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Proton Transfer Studies by Nuclear Magnetic Resonance. III. The Mean Life of the Amine–Water Hydrogen Bond in Aqueous Solution[1a]

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Isotopic hydrogen exchange rates in very strongly acidic solutions provide a method for measuring the mean life of hydrogen bonds between water molecules (as donors) and amine molecules (as acceptors). Applied to NH_3, CH_3NH_2 and $(CH_3)_3N$, the results yield a criterion for the formation of genuine molecular complexes. Mean lives, extrapolated to dilute aqueous solution, were, respectively, 2.0×10^{-12}, 1.2×10^{-11} and 1.0×10^{-10} sec.

In this paper we propose a method for measuring the mean life of the hydrogen bonds between molecules of amine (acting as acceptors) and water molecules in aqueous solution. We then apply this method to obtain results for NH_3, CH_3NH_2 and $(CH_3)_3N$. If correct, these results allow us to decide whether, or when, the amine–water interaction leads to the formation of genuine molecular complexes,[2,3] and they may provide further evidence of "iceberg formation" around organic molecules[4] in aqueous solution.

$H_3N \cdot HOH$ Hydrogen Bond.—For definiteness, we shall discuss our method while presenting results for the system HOH–NH_3. A certain amount of background information is necessary.

The rate of ionization of NH_4^+ in aqueous solution (eq. 1) has recently been measured with good

$$NH_4^+ + H_2O \xrightarrow{k_4} NH_3 + H_3O^+ \qquad (1)$$

accuracy by nuclear magnetic resonance (n.m.r.) techniques.[5] In the *p*H range 1–4, the rate law was found to be

$$\text{rate of ionization} = k_4[NH_4^+] \qquad (2)$$

Except for normal kinetic salt effects, the pseudo-first order rate constant, k_4, is independent of acidity in the *p*H range 1–4. At infinite dilution, $k_4^\circ = 24.4$ sec.$^{-1}$ at 25°, or $24.4/4 = 6.1$ sec.$^{-1}$ for each proton. Thus the mean life of the N–H covalent bond in NH_4^+ is 0.16 sec. in dilute, slightly acid aqueous solution.

On the other hand, it has been known for some time that in solutions which are *highly* concentrated both in a mineral acid and in an isotopically labeled ammonium salt, the half-life for the isotopic exchange is of the order of several minutes,[6,7] or more than a thousand times longer than in dilute aqueous solution! Although this extraordinary effect was unquestionably real, the reaction media used in these experiments[6,7] were so unconventional that a unique kinetic interpretation is not possible.

We now report rate constants for the isotopic exchange in sulfuric acid–water mixtures, using fairly low (0.2–0.4 *N*) concentrations of deuterium-labeled ammonium ion. The exchange was followed by measuring the peak heights of the n.m.r. lines due to ammonium ion as a function of time. The experiments were done in such a way that the exchange of the final deuteron ($NH_3D^+ + H^+ \rightarrow NH_4^+ + D^+$) was measured. The rate constant, k_e, for the isotopic exchange was then calculated from eq. 3a, where h_t is the peak height of the given n.m.r. line at time *t*.

$$k_e = \frac{1}{t} \ln \frac{h_\infty - h_0}{h_\infty - h_t} \qquad (3a)$$

Since the atom fraction, D/(D + H), is small (< 0.02 in our systems), we may write without appreciable error

$$k_e = \frac{\text{rate of deuteron–proton exchange}}{[NH_3D^+]} \qquad (3b)$$

The results are summarized in Table I. Within experimental error (±10%), k_e is independent of the concentration of ammonium ion over a twofold variation of the latter. We, therefore, conclude that the exchange is kinetically of the first order in NH_3D^+. Processes of higher order in $NH^+{}_4$, such as reaction 4 which is significant at low acidities and higher NH_4^+ concentrations,[5,8] may be neglected.

$$H_3ND^{\oplus} + \overset{H}{O}H + NH_3 \longrightarrow H_3N + \overset{H}{D}O + HNH_3^{\oplus} \qquad (4)$$

By contrast, k_e is highly sensitive to the acid concentration. For example, in 49.14 wt. % H_2SO_4, the half-life for the exchange is 105 sec.; in 58.37 wt. % H_2SO_4 it is 20 min.; and in 69.38 wt. % H_2SO_4 it is 15 hr. On account of this 500-fold increase in half-life, a number of plausible reaction mechanisms may immediately be ruled out.

Some relevant data for sulfuric acid-water mixtures are collected in Table II. First of all, the water activity is seen to decrease from 0.369 to 0.0498, or by a factor of 7.4 in this range. If the exchange were proceeding by a simple ionization mechanism (eq. 1, followed by rapid addition of a new proton to the ammonia molecule), k_e would be roughly proportional to the water activity, exact proportionality being perturbed by kinetic medium effects.[9] We would therefore expect a decrease in k_e of about one order of magnitude,

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[1] (a) Work supported by Air Force Office of Scientific Research, U.S.A.F., under contract no. AF 49(688)-287; (b) Alfred P. Sloan fellow, 1960; (c) Department of Physics.

[2] (a) T. Moore, *J. Chem. Soc.*, **91**, 1373 (1907); (b) T. Moore and T. Winmill, *ibid.*, **101**, 1635 (1912); (c) D. Berg and A. Patterson, THIS JOURNAL, **75**, 5197 (1953).

[3] E. Arnold, H. Freitag and A. Patterson, in "The Structure of Electrolytic Solutions," W. J. Hamer, editor, John Wiley and Sons, Inc., New York, N. Y., 1959, chapter 18.

[4] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

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

[6] A. I. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S.S.S.R.*, **74**, 513 (1950).

[7] L. Kaplan and K. E. Wilzbach, THIS JOURNAL, **76**, 2593 (1954).

[8] S. Meiboom, A. Loewenstein and S. Alexander, *J. Chem. Phys.*, **29**, 969 (1958).

[9] Previous measurements[5] of kinetic salt effects on k_4 indicate, however, that such medium effects should be relatively small.

