The Ammonium–Ammonia Proton Exchange in Liquid Ammonia

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Abstract: Liquid ammonia was prepared which contained significantly less than 10^{-6} *M* ammonium ion and which also contained significantly less than a 10^{-6} *M* concentration of all impurities capable of reacting with ammonium ion. Dilute ammonium chloride and ammonium bromide solutions in this highly purified liquid ammonia were prepared by the addition of gaseous HCl and HBr. Proton magnetic resonance spectra of the solutions were recorded as a function of concentration and temperature, and precise rate data were obtained for proton transfer. The data at the lowest concentrations (10^{-6}–10^{-5} *M*) were consistent with the proton exchange from "free" ammonium ion to ammonia in the case of both chloride and bromide solutions. The unimolecular rate constant for the transfer of a given proton from NH_4^+ to NH_3 is 6.9×10^9 sec^{-1} at 25°, and the activation parameters are 1.6 ± 0.5 kcal/mole for ΔH^* and -8 ± 2 eu for ΔS^*. The rate data at concentrations greater than 10^{-5} *M* are consistent with "ion association" and the conclusion that proton transfer is nondetectably slow from "associated" ammonium ions to ammonia. Stability constants and thermodynamic parameters are reported for the ammonium chloride and ammonium bromide ion pairs. These stability constants are compared with those calculated from continuum diffusion theory and are shown to be significantly larger. The secondary deuterium kinetic isotope effect was found to be negligibly small for both the ammonium–ammonia and ammonia–amide exchanges. Dilute solutions of water in ammonia were prepared from water vapor and the highly purified ammonia. The proton magnetic resonance spectra revealed that in agreement with a previous investigation the direct proton exchange from water to ammonia is nondetectably slow at room temperature and below in these dilute solutions and that the only detectable proton transfer is from free ammonium ions to ammonia. The data were used to obtain a combined ionization and ion-pair dissociation constant for dilute water in liquid ammonia.

As part of a more comprehensive study of the structures and reactions of "simple" solvated ions in solution investigators in this laboratory have been concerned with ions in liquid ammonia.[2,3] The first of these studies was a proton magnetic resonance investigation of proton transfer in dilute solutions of KNH_2 in highly purified liquid ammonia. Precise values were obtained for τ', the average lifetime of a given proton on a given ammonia molecule. This lifetime was found to be inversely proportional to the potassium amide concentration for three concentrations between *ca.* 10^{-5} and *ca.* 10^{-3} *M*. It was noted by the authors[2] that this result was unexpected in light of the value for the potassium amide ion-pair formation constant obtained from conductivity data[4] in that most of the amide ions should be "free" or unassociated with potassium ions at 10^{-5} *M* and the opposite should hold at 10^{-3} *M*.

There are four possible explanations for this result. First, the rate at which a given amide ion accepts a proton may indeed be independent of its state of association with a potassium ion. This is highly unlikely since the potassium ion must certainly tie up at least one amide ion lone pair to prevent proton acceptance at the position.

The next two possibilities involve the assumption that the ion-pair constant obtained from conductivity data is incorrect for some reason. If this is the case, then 10^{-5} to 10^{-3} *M* amide may correspond to almost totally free ions or almost totally associated ions. In either case τ' will be inversely proportional to the total amide concentration as was found experimentally.

The fourth possibility is that, since only three concentration points were given by the authors, some nonlinearity does exist over the concentration range studied, but the concentration measurements were not precise enough to detect it. A systematic dilution technique reported in this present paper is currently being applied to an extensive study of ammonia–amide solutions.

Swift, Marks, and Sayre[2] (SMS) reported a bimolecular rate constant for the transfer of the given proton from ammonia to amide. The physically meaningful quantity in this system is, however, the unimolecular rate constant for the protonation of a given amide ion lone electron pair if the following model is employed. Each amide ion is assumed to be strongly hydrogen bonded to two ammonia molecules, one at each of the amide ion lone pairs. The amide ion can be converted to an ammonia molecule by the acceptance of a proton at *either* lone pair. The diffusion equation to be employed subsequently in this paper calculates the rate constant for the separation of a given ammonia–amide pair; hence the proper experimental rate constant for comparison is $k_1'_{(NH_2^-)} = k_{1(NH_2^-)}/2$, where $k_{1(NH_2^-)}$ is the unimolecular rate constant for the conversion of amide ions to ammonia. The rate constant $k_1'_{(NH_2^-)}$ is related to τ' by eq 1.

$$k_1'_{(NH_2^-)} = 3[NH_3]/2[NH_2^-]\tau' = 3k_2[NH_3]/2 \quad (1)$$

In eq 1, $[NH_3]$ is the ammonia concentration, $[NH_2^-]$ is the amide concentration, and k_2 is the bimolecular rate constant of SMS.[2] At 25°, $k_1'_{(NH_2^-)}$ is 0.8×10^9 sec^{-1}, ΔH^* is 3.7 ± 0.5 kcal/mole, and ΔS^* is -5 ± 2 eu.

The question which arises concerns whether or not these values of k_1 and ΔH^* are characteristic of a diffusion-controlled process, which would be in this case the separation of an amide ion and an ammonia molecule.

