickelous ion was T_2 relaxation of the protons.

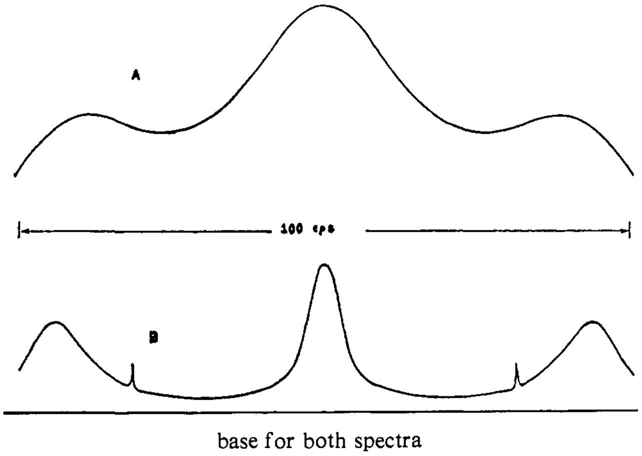

Figure 2. (A) Proton resonance spectrum at −38.5° for an anhydrous liquid ammonia solution for which $[Ni^{2+}]/[NH_3] = 5.70 \times 10^{-3}$. (B) Proton spectrum of anhydrous liquid ammonia at −38.5°.

Values of T_2 as a function of temperature were obtained in the following manner. Equation 2 is rather easily[7] converted to a polymonial relating η and η' to the value of X for which v possesses half the maximum value. Values of η as a function of temperature were determined by Swift, Marks, and Sayre,[7] and η' and T_2 could be determined for any given spectrum from the solution to the appropriate polynomial. The polynomials were solved through use of the Newton–Raphson iterative procedure on the Univac 1107 digital computer.

A plot of T_2 at four temperatures for a typical anhydrous solution is given in Figure 3. Strangely the anhydrous solutions could not be studied at temperatures above *ca.* 0°. At these temperatures the spectrum was observed to collapse into a singlet as a function of time, and the change was found to be irreversible.

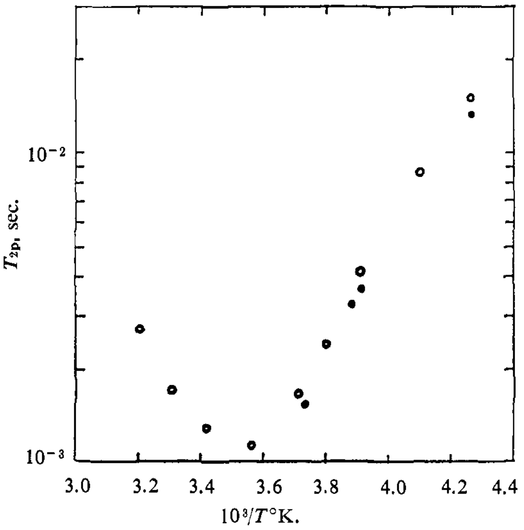

Figure 3. Log T_{2p} *vs.* $1/T$ for an anhydrous liquid ammonia solution for which $[Ni^{2+}]/[NH_3] = 5.70 \times 10^{-3}$. The solid circles were calculated from the triplet spectra, and the open circles are the results obtained from the collapsed spectra.

The source of this collapse is not known, but it did provide the opportunity for an excellent check of the T_2 values obtained from the triplet. T_2 values can easily be calculated from the half-line width at half-maximum intensity of any single Lorentzian signal such as the signal observed for any of the nickel(II)-ammonia solutions after the irreversible process had occurred.

Values of T_2 calculated from the singlet which resulted from the collapse of the triplet to which the data in Figure 3 apply are given as the second set of points in Figure 3. The agreement between the two sets of T_2 values is very good, showing conclusively that the analysis of the triplet line shapes was correct.

Two additional features of the results shown in Figure 3 are of considerable interest. At temperatures below about 0° the relaxation of protons appears to be controlled by the rate of a chemical reaction, since the temperature dependence of the relaxation rate is the Arrhenius type with a rather large slope.

The temperature dependence of T_2 above 0° is such as to strongly suggest that the proton relaxation mechanism is the "chemical shift" mechanism.[5] If this is the mechanism, the T_2 data may be used to obtain a value for A, the proton paramagnetic electron coupling constant.