TABLE I

KINETIC DATA BASED ON THE ISOTOPIC EXCHANGE OF DEUTERATED AMMONIUM SULFATE IN SULFURIC ACID–WATER MIXTURES

Temp., 25°; $K_A°$, 5.68×10^{-10} for NH^+_4[a]

Formal concn.					
$[NH_4^+]$	$[NH_3]$[b]	k_e, sec.$^{-1}$	k_H', sec.$^{-1}$	η/η_0	$k_H'(\eta/\eta_0)$
		49.14 wt. % H_2SO_4, h_0 = 1950			
0.422	1.23×10^{-13}	6.8×10^{-3}	13.2×10^{10}	3.71[c]	49×10^{10}
0.224	0.65×10^{-13}	6.4×10^{-3}	12.4×10^{10}	3.71	46×10^{10}
		58.37 wt. % H_2SO_4, h_0 = 18,600			
0.418	1.27×10^{-14}	5.7×10^{-4}	10.6×10^{10}	5.4	57×10^{10}
		69.38 wt. % H_2SO_4, h_0 = 376,000			
0.390	5.9×10^{-16}	1.35×10^{-5}	5.06×10^{10}	9.6	49×10^{10}
0.194	2.9×10^{-16}	1.20×10^{-5}	4.50×10^{10}	9.6	43×10^{10}
				Av.	$(49 \pm 5) \times 10^{10}$

[a] R. G. Bates and G. Pinching, THIS JOURNAL, **72**, 1393 (1950). [b] Computed from eq. 17. Note that $[NH_3]$ is extremely small. This is why k_e is measurable even though k_H' is very large. [c] "International Critical Tables."

TABLE II

DATA FOR SULFURIC ACID–WATER MIXTURES, 25°

H_2SO_4 (wt. %)	a_w[a]	Molar concentration[b]			Mole fraction[b]	$\frac{Y_{PhCO_2H})^2}{Y_{Ph_4P^+} \times Y_{ClO_4^-}}$	h_0[c]	k_e, sec.$^{-1}$	
		$SO_4^=$	HSO_4^-	H_3O^+	H_3O^+			reacn. 5 (eq. 10)	Obsd.
49.14	0.369	1.8	5.14	8.74	0.19	149[d]	1,950	2.1×10^{-6}	6.6×10^{-3}
58.37	.189	1.6	7.21	10.41	.24	576[d]	18,600	4.4×10^{-7}	5.7×10^{-4}
69.38	.0498	1.0	10.3	12.3	.32	1350[d]	376,000	1.35×10^{-7}	1.3×10^{-5}

[a] W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, THIS JOURNAL, **82**, 62 (1960). [b] T. F. Young, L. F. Maranville and H. M. Smith in "The Structure of Electrolytic Solutions," W. J. Hamer, editor, John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 4. [c] Ref. 12b. [d] Ref. 13, 14.

instead of the observed factor of 500. The simple ionization mechanism must therefore be ruled out.

Using data in Table II, we can eliminate by entirely analogous arguments any reaction mechanisms in which the rate-determining step is transfer of a hydrogen ion from ammonium ion to $SO_4^=$ or HSO_4^-.

In seeking a reaction mechanism to fit the observed sharp decrease in k_e with increasing acid concentration, we considered that reaction with hydroxide ion is rate-determining

$$H_3ND^+ + OH^- \xrightarrow{k_5} H_3N + DOH \qquad (5)$$

However, we shall show that this reaction is too slow to account for more than a small fraction of the observed rate of exchange. For *proton* transfer in dilute aqueous solution, Eigen and Schoen[10] have reported that $k_5 = 3 \times 10^{10}$ sec.$^{-1}M^{-1}$, or $3 \times 10^{10}/4$ sec.$^{-1}M^{-1}$ for each proton in NH^+_4. Neglecting kinetic salt effects and deuterium isotope effects (they are in such a direction as to lower k_5), we obtain

$$k_e \text{ (reaction 5)} = 0.75 \times 10^{10} [OH^-] \qquad (6)$$

In these super-acid media, the hydroxide concentration must be very small, but it is difficult to estimate it. A convenient approach is to apply the Hammett acidity function,[11] h_-, to the ionization of water. Thus

$$[OH^-] = K_w a_w / h_- \qquad (7)$$

where a_w is the activity and K_w is the ion product of water. At 25°, $K_w = 1.01 \times 10^{-14}$. Unfortunately, values of h_- are not available for our systems. We have therefore estimated them as follows:

We begin with known values of the acidity function, h_0.[11,12] By definition

$$h_- = h_0 \times \frac{Y_{A^-}}{Y_{HA}} \times \frac{Y_{BH^+}}{Y_B} \qquad (8)$$

where Y_i denotes the molar activity coefficient of the i-th species, and HA-A^- and BH^+-B denote any two conjugate acid–base couples of the charge-types indicated.[11] In principle, the quotient of activity coefficients in (8) can be evaluated from thermodynamic data for suitable model substances. In practice, the required data are not available, and we have assumed—somewhat arbitrarily—that

$$\frac{Y_{A^-} Y_{BH^+}}{Y_{HA} Y_B} \approx \frac{Y_{Ph_4P^+} Y_{ClO_4^-}}{(Y_{PhCO_2H})^2} \qquad (9)$$

Tetraphenylphosphonium perchlorate and benzoic acid were chosen, not because they are necessarily the best model substances for which data are available,[13,14] but because they seemed to lead to the lowest values for h_- and hence an *upper* limit on k_e for this mechanism. Combining eq. 6–9, we obtain

$$k_e \text{ (reaction 5)} = \frac{0.76 \times 10^{-4} a_w}{h_0} \frac{(Y_{PhCO_2H})^2}{(Y_{Ph_4P^+})(Y_{ClO_4^-})} \qquad (10)$$

Results of this calculation are shown in Table II. The value of k_e predicted for reaction 5 is smaller by 2–3 orders of magnitude than the experimental value. Since the prediction was made in such a way as to obtain an upper limit, we con-

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(10) M. Eigen and J. Schoen, *Z. Elektrochem.*, **59**, 483 (1955); *Z. physik. Chem.* (*Frankfurt*), **3**, 126 (1955).

(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 269.

(12) (a) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(13) L. P. Hammett and R. Chapman, THIS JOURNAL, **56**, 1282 (1934).

(14) N. C. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

clude that reaction 5 contributes at most 1% to the observed rate of exchange.