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[1] To whom inquiries should be addressed.

[2] T. J. Swift, S. B. Marks, and W. G. Sayre, *J. Chem. Phys.*, **44**, 2797 (1966).

[3] (a) T. J. Swift and H. H. Lo, *J. Am. Chem. Soc.*, **88**, 2994 (1966); (b) *ibid.*, **89**, 3988 (1967).

[4] W. W. Hawes, *ibid.*, **55**, 4422 (1933).

Emerson, Grunwald, and Kromhout[5] have presented an extensive discussion of a similar separation, namely, the breaking of an ammonia–water hydrogen bond in aqueous solution, and the authors' analysis should apply to ammonia–amide separation in liquid ammonia as well.

If hydrogen-bond rupture is the rate-determining step, then $2k_1'_{(NH_2^-)}$ is equal to $1/\tau_D + 1/\tau_R$, where $1/\tau_D$ is the rate constant for diffusion and $1/\tau_R$ is the rate constant for rotation. The factor of 2 arises since there is a 50% probability that the proton remains with the ammonia molecule as the two species separate.

As discussed by the authors,[5] $1/\tau_D$ can be estimated if it is assumed that the Einstein theory of Brownian motion applies. Thus $1/\tau_D$ is given by

$$1/\tau_D \simeq 6(D_{NH_2^-} + D_{NH_3})/s^2 \qquad (2)$$

where the D's are diffusion coefficients and s is the distance between nearest sites in the solvent liquid ammonia. Diffusion coefficients at 25° are not available, but at $-34°$, D_{NH_3}[6] is 5.2×10^{-5} cm^2/sec and $D_{NH_2^-}$[7] is 3.7×10^{-5} cm^2/sec. The distance, s, was taken as 3.5 Å, the nearest neighbor N–N distance in liquid ammonia as determined by solution X-ray studies.[8]

With these values $1/\tau_D$ was calculated to be 4.2×10^{11} sec^{-1} at $-34°$. The rate constant for rotation of ammonia[9] in liquid ammonia at $-34°$ is approximately 8×10^{11} sec^{-1}, and this rotation constant for ammonia is one of the contributions to $1/\tau_R$. The other contribution is the rotation constant for the amide ion.

It is quite clear that $1/\tau_D + 1/\tau_R$ estimated in this manner is much larger than $2k_1'_{(NH_2^-)}$, which is 2.8×10^8 sec^{-1} at $-34°$. The two possible explanations for this very large difference between calculated and observed values are that proton transfer and not bond breaking is the rate-determining step or that the ammonia–amide hydrogen bond is a particularly strong one, and the calculated values of τ_D and τ_R simply do not apply.

In view of the questions raised by this study, a further investigation was undertaken of the ammonium–ammonia proton transfer. Previous work[5,10,11] has shown that the bimolecular ammonium–ammonia exchange process in aqueous solution is quite likely diffusion controlled. As such the unimolecular reaction in liquid ammonia could provide an excellent test of diffusion theory in ammonia as well as a reflection of the strength of ion–dipole bonds in this medium.

In addition, ion-pair formation constants for the ammonium chloride and ammonium bromide ion pairs have been determined in liquid ammonia from conductivity data.[7] The effect of ion pairing on τ' is more easily studied with ammonium ion since a wider range of concentration may be employed in a precise manner than with the amide.

Ogg[12] first observed that the addition of an acid to anhydrous liquid ammonia caused the proton resonance spectrum to collapse from a triplet to a singlet. Although his work was little more than qualitative in nature, it did reveal that proton resonance is certainly applicable to the study of proton transfer in such solutions.

SMS[2] further modified the set of modified Bloch equations for the protons of liquid ammonia to include the effect of proton exchange. The same set of equations with the same definition of τ' given by SMS apply to the ammonium–ammonia system as well as the ammonia–amide system. Likewise the treatment of the spectral data for the extraction of τ' remains the same.

Experimental Section

A. **Purification of Ammonia.** The method of ammonia purification and cleansing of the apparatus used by SMS[2] was found to be inadequate for the study of acidified solutions. The Pyrex apparatus drawn in Figure 1, but without stopcock 4 and volume D, was used in the majority of the experiments to be reported.

Doubly distilled potassium was distilled into bulb B, and then Matheson anhydrous ammonia was distilled into the apparatus from a container of potassium–ammonia solution stored on a high-vacuum line. The apparatus was then removed from the vacuum line and the ammonia was distilled from bulb B to bulb C through the fritted-glass filter, which was inserted to prevent contamination by potassium of the portion of the apparatus to the left of the filter.

This portion of the apparatus was washed with the distilled ammonia after which the ammonia was washed back into bulb B. This procedure was repeated 25 to 30 times until a stable, reproducible triplet was obtained as the proton resonance spectrum. It was found to be necessary to perform this tedious and time-consuming washing technique in order to obtain reproducible results for acidified solutions.

When the SMS procedure was followed, the apparent amount of acid subsequently added was always less than the actual amount added. The SMS ammonia apparently contained small concentrations of impurities such as K or OH$^-$. While these impurities will not affect the proton spectrum of the "pure "ammonia[13,14] or interfere with the ammonia–amide study, they will both react with added ammonium ions.