The experiments and results described above were quite interesting in a qualitative sense; but, in order that the original purpose of this investigation might be served, it was necessary to continue the study in somewhat greater detail.

Data such as that given in Figure 3 showed that it is easiest and most profitable to study the proton resonance signals of nickel(II)-ammonia solutions to which a small amount of ammonium ion had been added. The addition of the NH_4^+ resulted in the collapse of the ammonia triplet spectrum, and the values of T_2 were easily obtained. These solutions were prepared by the procedure outlined in the preceding section.

The values of T_{2p} as a function of temperature are given for three such solutions in Figure 4. T_{2p} is defined by Swift and Connick[5] as the relaxation time arising from the interaction of the nucleus studied with the paramagnetic species studied.

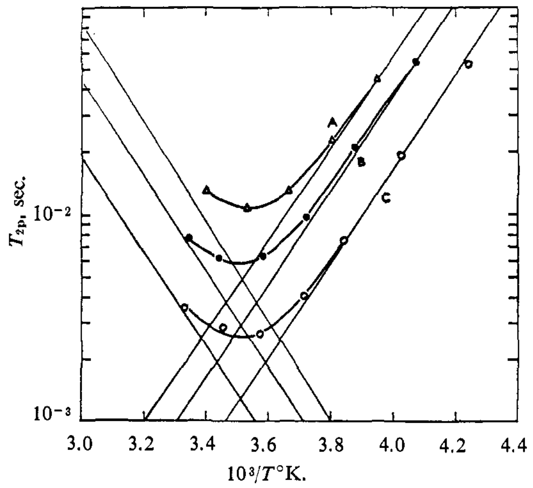

Figure 4. Log T_{2p} *vs.* $1/T$ for three acidified $Ni(NH_3)_6(ClO_4)_2$ solutions in liquid ammonia. The concentrations were (A) $[Ni^{+2}]/[NH_3] = 4.19 \times 10^{-4}$, $[ClO_4^-] = 6.94 \times 10^{-2}$ *M*; (b) $[Ni^{+2}]/[NH_3] = 7.38 \times 10^{-4}$, $[ClO_4^-] = 8.85 \times 10^{-2}$ *M*; (C) $[Ni^{+2}]/[NH_3] = 1.60 \times 10^{-3}$, $[ClO_4^-] = 0.153$ *M*.

Discussion

The temperature region of chemical exchange controlled relaxation is the same for all three solutions. Values of k_1, the reciprocal of the average lifetime of a given proton in the first coordination sphere of a nickelous ion, were calculated to be 1.96×10^5, 1.84×10^5, and 1.95×10^5 sec^{-1} at 25° for the three solutions in the order of decreasing concentration.

The average value was taken to be $1.9 \pm 0.1 \times 10^5$ sec^{-1}. The values of ΔH^* and ΔS^* were calculated to be 10.1 ± 0.5 kcal/mole and -0.5 ± 1 eu, respectively. All of these numbers are in sufficient agreement with those given for the previous ^{14}N study[3] that there is no doubt that the process measured is the exchange of whole ammonia molecules.

In addition it may be seen that the proton resonance results are in complete agreement with those from the ^{14}N study in that no dependence of k_1 was observed on the concentration of ClO_4^- or on the ionic strength.

The data in Figure 4 near and above the temperature of the bend-over were fit with the assumption that the relaxation is produced by the "chemical shift" mechanism[5] and that the curve-fitting problem was identical with that encountered by Swift and Connick[5] in the ^{17}O resonance study of Ni^{2+} in aqueous solution. The average value of A/h obtained for the three solutions of Figure 4 is $3 \pm 1 \times 10^6$ cps. This value is considerably larger than the value of 1.1×10^5 cps given by Wayland and Rice[9] for the proton–electron coupling constant for $Ni(H_2O)_6{}^{2+}$ in aqueous solutions.

The results of this investigation show quite clearly that proton resonance may be of considerable value in the study of paramagnetic ions in liquid ammonia. In addition, nickelous ion has been established as a probe reagent for the study of ion solvation in liquid ammonia since it meets each of the three requirements outlined.

Acknowledgment. The authors wish to acknowledge the support of the National Science Foundation in the form of Grant No. GP3198.

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(9) B. B. Wayland and W. L. Rice, *Inorg. Chem.*, 5, 54 (1966).