Having eliminated these reasonable alternatives, we now consider a kinetic scheme first used by Swain and co-workers[15,16] to explain the kinetics of proton exchange between triethylammonium ion and methanol in acidic methanol solution. For simplicity, we shall first consider the case of proton–proton exchange, and then correct the final expression so that it may be applied to proton–deuteron exchange. The proton transfer is represented as occurring in two steps

$$H_3{}^+N\text{–}H^*\ldots OH_2 \underset{k'_{-4}}{\overset{k_4'}{\rightleftarrows}} H_3N\ldots H^* - OH + H^+ \qquad (11)$$

$$H_3N\ldots H^* - OH \xrightarrow{k_H'} H_3N + OHH^* \qquad (12)$$

In eq. 11, the starred proton, having been transferred to a water molecule in the solvation shell, is still in position to return to its original nitrogen atom, and will do so if the reaction is reversed before the $H_3N\ldots H^*\text{—}OH$ hydrogen bond is broken. In eq. 12, this bond is broken, thus completing the exchange. The rate law for the exchange is then given by eq. 13

$$\text{rate of proton exchange} = k_4'[NH_4{}^+]\,\frac{k_H'}{k_H' + k'_{-4}[H^+]} \qquad (13)$$

where the rate "constants" (k_4', k'_{-4} and k_H') are subject to medium effects. In dilute acid, $k_H' >> k'_{-4}\,[H^+]$, and equation 13 reduces to 2. In sufficiently strong acid, $k_H' << k'_{-4}\,[H^+]$, and we obtain eq. 14.

$$\text{rate of proton exchange (in strong acid)} = \frac{k_4'k_H'[NH^+{}_4]}{k'_{-4}[H^+]} \qquad (14)$$

Equation 14 has the desired property that the rate decreases with increasing acidity.

In order to correct for medium effects on k_4' and k'_{-4}, it is convenient to use the acidity function, h_0.[11,12] Supposing again that $k_H' << k_{-4}\,[H^+]$, we may write

$$\text{rate of proton exchange} = k_H'\,[H_3N\ldots H^*\text{–}OH] \qquad (15)$$

The concentration of the $H_3N\ldots H^*\text{—}OH$ pair is related to the *formal* concentration of ammonia, NH_3, by the ratio[17]

$$\frac{[H_3N\ldots H^*\text{–}OH]}{[NH_3]} = \frac{k'_{-4}[H^+]}{k'_{-4}[H^+] + k_H'} \qquad (16)$$

which is approximately unity by hypothesis. Furthermore, $[NH_3]$ is related to the acidity of the medium by eq. 17

$$[NH_3] = K_A{}^0[NH_4{}^+]/h_0 \qquad (17)$$

where $K_A{}^0$ is the acid dissociation constant of $NH_4{}^+$ in water at infinite dilution. Thus we obtain eq. 18 for the rate of proton exchange

$$\frac{\text{rate of proton exchange}}{[NH_4{}^+]} = \frac{k_H'K_A{}^0}{h_0} \qquad (18)$$

Thus far we have considered only proton–proton exchange. However, we actually measure deuteron–proton exchange, as shown in eq. 3b. In order to calculate k_H' from k_e, we must correct k_e for the kinetic isotope effect, and multiply by a statistical factor, g, which is equal to the number of equivalent exchangeable N–H bonds.

For $NH_4{}^+$, $g = 4$. To correct for the deuterium-isotope effect on k_e, we multiply by $\sqrt{2}$. This factor was chosen because, for the analogous exchange of $(C_2H_5)_3NH^+$ in acidic methanol, Swain, McKnight and Kreiter[16] found

$$\frac{\text{deuterium isotope effect}}{\text{tritium isotope effect}} \approx \frac{\sqrt{3}}{\sqrt{2}}$$

Thus we obtain the final expression

$$k_H' = \frac{g\,\sqrt{2}\,k_e\,h_0}{K_A{}^0} \qquad (19)$$

where k_H' is the rate constant for the dissociation of the amine–water hydrogen bond.

Values of k_H' for the dissociation of $H_3N\ldots H^+OH$ have been computed from eq. 19 and are listed in Table I. The values are very large, ranging from 5×10^{10} to 13×10^{10} sec.$^{-1}$, and decrease systematically with increasing acid concentration.

In order to see whether these values are of a reasonable magnitude, we shall estimate a theoretical upper limit to k_H' by assuming that H_3N and H^* OH behave as if they were independent kinetic units. Proton exchange is completed if either molecule diffuses to an adjacent lattice site or rotates on its present site. Thus

$$k_H' = \frac{1}{\tau_D} + \frac{1}{\tau_R} \qquad (20)$$

where τ_D and τ_R denote the relaxation times for diffusion and rotation. We shall further assume that the solvent is a viscous continuum, and hence that k_H' is inversely proportional to the viscosity of the medium. Consequently

$$k_H'\,\eta/\eta_0 = k_H \qquad (21)$$

where η is the viscosity of the reaction medium, η_0 that of pure water, and k_H is the rate constant for the rupture of the $N\ldots H^*$ bond in water.

The use of eq. 21 is consistent with the assumption that the H_3N and H^*OH molecules are independent kinetic units. In applications of the viscous continuum model to a series of solvents, it is usually assumed that gross deviations are to be expected only if the composition of the kinetic units changes with the solvent. For example, gross deviations from Walden's rule for the mobility of ions are usually taken to indicate changes in the nature of the tight solvation shells surrounding the ions.

Values of k_H calculated *via* eq. 21 are listed in the final column of Table I. The values are satisfactorily constant over a nearly threefold variation in viscosity and a 200-fold variation in h_0, thus supporting our assumptions. The average for k_H is $(49 \pm 5) \times 10^{10}$ sec.$^{-1}$.

It is possible to compare this value with a completely independent estimate; $1/\tau_D$ in eq. 20 may be estimated from Einstein's theory of the Brownian movement.[18] The mean time required for

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[15] C. G. Swain and M. M. Labes, THIS JOURNAL, **79**, 1084 (1957).

[16] C. G. Swain, J. T. McKnight and V. P. Kreiter, *ibid.*, **79**, 1088 (1957).

[17] Equation 16 is derived by making the steady-state approximation that $d[NH_3]/dt = d[H_3N\cdot H^*OH]/dt = 0$.

[18] A. Einstein, "Investigations on the Theory of the Brownian Movement," Methuen and Co., Ltd., London, 1926.