B. **Purification of HCl, HBr, and H_2O.** Gaseous HCl and HBr (both Matheson) were further purified by several bulb-to-bulb distillations on a high-vacuum line. In each distillation only the middle fraction was retained. The HCl was also passed through a column containing PCl_5 to remove any traces of water which might remain.

The walls of the vacuum system were "conditioned" to each of these gases through a contact time of at least a week.

Degassed distilled water was further degassed under high vacuum and then distilled into a bulb containing reagent grade zinc oxide. The vacuum line was then conditioned to water vapor for at least a week. Water stored in this way has a pH which is very close to 7, and the water vapor may be used without fear of adding either acidic or basic impurities to the liquid ammonia.

C. **Preparation of Liquid Ammonia Solutions.** After the ammonia had been purified, various amounts of HCl, HBr, or H_2O were added in one of two ways. The first was a dilution technique in which the apparatus of Figure 1, including stopcock 4 and volume D, was employed.

Volume D, precalibrated for the temperature employed, was immersed in a constant-temperature 2-propanol–Dry Ice bath, and ammonia was distilled from bulb B into volume D up to the mark shown in Figure 1. This operation was performed with stopcock 4 closed. Stopcock 4 was then opened, stopcock 3 was closed, and the ammonia was distilled into bulb C.

The apparatus was then attached to the high-vacuum line, and a measured pressure of HCl, HBr, or H_2O was introduced into the precalibrated volume A. The known amount of HCl, HBr, or H_2O was condensed into bulb C by cooling with liquid nitrogen. The

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(5) M. T. Emerson, E. Grunwald, and R. Kromhout, *J. Chem. Phys.*, 33, 547 (1960).

(6) D. W. McCall, D. C. Douglas, and E. W. Anderson, *Phys. Fluids*, 4, 1317 (1961).

(7) C. A. Kraus and W. C. Bray, *J. Am. Chem. Soc.*, 35, 1314 (1913).

(8) R. F. Kruth, and J. I. Pets, *J. Chem. Phys.*, 41, 890 (1964).

(9) K. Fish, R. C. Miller, and C. P. Smyth, *ibid.*, 29, 745 (1958).

(10) S. Meiboom, A. Loewenstein, and S. Alexander, *ibid.*, 29, 969 (1958).

(11) T. M. Connor and A. Loewenstein, *J. Am. Chem. Soc.*, 83, 560 (1961).

(12) R. A. Ogg, *Discussions Faraday Soc.*, 17, 215 (1954).

(13) T. Birchall and W. L. Jolly, *J. Am. Chem. Soc.*, 87, 3007 (1965).

(14) T. J. Swift and S. B. Marks, unpublished results on the proton spectra of dilute potassium–ammonia solutions.

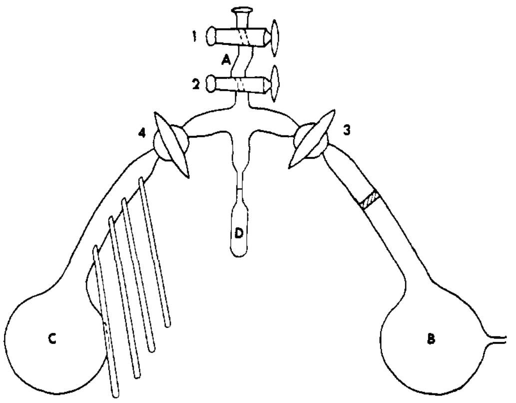

Figure 1. Pyrex apparatus used in the purification of ammonia and in the preparation of ammonium–ammonia solutions.

frozen mixture was warmed to *ca.* −70° to produce the solution of known concentration.

Finally a small portion was poured into one of the standard wall, 5-mm o.d., nmr tubes, and the tube was sealed and removed. The pmr spectra were recorded as a function of temperature between *ca.* −70 and *ca.* 30° with a Varian A-60A spectrometer equipped with the standard temperature control. All spectra were recorded within 24 hr after solution preparation, and the spectra were highly reproducible within this period and for periods of approximately a week after.

Additional solutions were prepared by dilution of the first solution with additional ammonia obtained from bulb B in the manner given above. This technique was limited to an over-all tenfold dilution because of the amount of ammonia available in bulb B.

The following technique was used to expand the range of concentrations studied with any given amount of purified ammonia and also to test the procedure given above for possible systematic errors. Stopcock 4 and volume D were removed from the apparatus. All of the purified ammonia was distilled from bulb B to bulb C and stopcock 3 was closed. The apparatus was attached to the vacuum line, and again a known amount of HCl, HBr, or H_2O was added to the ammonia *via* volume A. Successively increasing concentrations were obtained by adding additional amounts of acid. This technique and the technique previously outlined yielded identical results.

D. Concentration Determination. Account had to be taken of the fact that ammonia was removed from bulb C to the nmr sample tubes during a series of solution preparations. At the conclusion of a series the ammonia from bulb C was distilled into a degassed and weighed bulb of sulfuric acid on the vacuum line. The amount of ammonia was determined by the gain in weight of this container. After the spectra were recorded each nmr tube was weighed, opened, and reweighed to determine the ammonia content. With this information together with the volumes of A and D and the measured pressures of HCl, HBr, and H_2O employed, the concentrations of all solutions in a given series were determined.

E. Preparation of ND_3. Deuterioammonia for secondary kinetic isotope studies was prepared from Columbia Organic Chemicals 99.7% deuterium oxide and technical grade magnesium nitride obtained from City Chemical, New York, N. Y. The apparatus was set up on a high-vacuum line and the D_2O was dropped slowly into a bulb containing the nitride. The ND_3 formed was passed several times through a column containing magnesium nitride to remove the last traces of D_2O. A pmr spectrum showed no trace of any proton signal for the product ND_3.

The ND_3 was used to prepare 92% deuterated ammonia by mixing with NH_3, and this partially deuterated material was used for the secondary isotope study of the ammonium–ammonia exchange. Secondary isotope work was also done with the ammonia–amide system and 83.3 and 91.6% deuterated ammonia was employed.

Results

A. Ammonium Chloride and Ammonium Bromide. Plots of $1/\tau'$ *vs.* total ammonium concentration at various temperatures are shown for the chloride in Figure 2 and for the bromide in Figure 3. In both cases $1/\tau'$ varies linearly with total acid in the concentration range between *ca.* 10^{-6} and *ca.* 10^{-5} *M*. It is this linearity and the fact that all the plots extrapolate to the origin which are used as the strictest test of the purity of the ammonia used for solution preparation.

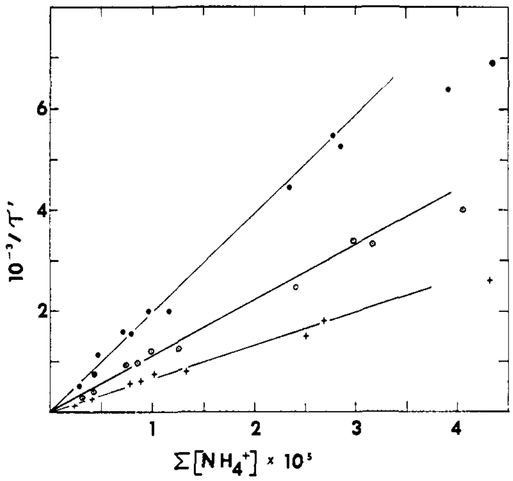

Figure 2. Plots of $1/\tau'$ *vs.* total NH_4Cl concentration at various temperatures: 25° (●), −10° (⊙), −36.5° (+).

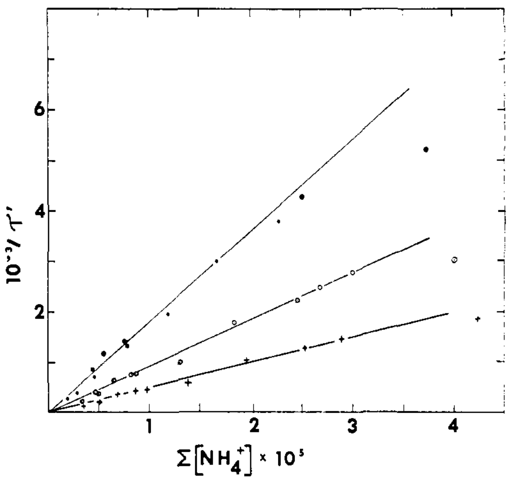

Figure 3. Plots of $1/\tau'$ *vs.* total NH_4Br concentration at various temperatures: 25° (●), −10° (⊙), −36° (+).

At concentrations above *ca.* 10^{-5} *M*, both plots reveal a marked negative deviation from linearity at all temperatures. This deviation is shown for a wider concentration range in the log–log plots of Figures 4 and 5. The plots show the low concentration region with a slope of unity, while at higher concentrations the slope appears to be one-half, and at the highest concentrations shown the slope is significantly less than one-half.

The temperature dependence is shown more clearly in Figures 6 and 7. The important result obtained from these plots is that the slope of the lines is independent of concentration within experimental uncertainty even in the relatively high concentration regions. This was a strong indication that proton transfer was occurring from the same species at all concentrations. At the lowest concentration this species is certainly unassociated NH_4^+, and hence it is reasonable to assume that this is the only effective species in the proton transfer to ammonia. This conclusion is strongly supported by

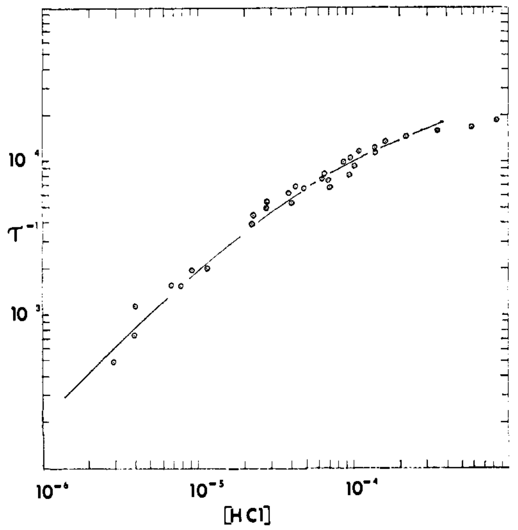

Figure 4. Plot of $-\log \tau'$ vs. log (total NH_4Cl concentration) at 25°.