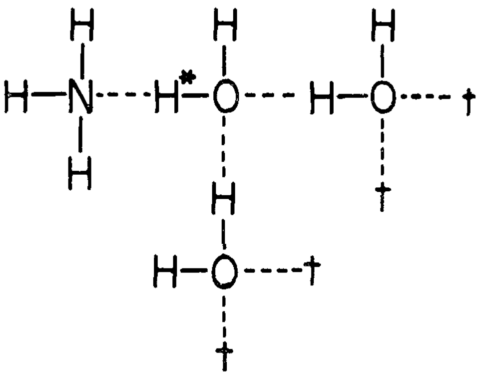

Fig. 1.—Model for proton transfer to NH_3.

the diffusion of a molecule through a distance s in an arbitrary direction is $s^2/6D$, where D is the macroscopic diffusion coefficient (in cm.²/sec.). Thus, for the separation of an *i-j* pair by a distance s, the relaxation time, τ_D, is given by

$$\frac{1}{\tau_D} = \frac{6(D_i + D_j)}{s^2} \tag{22}$$

Strictly speaking, eq. 22 is valid only when s is large compared to molecular dimensions. But if s is exactly the distance from one site to the next, we may expect, on the basis of arguments proposed by von Smoluchowski,[19] that eq. 22 is not a bad approximation. Numerical data needed for the calculation of $1/\tau_D$ are given in Table III.

The quantity $1/\tau_R$ may be obtained from dielectric relaxation data.[20] The calculation of k_H then proceeds as

$$\text{hypothesis: } H_3N\ldots H^*\text{–}OH \xrightarrow{k_H = \frac{1}{\tau_D} + \frac{1}{\tau_R}} H_3N + OHH^*$$

(diffusion and rotation of independent kinetic units)

Diffusion: $[6(2.44 + 2.39)/(2.9)^2] \times 10^{11}$		34×10^{10} sec.$^{-1}$
Rotation: HOH (same as in pure water)		12×10^{10} sec.$^{-1}$
NH_3 (about the same ?)		12×10^{10} sec.$^{-1}$?
k_H (predicted)	about	58×10^{10} sec.$^{-1}$
experimental value of $k_H' \eta/\eta_0$		49×10^{10} sec.$^{-1}$

The agreement between the predicted value of k_H and the experimental value of $k_H'\eta/\eta_0$ is excellent, lending further strong support to our assumptions. We therefore suggest that H_3N and H^*–OH on adjacent sites should be regarded as independent kinetic units.

A critical remark is now in order. We have seen that k_H' is very large, and there is some question whether k'_{-4} [H+] can plausibly be assumed to be much larger. We wish to discuss this question in two parts. First, we shall reason that $k'_{-4}[H^+]$ is at least of comparable magnitude to k_H'; and second, that the preceding estimates of k_H are at worst *lower limits*, so that our conclusion that H_3N and H^*OH are independent kinetic units remains in any case correct.

TABLE III

DATA USED IN THE CALCULATION OF $1/\tau_D$ IN AQUEOUS SOLUTION AT 25°

Species	10^5 D, cm.²/sec.	Species	10^5 D. cm.²/sec.
H_2O	2.44^a	H_3O^+	9.31^a
NH_3	2.39^b	$(CH_3)_3N$	$\sim 1.26^c$
		CH_3NH_2	$\sim 1.99^b$

Nearest-neighbor distance in liquid water: $s = 2.9$ Å.[d]

[a] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, New York, N. Y., 1955, p. 317, and Appendix 6.2. See also D. C. Douglass and D. W. McCall, *J. Chem. Phys.*, **31**, 569 (1959). [b] Data in temperature range 4–17° were fitted to the equation, log $D_{NH_3} = -0.802 - 1139/T$, from which the value at 25° was calculated. Data taken from Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, 1923, p. 246. [c] Assumed to be the same as for $(CH_3)_3NH^+$ (note *a*). [d] J. Morgan and B. E. Warren, *J. Chem. Phys.*, 6, 666 (1938); G. W. Brady and W. J. Romanow, *ibid.*, **32**, 306 (1960).

Regarding the magnitude of $k'_{-4}[H^+]$, our previous study of the reaction of hydrogen ion with ammonia in dilute aqueous acid indicates that the formula, $H_3N\ldots H^*OH$, is an oversimplification. Probably a better model would be that shown in Fig. 1, since proton transfer to NH_3 from the starred position is virtually instantaneous after attachment of an additional proton at any one of the four daggered positions.

In dilute acid, the hydronium ion must diffuse through a considerable distance on the average before attachment at a daggered site. In strong acid (50 to 70%), the concentration of H_3O^+ is so large that the average diffusion distance approaches that between adjacent sites. If we wish to obtain a conservative estimate for $k'_{-4}[H^+]$ from eq. 22, we use the macroscopic diffusion constants for H_3O^+ and NH_3 (Table III), and the intersite distance, 2.9 Å., appropriate to molecular diffusion. The value found in this way is 82×10^{10} sec.$^{-1}$ at 25°. The comparable value of k_H (k_H' corrected to dilute aqueous solution) has been previously estimated as 49×10^{10} sec^{-1}.

On this basis, $k'_{-4}[H^+]$ may not be very much greater than k_H'. Going back to eq. 15 and 16, it can be shown that the quantity which has been denoted as k_H' in Table I is really equal to

$$k_H' \times \frac{k'_{-4}[H^+]}{k'_{-4}[H^+] + k_H'} \equiv k_H' \times F \tag{23}$$

In Table I, F is assumed to be unity. If $k'_{-4}[H^+]$ were not an order of magnitude greater than k_H', F would be significantly less than one, and the true value of k_H' would actually be greater than the value listed in the table.

$CH_3NH_2 \cdot HOH$ Hydrogen Bond.—The results of the experiments on methylammonium ion are shown in Table IV. The kinetic pattern is completely analogous to that for ammonium ion. The rate constant for the isotopic exchange, k_e, is independent of $[CH_3NH_2D^+]$ over a twofold range of concentration. Reaction mechanisms involving direct reaction with OH^-, $SO_4^=$ or H_2O may again be ruled out. Assuming a reaction mechanism similar to that shown in eq. 11 and 12, values of k_H' were computed from eq. 19 with $g = 3$. The quantity k_H' η/η_0 is again constant within experimental error over a more than twofold variation in viscosity and a 200-fold variation in h_0.

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(19) M. von Smoluchowski, *Physik Z.*, **17**, 557, 585 (1916).

(20) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).