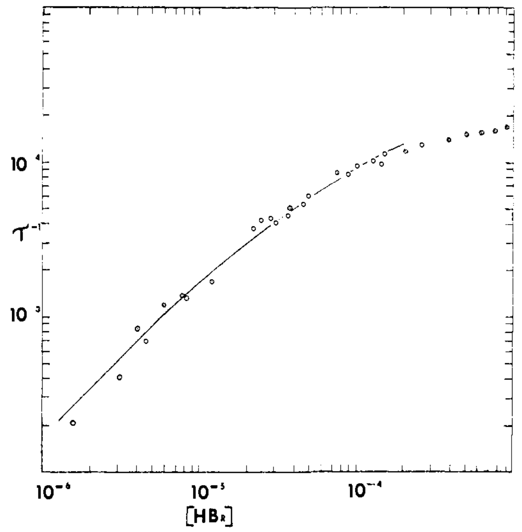

Figure 5. Plot of $-\log \tau'$ vs. log (total NH_4Br concentration) at 25°

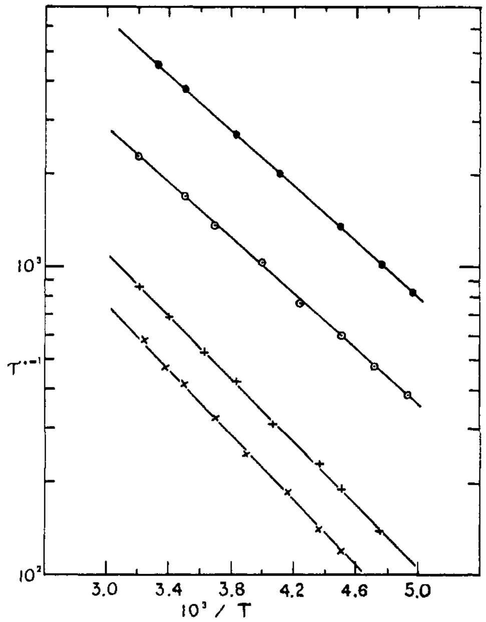

Figure 6. Plots of $-\log \tau'$ vs. $1/T$ for various total NH_4Cl concentrations. $[NH_4Cl]/[NH_3]$ is 7.6×10^{-7} (●), 2.6×10^{-7} (⊙), 9.5×10^{-8} (+), 6.2×10^{-8} (×).

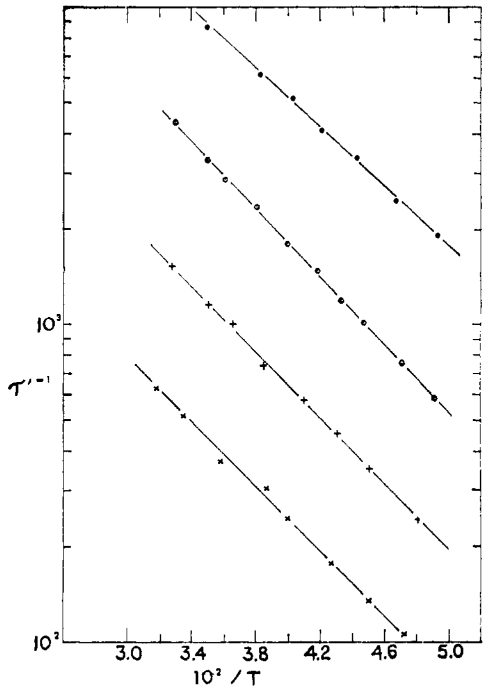

Figure 7. Plots of $-\log \tau'$ vs. $1/T$ for various total NH_4Br concentrations. $[NH_4Br]/[NH_3]$ is 3.7×10^{-6} (●), 8.2×10^{-7} (⊙), 2.2×10^{-7} (+), 8.7×10^{-8} (×).

the detailed analyses given below of Figures 4 and 5.

The model assumed for ammonium–ammonia proton transfer involves the ammonium ion being strongly hydrogen bonded to four ammonia molecules through each of the four protons. The proper unimolecular rate constant for comparison with diffusion theory is then ${k_1}'_{(\mathrm{NH_4^+})} = k_{1(\mathrm{NH_4^+})}/4$, where $k_{1(\mathrm{NH_4^+})}$ is the unimolecular rate constant for ammonium–ammonia conversion.

Values of ${k_1}'_{(\mathrm{NH_4^+})}$, given as $[NH_3]/[NH_4^+]\tau'$, are easily obtained from the linear regions of Figures 2 and 3, and they are given together with the activation parameters in Table I.