TABLE IV

KINETIC DATA BASED ON THE ISOTOPIC EXCHANGE OF N-DEUTERATED METHYLAMMONIUM CHLORIDE IN SULFURIC ACID–WATER MIXTURES

Temp., 25°; $K_A°$, 2.38 × 10^{-11} for $CH_3NH_3^{+a}$

H_2SO_4 (wt. %)	$[CH_3ND_3^+]$	k_e, sec.$^{-1}$	10^{-10} k_H', sec.$^{-1}$	η/η_0	10^{-10} k_H' (η/η_0)
34.23	0.26	1.97×10^{-3}	2.71	2.28^b	8.2
(h_0 = 102)	.45	1.75×10^{-3}	2.41	2.28	7.3
49.10	.29	6.86×10^{-5}	1.79	3.70	8.7
(h_0 = 1930)	.58	6.88×10^{-5}	1.79	3.70	8.8
54.27	.30	1.76×10^{-5}	1.61	4.61	9.8
(h_0 = 6760)	.59	1.42×10^{-5}	1.30	4.61	7.9
58.86	.27	3.91×10^{-6}	1.16	5.6	8.5
(h_0 = 21,900)	.49	3.72×10^{-6}	1.10	5.6	8.1
				Av.	8.4 ± 0.8

[a] D. F. Everett and F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941). [b] "International Critical Tables."

TABLE V

KINETIC DATA BASED ON THE ISOTOPIC EXCHANGE OF $(CH_3)_3ND^+$ IN SULFURIC ACID–WATER MIXTURES

Temp., 25°· K_A^0, 1.57 × 10^{-10} for $(CH_3)_3NH^{+a}$

H_2SO_4 (wt. %)	$[(CH_3)_3ND^+]$	k_e, sec.$^{-1}$ Reacn. 5 (eq. 10)	k_e, sec.$^{-1}$ Exptl. value	$10^{-9}k_H'$, sec.$^{-1}$	η/η_0	$10^{-9}k'_H$ (η/η_0)
24.86	0.485	(2.6×10^{-5})	8.66×10^{-3}	1.79	1.76^b	3.14
(h_0 = 22.9)						
27.52	.208	(2.1×10^{-5})	5.16×10^{-3}	1.63	1.89	3.08
(h_0 = 35.1)	.461		4.86×10^{-3}	1.54	1.89	2.91
31.43	.219	(1.4×10^{-5})	1.76×10^{-3}	1.05	2.10	2.21
(h_0 = 66.0)	.499		1.72×10^{-3}	1.02	2.10	2.14
36.15	.446	(1.0×10^{-5})	5.4×10^{-4}	0.67	2.40	1.62
(h_0 = 138)						
54.27	.188	(1.2×10^{-6})	2.59×10^{-6}	0.158	4.61	0.73
(h_0 = 6760)	.537		2.78×10^{-6}	0.169	4.61	0.78

[a] H. P. Marshall and E. Grunwald, THIS JOURNAL, **76**, 2000 (1954). D. F. Everett and F. K. Wynne-Jones, *Proc. Roy Soc.* (*London*), **A177**, 499 (1941). [b] "International Critical Tables."

However, the average value of k_H, 8.4 × 10^{10} sec.$^{-1}$, is an order of magnitude smaller than the corresponding constant for ammonium ion.

If we assume again that the amine and the water molecules behave as independent kinetic units, we predict that k_H should have nearly the same value as for the $H_3N...HOH$ "complex." The much smaller value obtained experimentally can be understood only if the $CH_3.H_2N...HOH$ "complex" is a genuine kinetic unit which remains intact for several diffusive jumps.

$(CH_3)_3N·HOH$ Hydrogen Bond.—The results for experiments on trimethylammonium ion are shown in Table V. The rate constants for exchange, k_e, are again independent of the salt concentration, but fall into a kinetic pattern which deviates from that for the other two ammonium salts. Values of k_H' were computed from eq. 19 with $g = 1$. However, when these values are multiplied by η/η_0, the product is no longer constant but decreases markedly with increasing acid concentration (Table V). Moreover, the values of k_H' are appreciably smaller than those obtained for the other ammonium salts, being two orders of magnitude smaller than those for ammonium ion.

Two interpretations suggest themselves: either the kinetic scheme shown in eq. 11 and 12 does not apply; or the medium effect on k_H' is not given correctly by eq. 21. We favor the second interpretation.

The relevant equilibrium and rate constants for the system $(CH_3)_3NH^+$–H_2O, as far as they are known, provide no basis for abandoning the kinetic scheme shown in eq. 11 and 12. The value of K_A^0 for $(CH_3)_3NH^+$ is intermediate between values for NH_4^+ and for $CH_3NH_3^+$. In dilute acid, the rate constant k_{-4} for the reaction of $(CH_3)_3N$ with H_3O^+ is virtually identical with that for the analogous reaction involving ammonia.[21] Thus the assumption that $k'_{-4}[H^+] >> k_H'$ is likely to be justified. The value of k_4 is of the same order of magnitude as for NH_4^+.[21] The rate constant k_5 for reaction with hydroxide ion cannot be much greater than that for the analogous reaction 5 of NH_4^+, since the latter reaction is already occurring at nearly every encounter. Calculation based on eq. 10 shows that this reaction does not contribute significantly to the experimental value of k_e except possibly in 54% H_2SO_4 (compare columns 3 and 4, Table V).

In searching for possible alternative kinetic schemes, we plotted log k_e *vs.* log h_0. As shown in Fig. 2, the plot is accurately linear, the slope being −1.44. However, we have as yet been unable to conceive of a plausible kinetic scheme which (except for medium effects on rate constants) will give a slope more negative than −1. The scheme shown in eq. 11 and 12 is the most plausible in this group.

Since eq. 21 does not fit, we have evaluated k_H by more empirical methods of extrapolation to zero per cent. H_2SO_4. The best of these is shown in Fig. 3: the plot of log ($k_H'\eta/\eta_0$) *vs.* weight per cent. H_2SO_4 is accurately linear. The intercept of 10.06, which is equal to log k_H, leads to k_H = 1.15 × 10^{10} sec.$^{-1}$. Other methods of extrapolation lead to estimates ranging from 0.7 to 1.3 × 10^{10} sec.$^{-1}$.

Although some uncertainty attaches to the precise value of k_H, there is no doubt that it is appreciably smaller than one would expect if the adjacent $(CH_3)_3N$ and H^*OH molecules were behaving as independent kinetic units. Using eq. 22 and numerical data in Table III, we estimate $1/\tau_D$ for such a model as 26 × 10^{10} sec.$^{-1}$. Thus the two ligands in the $(CH_3)_3N·HOH$ complex move as

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[21] E. Grunwald, P. J. Karabatsos, R. A. Kromhout and E. L. Purlee, *J. Chem. Phys.*, **33**, 556 (1960).

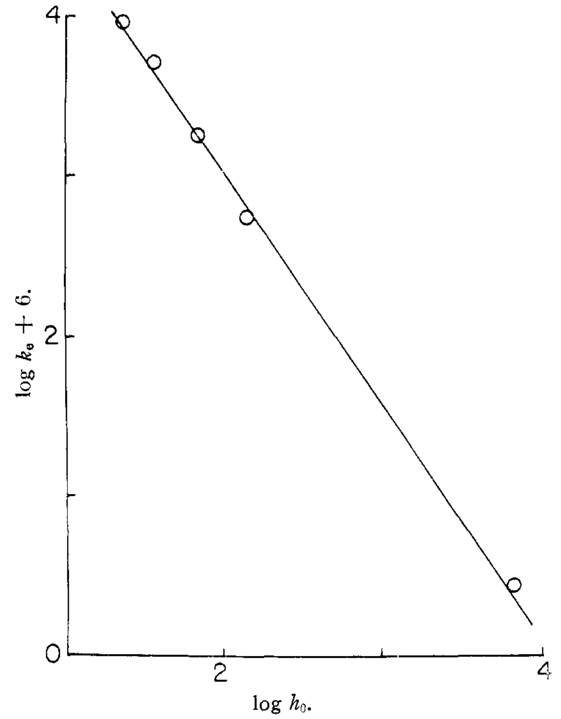

Fig. 2.—Plot of log k_e vs. log h_0 for trimethylammonium ion in sulfuric acid–water mixtures, 25°.

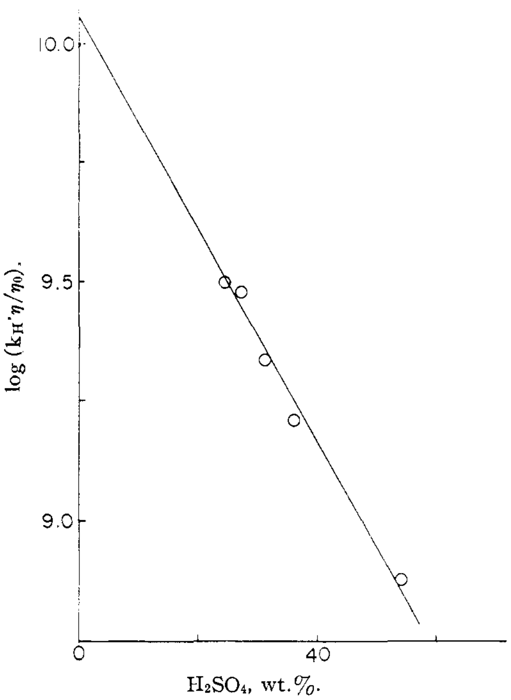

Fig. 3.—Plot of log ($k_H'\eta/\eta_0$) vs. weight per cent. sulfuric acid for trimethylammonium ion, 25°.

a single kinetic unit which remains intact for something of the order of ten diffusive jumps.

Discussion

Relative values of k_H are in the sequence: NH_3, >50; CH_3NH_2, 8; $(CH_3)_3N$, 1. In interpreting this sequence, two alternative hypotheses suggest themselves, namely (i) that the rate depends primarily on the strength of the N· · ·H hydrogen bond; or (ii) that it depends primarily on the stability of the solvation shells surrounding the amines.

If we accept the first hypothesis, then our data indicate that the strength of an N· · ·H hydrogen bond increases in the sequence, $NH_3 < CH_3NH_2 < (CH_3)_3N$. According to organic chemical theory, this result is reasonable. The CH_3–group is electron-releasing compared to hydrogen,[22] so that electron supply to the nitrogen atom should increase in the sequence, $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$. Unfortunately there is almost no independent evidence in support of this prediction. Basicity constants in water are not reliable indicators of electron supply because of complicating solvation and steric effects.[23–25] On the other hand, in non-polar solvents, where the effects of electron supply are less likely to be masked by solvation effects, basicity *is* often found to be in the hoped-for sequence $RNH_2 < R_2NH < R_3N$ (where R is any small *n*-alkyl radical).[23,26] As far as we know, there have not been any directly relevant studies of hydrogen bonding for a series of amines with a single donor under conditions where unambiguous measures of relative hydrogen-bond strength are obtained. However, the available data at least do not invalidate our hypothesis. For example, shifts of the infrared stretching frequency of chloroform consequent to hydrogen bonding are 32 cm.$^{-1}$ for $Cl_3CH·NH_3$ in carbon tetrachloride and 110 cm.$^{-1}$ for $Cl_3CH·N(C_2H_5)_3$ in tetrachloroethylene,[27] suggesting that the hydrogen bond to ammonia is much the weaker of the two.

The second hypothesis involves quite a different model of the amine–water interaction. Instead of regarding the hydrogen-bonded complex as a bimolecular unit, one assumes that the amine molecule is surrounded by a solvation shell in which a number of water molecules coöperate to form a well-ordered configuration of low potential energy. This ordered configuration may be a continuous structure which envelops the entire solute molecule, as suggested by Claussen for hydrocarbons in water[28]; or it may consist of a few "patches of ice" which are formed next to the solute molecule, but which do not necessarily fuse to form a single enveloping structure.[4] Because of the relatively low potential energy of the solute plus its solvation shell, the relaxation times for rotation and diffusion are longer than they would be in a less ordered structure of higher potential energy. On this basis, the magnitude of k_H is an index of the relative stability of the amine plus its solvation shell,

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(22) See, for example, R. W. Taft, in "Steric Effects in Organic Chemistry," M. S. Newman, editor, John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 619, 635.

(23) R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

(24) H. C. Brown, H. Bartholomay and M. D. Taylor, This Journal, **66**, 435 (1944).

(25) R. G. Pearson and F. V. Williams, *ibid.*, **76**, 258 (1954).