The slope of one-half in Figures 4 and 5 is strongly indicative of ammonium chloride and ammonium bromide ion-pair formation where the ions pairs are much poorer proton donors than the unassociated ammonium ion. If the assumption is made that $1/\tau'$ is proportional to $[NH_4^+]$, the free ammonium ion concentration, theoretical lines obtained from eq 3 can be fit to the data of Figures 4 and 5, and these are the solid lines shown in the figures.

$$\sum[\mathrm{NH_4^+}] = \frac{[\mathrm{NH_3}]}{\tau'{k_1}'_{(\mathrm{NH_4^+})}}(1 + K_x[\mathrm{NH_3}]/\tau'{k_1}'_{(\mathrm{NH_4^+})})$$

$$K_x = [\mathrm{NH_4X}]/[\mathrm{NH_4^+}][\mathrm{X^-}] \qquad (3)$$

In eq 3, $\Sigma[NH_4^+]$ is the total ammonium ion concentration and X is either chloride or bromide. Activity corrections are not significant in liquid ammonia at

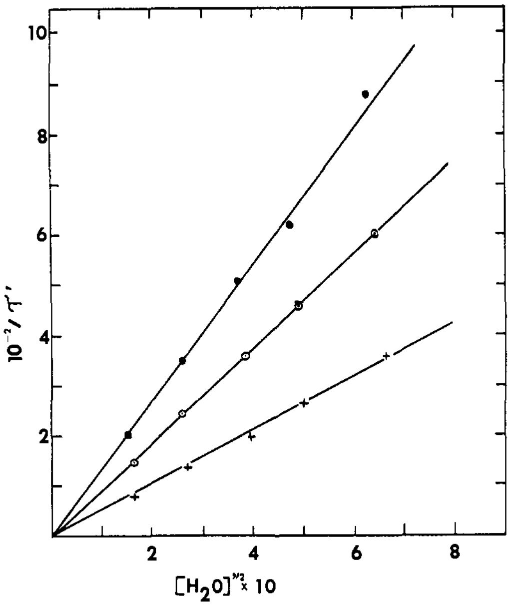

Figure 8. Plots of $1/\tau'$ *vs.* square root of water concentration at various temperatures: 25° (●), −1.5° (⊙), −30° (+).

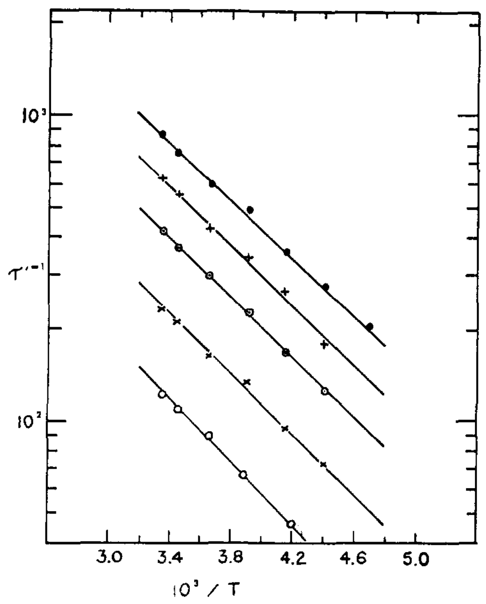

Figure 9. Plots of $-\log \tau'$ *vs.* $1/T$ for various water concentrations. $[H_2O]/[NH_3]$ is 7.7×10^{-3} (●), 3.8×10^{-3} (+), 1.9×10^{-3} (⊙), 9.1×10^{-4} (X), 2.2×10^{-4} (O).

the concentrations of interest although they are appreciable at the highest concentrations of Figures 4 and 5. No attempt was made to fit the data at these highest concentrations, although qualitatively the data appear to reflect the formation of triple ions and perhaps higher ionic aggregates.

Table I.

	NH_4Cl		NH_4Br		NH_3-OH_2
	25°	−34°	25°	−34°	25°
$k_1'_{(NH_4^+)} \times 10^{-9}$ sec^{-1}	6.9	2.5	6.4	2.1	...
$K_x \times 10^{-4}$ l./mole	3.1	2.1	1.4	0.9	...
$K_{ion} \times 10^{12}$ mole/l.	...	...	...	...	3 ± 1
ΔH^*, kcal	1.6 ± 0.5	...	1.6 ± 0.5	...	...
ΔS^*, eu	−8 ± 2	...	−8 ± 2	...	...
$\Delta H°$, kcal	1.0 ± 1	...	1.0 ± 1	...	...
$\Delta S°$, eu	24 ± 5	...	24 ± 5	...	...

Values of K_x together with values of $\Delta H°$ and $\Delta S°$ for ion-pair formation as determined by curve fitting are given in Table I.

The results of the study of the 92% deuterated solution were identical within experimental error with those of the 100% protonated system. There was no detectable secondary kinetic isotope effect where a 10% effect represented the lower limit of detectability. A similar study of the ammonia–amide system led to an identical conclusion for it.

B. Water. A plot of $1/\tau'$ *vs.* the concentration of water for various dilute solutions of water in ammonia does not show a linear region down to the smallest concentrations which yield a measurable value of $1/\tau'$. However, the plot of $1/\tau'$ *vs.* $[H_2O]^{1/2}$ shown in Figure 8 is linear, indicating that undissociated water does not contribute to $1/\tau'$ but that NH_4^+, the dissociation product, is the exchanging species.

The temperature dependence of $1/\tau'$ shown in Figure 9 supports this conclusion since the slope is independent of concentration and identical with the slope of Figures 6 and 7.