(26) E. A. Yerger and G. M. Barrow, *ibid.*, **77**, 6206 (1955).

(27) (a) C. G. Cannon, *Spectrochim. Acta*, **10**, 429 (1958); (b) R. E. Glick, *Chemistry & Industry*, 413 (1956).

(28) W. F. Claussen, *J. Chem. Phys.*, **19**, 259, 662, 1425 (1951); W. F. Claussen and M. F. Polglase, This Journal, **74**, 4817 (1952).

or at least of the amine plus that portion of the solvation shell which is in contact with the nitrogen atom.

From this point of view, it is a most satisfying aspect of our results that k_H for the ammonia–water "complex" is of such a magnitude as to suggest that we are dealing with independent kinetic units. Because of the close similarity of molecular structure, we may assume that NH_3 fits into the quasi-crystalline lattice of liquid water with a minimum of distortion. Thus the presence of the NH_3 molecule should exert little influence on the configuration and hence on the kinetic properties of the surrounding water molecules. On the other hand, as first one and then three CH_3- groups are substituted for hydrogen atoms, the progressive decrease in k_H suggests that there is a progressive increase in the stability of the "iceberg" that is built up next to the nitrogen atom. In view of the known increase in the importance of the iceberg phenomenon with increasing size of the solute molecule,[4] such an observation is plausible.

While at this time there is no basis for preferring either the first or the second hypothesis, such a basis may form as data for similar structures accumulate.

Finally, there is the problem of the medium effect on k_H'. It is difficult to explain why the data for NH_3 and CH_3NH_2 are fitted perfectly by eq. 21, while the data for $(CH_3)_3N$ deviate greatly. Neither of the two hypotheses provides a reasonable *and* consistent explanation. For example, one might ascribe the deviation from eq. 21 for $(CH_3)_3N$ to a progressive change in the average composition of the kinetic units caused, perhaps, by the substitition of $SO_4^=$ or HSO_4^- for H_2O in the solvation shell. However, one is then hard-put to explain the complete absence of this phenomenon for CH_3NH_2. The solution to this problem must also await accumulation of data on similar systems.

Kinetic Part

Materials.—Ammonium sulfate, methylammonium chloride and trimethylammonium chloride were reagent grade chemicals, the latter two being further purified by recrystallization from ethyl alcohol. The exchangeable hydrogen in each of these salts was replaced by deuterium from heavy water, as described previously for NH_4^+.[5] Sulfuric acid–water mixtures were prepared from reagent grade sulfuric acid and doubly distilled water. (The final distillation of the water was from alkaline permanganate in an all-glass apparatus.) The weight per cent. of H_2SO_4 in each of the mixtures was calculated from the measured acid normality or density.

Reaction solutions were prepared as needed by adding a known weight of the salt to 10 ml. of a stock acid solution. Complete solution was accomplished as quickly as possible, and a 0.5-ml. portion was then pipetted into a standard n.m.r. sample tube. With practice it became possible to start taking n.m.r. spectra within 90 seconds after mixing the salt and acid.

All solution preparations and kinetic measurements were made in an air-conditioned room at 25 ± 0.5°. When the half-lives were longer than about 1 hour, the samples were stored in a water thermostat at 25.00° between n.m.r. measurements.

Ammonium Ion.—The n.m.r. spectrum of the NH_4^+ protons in strongly acid solutions consists of 3 sharp, widely separated lines of nearly equal intensity.[5] On the other hand, completely deuterated ammonium ion of course shows no proton resonance absorption. Also present are the various intermediates of exchange—ND_3H^+, $ND_2H_2^+$ and NDH_3^+—all of which contribute to the proton resonance. The effect of the deuterium atoms on the proton spectra of these intermediates is to cause each of the 3 proton lines to be split further by spin–spin coupling to the deuterium nuclei. Since the coupling is small the observed effect is to broaden each of the proton resonance lines into an unresolved multiplet.

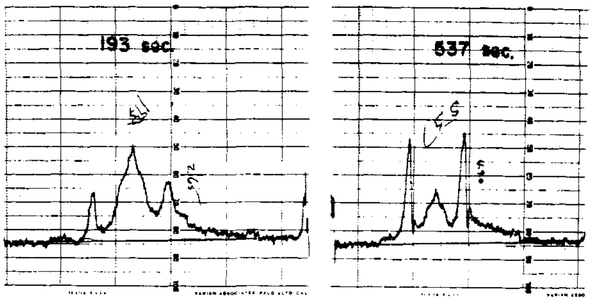

Fig. 4.—Typical n.m.r. spectra for the isotopic exchange of 0.5 *M* $(CH_3)_3ND^+$ in 31.43 wt. % H_2SO_4–H_2O at 25°.

One possible way to follow the displacement of deuterium by hydrogen is to measure the *area* of the proton resonance lines as a function of time. This, however, was unsatisfactory owing to uncontrollable changes in scanning rate caused by drift of the electronic equipment. A more practical method was based on the measurement of peak heights. Here one waits until the concentration of ND_4^+, ND_3H^+ and $ND_2H_2^+$ has become negligible, and then uses eq. 3a for calculating the rate constant for the conversion of NH_3D^+ to NH_4^+. We found that when $h_t >$ about 0.5 h_∞, the proton lines become sharp and the plot of log $(h_\infty - h_t)$ *vs.* t becomes linear. The peak heights were found to be quite stable, and whatever small drifts did exist could be corrected for by periodic measurement of a reference height.

Trimethylammonium Ion.—The resonance lines of the N–H protons are not suitable for following the exchange because of the large amount of broadening of these lines by quadrupole relaxation of the nitrogen atom. However, the reaction may be followed by following the change in the CH_3 resonance lines.

In $(CH_3)_3ND^+$, the deuterium splits the CH_3- resonance into a (1,1,1) triplet, the line separation being 1.0 c.p.s. In $(CH_3)_3NH^+$, the N-proton splits the CH_3- resonance into a (1,1) doublet, the line separation being 6.5 c.p.s. Since the triplet splitting in $(CH_3)_3ND^+$ is only about twice the line width, one observes a broadened "singlet," the triplet character of which is just barely recognizable. The intensity of this peak decreases with time, while a symmetrical sharp doublet appears in its place. Typical spectra are shown in Fig. 4. The reaction is easily followed by measuring the height of either the "singlet" or doublet as a function of time. In any given run, values of k_e obtained by the two methods agreed closely.