At relatively high water concentrations (*ca.* 0.1 *M*), the pmr signal of water was observed at the same position as that observed by Birchall and Jolly.[13] This signal is much too sharp to account for the observed $1/\tau'$, and hence the direct proton transfer from H_2O to NH_3 is nondetectably slow under the conditions employed in agreement with the results of Birchall and Jolly.[13] The rapid proton exchange certainly occurs from ammonium ion to ammonia.

Figure 8 and eq 4 may be used to obtain a value of K_{ion}, the equilibrium constant for the following reaction.

$$(1 + x)H_2O + NH_3 \rightleftharpoons NH_4^+ + OH(H_2O)_x$$

This net reaction is not the reaction at infinite dilution of water in ammonia since in the latter case the hydroxide ion cannot be solvated by water. The importance of this solvation has been pointed out by Jolly,[15] and it also appears to be quite important in the present case since the value of K_{ion} of Table I is much larger than the value of 10^{-18} given by Jolly[15] for K_{ion} at $x = 0$. The large difference undoubtedly reflects the solvating effect of water on hydroxide.

$$1/\tau' = k_1'_{(NH_4^+)} K_{ion}^{1/2} [H_2O]^{1/2}/[NH_3]$$

$$K_{ion} = [NH_4^+][OH^-]/[H_2O] \qquad (4)$$

The value of K_{ion} at 25° is given in Table I. The process characterized by K_{ion} may be viewed as made up of two separate equilibria. The first is the proton transfer from water to ammonia to produce a contact ion pair, and the second is the separation of the ion pair into the free ions.

In water K_{ion} is given to a good approximation by the equilibrium constant for the first step, the proton transfer. This value is 1.8×10^{-5} *M* at 25° and after cor-

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(15) W. L. Jolly, *J. Chem. Educ.*, 44, 304 (1967).

rection for the concentrations of bulk solvent in water and liquid ammonia the value is 1.2×10^{-5} *M* in liquid ammonia at 25°.

The equilibrium constant for the ion-pair separation should be reasonably approximated by K_z^{-1} of Table I for ammonium chloride at 25°. It is seen that K_{ion} for water in liquid ammonia is significantly smaller than $(1.2 \times 10^{-5})K_z^{-1}$ indicating that the NH_4OH ion pair is a particularly stable one and/or that the constant for step 1 differs significantly between water and ammonia.

Discussion

One of the principal purposes of this study was the investigation of ion-pairing effects on proton-transfer reactions. The results presented here are certainly consistent with the conclusion that a paired ammonium ion is a much poorer proton donor that a free ammonium ion. This leads to pmr being a very sensitive method for the determination of ion-pair formation constants. The ion-pair constants determined in this manner are significantly larger than those determined from conductivity data. This may be due to the fact that precise nmr data may be obtained at much lower concentrations than with the conductivity data. In addition $1/\tau'$ appears to be a function of the concentration of the free ammonium ion only and hence is a rather sensitive "pH meter" in liquid ammonia while conductivity is sensitive to all conducting species including triple ions, etc. Lastly, nmr provides a very sensitive test of solvent purity in the case of liquid ammonia. For these reasons we feel that the ion-pair formation constants reported here are more reliable than those determined from conductivity data.

Since it has been shown that solvent purification involves a quite tedious procedure, but that the purification can be checked by pmr, it is of special interest to repeat the conductivity studies with highly purified solvent. Such conductivity studies will be undertaken in this laboratory.

It is of interest to compare the ion-pair formation constants of Table I with the values calculated from diffusion theory.[16] The theoretical expression for K_z in the case of charges of +1 and −1 is

$$K_z = \frac{4\pi a^3 N}{3000}\exp(\Phi_z) \qquad \Phi_z = e_0^2/\epsilon akT \tag{5}$$

where *N* is Avogadro's number, *a* is the distance of closest approach of the two ions, and ϵ is the effective dielectric constant over an ionic separation from *a* to infinity in the solvent.

If the ion pairs are taken to be contact ion pairs, *i.e.*, the two ions are not separated by one or more solvent molecules, *a* may be taken as the sum of the ionic radii, and it is 3.26 Å for NH_4Cl and 3.40 for NH_4Br. If the bulk dielectric constant of 23 for ammonia at −34° is used for ϵ, K_z is calculated to be 8.7×10^2 for the chloride and 7.5×10^2 for the bromide.

There is a very sizable discrepancy in both cases between these calculated values and the measured values of Table I. This large discrepancy in the direction in which it occurs is by no means wholly unexpected. The use of the bulk dielectric constant for ϵ in eq 5 is a highly questionable procedure at best. The true dielectric constant at interionic distances of the order of *a* to *a* plus the diameter of several ammonia molecules is in all likelihood significantly less than the bulk value leading to significantly larger ion-pair stability constants.

Water would appear to present a special case in that by a fortuitous set of circumstances[17] the effective dielectric constant is quite near the bulk value both theoretically[17] and experimentally.[16, 18]

There is little reason to believe that this must hold for other solvents, however. In the present case, dielectric constants of 14 between *a* and *a* + 3.26 Å and 23 between *a* + 3.26 Å and infinity lead to the calculation of the measured value of K_z for both the ammonium chloride and ammonium bromide ion pairs. This dielectric constant value of 14 is by no means unreasonably low for that range of interionic separation. This point concerning the effective dielectric constant is far from settled, however, and a reasonably large set of highly reliable ion-pair stability constants in liquid ammonia is required.

From the results and interpretation presented in this work concerning the role of ion pairing in proton transfer and the values of the ion-pair constants, it appears likely that the ion-pair constant for KNH_2 may be much higher than that calculated from conductivity data and that the kinetic parameters reported by SMS[2] refer to proton transfer between ammonia and KNH_2 ion pairs. As was mentioned in the introductory section, precise dilution studies at low concentrations are being performed in this laboratory on the ammonium–amide reaction to ascertain if such is indeed the case.

Finally, the rate parameters for the ammonium–ammonia exchange can be compared with those calculated from diffusion theory. The diffusion coefficient of NH_4^+ in liquid ammonia at −34° is 2.75×10^{-5} cm^2/sec,[7] and therefore from eq 2 $1/\tau_D$ is 3.5×10^{11} sec^{-1}. As with the ammonia–amide reaction, a calculated lower limit for $1/\tau_R$ is obtained from the rotation rate of ammonia and is 8×10^{11} sec^{-1} at −34°.

The value of $2k_1'_{(NH_4^+)}$ at −34° is only 5.0×10^9 sec^{-1}, and this is clearly much smaller than $1/\tau_D + 1/\tau_R$. This result indicates one of two possibilities as outlined in the introductory section; either the proton transfer is rate determining or the NH_4^+–NH_3 hydrogen bond is much stronger than the NH_3–NH_3 bond, so much so that the diffusion data do not apply.

Some indication of which of these two possibilities is actually the case can be obtained from an examination of the activation parameters. An effective ΔH^* can be obtained for $1/\tau_D$ from the measured[6] temperature dependence of the diffusion coefficients, and this ΔH^* is 1.5 kcal/mole. Likewise the temperature dependence of the dielectric relaxation time of ammonia is available[9] and ΔH^* for ammonia rotation is 1.0 kcal/mole. The measured ΔH^* from Table I is 1.6 kcal/mole. While these calculated values of ΔH^* are

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[16] M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, 2, 285 (1964).

[17] S. Levine and D. K. Rosenthal in "Chemical Physics of Ionic Solutions," B. E. Conway and R. G. Barradas, Ed., John Wiley and Sons, Inc., New York, N.Y., 1966.

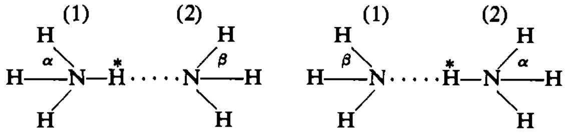
[18] We are indebted to Professor John E. Stuehr of this department for several very helpful discussions concerning this point and for his suggestions leading to the conclusions presented concerning the effective dielectric constant in nonaqueous solutions.

close to the measured values, it must be kept in mind that they must refer to processes quite different from that which is characterized by the rate constant, $2k_1'_{(NH_4^+)}$, due to the large discrepancy between the calculated and observed rate constants.

If $2k_1'_{(NH_4^+)}$ is indeed given by $1/\tau_D + 1/\tau_R$ for the breaking of an unusually strong hydrogen bond, the process which occurs is not diffusion but is quite similar to the breaking of a coordinate bond such as is involved in ammonia exchange with $Ni(NH_3)_6^{2+}$ in liquid ammonia. This exchange with the nickel complex has been studied by both ^{14}N resonance[19] and proton resonance.[3a] The ΔS^* is zero within experimental error, a result which is typical[20] of a simple unimolecular process in solution and should apply to the breaking of a strong NH_4^+–NH_3 hydrogen bond. With this model the activation parameters expected with a rate constant of 5.0×10^9 sec^{-1} at $-34°$ are 3.0 kcal/mole for ΔH^* and zero entropy units for ΔS^*. These are quite different from the observed values and provide an argument against bond breaking as the rate-determining step in the exchange reaction.

The question which then arises is whether or not the measured activation parameters are consistent with proton transfer across (or through) an energy barrier as the rate-determining step. In particular is it reasonable that the entropy barrier should be relatively large and negative?

Consider the ammonium–ammonia pair shown below. On the left nitrogen 1 is part of an ammonium ion and α, the H–N–H angle, is the tetrahedral angle.



Nitrogen 2 is part of an ammonia molecule and β, the H–N–H angle, is in all likelihood significantly larger than the tetrahedral angle. In addition, the solvent structure around nitrogen 1 is undoubtedly different from that around nitrogen 2 because of the stronger hydrogen-bonding ability of the ammonium ion.

This situation is completely reversed in the proton-transfer product on the right side and considerable rearrangement has occurred. In addition, the principle of microscopic reversibility demands that rearrangement accompany proton transfer on the average rather than simply follow it. Such necessary rearrangement represents an entropy barrier which could account for the measured value of ΔS^*. It may be possible to check this conclusion through a study of a reaction such as the pyridinium–pyridine exchange.

Further studies are being performed on the ammonium–ammonia system, among them being the ND_4^+–ND_3 exchange studied by means of deuterium resonance.

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(19) H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 4, 206 (1965).

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