Methylammonium Ion.—Again it is necessary to follow the isotopic exchange by measuring the CH_3- proton resonance as a function of time. However, the spectral analysis is now much more complicated because the reaction proceeds through a series of steps. Under our experimental conditions of large proton excess, the exchange goes virtually to completion, and the kinetics may be represented by the scheme

$$\begin{aligned} CH_3ND_3^+ + H^+ &\xrightarrow{3k_e} CH_3ND_2H^+ + D^+ \\ CH_3ND_2H^+ + H^+ &\xrightarrow{2k_e} CH_3NDH_2^+ + D^+ \\ CH_3NDH_2^+ + H^+ &\xrightarrow{k_e} CH_3NH_3^+ + D^+ \end{aligned} \tag{24}$$

This scheme leads to the rate equations

$$\begin{aligned} d[D_3]/dt &= -3k_e[D_3] \\ d[D_2]/dt &= -2k_e[D_2] + 3k_e[D_3] \\ d[D_1]/dt &= -k_e[D_1] + 2k_e[D_2] \\ d[D_0]/dt &= k_e[D_1] \end{aligned} \tag{25}$$

where D_3, D_2, D_1 and D_0 denote, respectively, the molar concentrations of $CH_3ND_3^+$, $CH_3ND_2H^+$, $CH_3NDH_2^+$

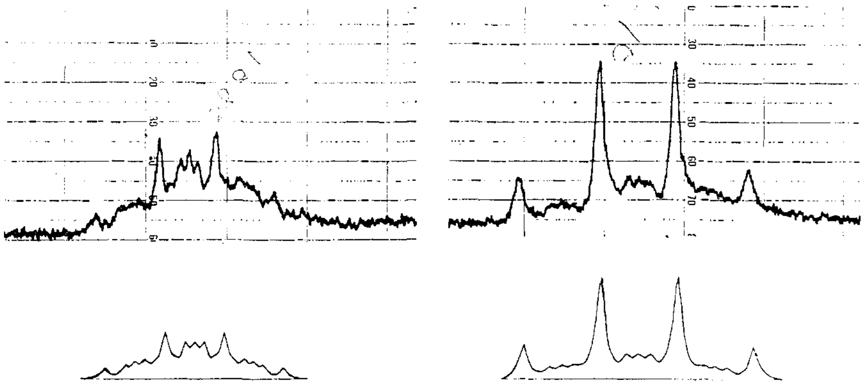

Fig. 5.—Theoretical (bottom) and experimental n.m.r. spectra during the isotopic exchange of $CH_3ND_3^+$ in 36% H_2SO_4–H_2O at 25°: left, $k_et = 1.0$; right, $k_et = 2.2$.

and $CH_3NH_3^+$ at time t. When this set of simultaneous equations is solved for the boundary condition that at $t = 0$, $D_3 = c_0$ and $D_2 = D_1 = D_0 = 0$, one obtains

$$\begin{aligned}[D_3]/c_0 &= e^{-3k_et}\\ [D_2]/c_0 &= 3e^{-2k_et} - 3e^{-3k_et}\\ [D_1]/c_0 &= 3e^{-3k_et} - 6e^{-2k_et} + 3e^{-k_et}\\ [D_0]/c_0 &= -e^{-3k_et} + 3e^{-2k_et} - 3e^{-k_et} + 1\end{aligned} \qquad (26)$$

The concentration of each of the four isotopic species can thus be calculated as a function of the dimensionless parameter k_et. This permits the construction of theoretical n.m.r. spectra as a function of k_et.

TABLE VI

PREDICTED MULTIPLET STRUCTURE OF CH_3-RESONANCE BANDS

Isotopic species	ν_0^i(c.p.s.)	h_i	Isotopic species	ν_0 (c.p.s.)	h_i
$CH_3ND_3^+$	±2.91	1/27	$CH_3NDH_2^+$	±7.28	1/12
	±1.94	3/27		±6.31	1/12
	±0.97	6/27		±5.34	1/12
	0.00	7/27		±0.97	2/12
				0.00	2/12
$CH_3ND_2H^+$	±5.095	1/18			
	±4.125	2/18	$CH_3NH_3^+$	±9.465	1/8
	±3.55	3/18		±3.155	3/8
	±2.185	2/18			
	±1.215	1/18			

The CH_3– resonance of each isotopic species is a multiplet due to spin–spin coupling to the N– protons and deuterons. The corresponding coupling constants were found to be 6.31 and 0.97 c.p.s., respectively. Using these coupling constants, the positions of the resonance peaks, ν_0^i (measured from the center of the CH_3– resonance band), and their relative intensities, h_i, were calculated for each isotopic species and are listed in Table VI. The n.m.r. spectrum for each isotopic species was then predicted by adding up the intensities of the multiplet components, assuming Lorentzian line shapes

$$g(\nu) = \sum_i h_i \frac{2T_2}{1 + 4\pi^2T_2^2(\nu_0^i - \nu)^2} \qquad (27)$$

where the summation extends over the entire set of multiplet lines expected for the given isotopic species. Finally, to obtain the composite spectrum for the mixture of isotopic species for any given value of k_et, the relative concentrations D_3/c_0, D_2/c_0, etc., are calculated, and the corresponding $g(\nu)$ are added, each being weighted in proportion to the amount present

$$G(\nu) = \sum_{j=0}^{3} (D_j/c_0)\, g_j(\nu) \qquad (28)$$

Theoretical spectra were calculated on an IBM 650 computer for a series of values of the parameter, k_et. For T_2, the experimental value of 0.32 sec. was used. Two such theoretical spectra are shown in Fig. 5, along with experimental spectra corresponding to closely similar values of k_et. The agreement is very good.

To simplify the comparison of experimental with theoretical spectra, the ratio, r, of the center peak to the two larger members of the $CH_3NH_3^+$ quadruplet was calculated from the theoretical curves as a function of k_et, and a smooth plot of r vs. k_et was prepared. By measuring experimental peak heights, we then obtained experimental values of r as a function of time. By interpolating on the theoretical plot[29] of r vs. k_et, we derived quasi-experimental values of k_et as a function of time. Plots of the quasi-experimental k_et vs. time were nicely linear, the slope being equal to the desired rate constant k_e.

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[29] The plot of r has been filed with the American Documentation Institute.