

measurement on the solid at 77°K. If the effect of temperature decrease could be associated definitely and uniquely with reduction of non-radiative processes, such as amplitudes of crystal vibrations, then it might be possible to obtain a significant value of τ_0 by extrapolation of measured τ at various low temperatures. A more thorough study of this point will be made, but the necessary equipment is not available at present. Values of τ_0 from absorption data, quoted by Mulliken, range from 1.3×10^{-2} to 2.2×10^{-3} , and are considerably longer than our value 5×10^{-3} second.

But the orders of magnitude of τ_0 associated with the two electronic states of SO_2 show at least that the first excited state has a longer lifetime

than would correspond to the usual singlet-singlet transition. This suggests that the first excited state may be a triplet state. Douglas²⁵ has observed an effect of a magnetic field on the first electronic state but no such effect on transition to the second electronic state. He attributed his observations to a triplet character of the first excited state. We observed no preferential quenching of the fluorescence from the first excited state by O_2 , but the pressure of O_2 probably was not sufficiently high, and our observation is not sufficient for rejection of the hypothesis that the first excited state may be a triplet.

(25) A. E. Douglas, *Can. J. Phys.*, **36**, 147 (1958).

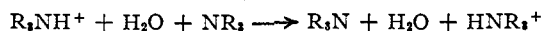
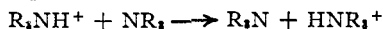
[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK]

The Activation Energies of Proton Transfer Reactions in Ammonium and Methylammonium Solutions Measured by the Nuclear Magnetic Resonance Technique¹

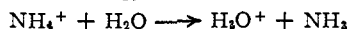
BY T. M. CONNOR² AND A. LOEWENSTEIN³

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The activation energies of proton transfer processes of the types (R = H or Me)



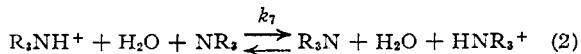
have been measured by the nuclear resonance technique in aqueous solutions of ammonium and methylammonium chlorides and have values very close to zero. An activation energy of 12.2 ± 0.5 kcal. mole⁻¹ was found for the reaction



The significance of these results in terms of diffusion controlled reaction mechanisms is discussed. The thermodynamic functions ΔH^* , ΔF^* and ΔS^* have been calculated for these reactions and indicate that for those reactions where $\Delta E \approx 0$, the free energy of activation is ≈ 5 kcal. mole⁻¹.

The rates and mechanisms of proton transfer reactions have been studied previously in aqueous solutions of ammonium⁴⁻⁶ and methylammonium^{7,8} ions at room temperature by the nuclear magnetic resonance (n.m.r.) technique. We have extended these studies by measuring the proton transfer rates as a function of the temperature and have evaluated the activation energies associated with these processes.

It was found⁴⁻⁸ that the main contribution to the total rate of exchange can be attributed to the mechanisms



where R denotes the methyl or hydrogen radicals in the ammonium or methylammonium ions. The

notation of the rate constants is the same as that used in references 5-8. The ratio k_6/k_7 was found^{6,8} to be independent of the ammonium or methylammonium concentrations.

Two additional exchange mechanisms are the direct proton exchange between the ammonium ion and the hydroxyl ions or the water molecules, respectively. The first of these is a very fast reaction⁹ ($k_5 \approx 10^{11}$ sec.⁻¹M⁻¹), but its contribution to the total rate of exchange is negligible because of the small concentration of the hydroxyl ions in the pH range in which the rates were measured (pH 1 to 4). The second reaction (exchange with water) is a very slow reaction in both the ammonium and methylammonium cases. However, the rate in ammonium solutions⁶ ($k_4 = 24.4$ sec.⁻¹) is large compared with the rate in methylammonium solutions⁸ ($k_4 = 1.2$ sec.⁻¹), and hence its contribution to the total rate has been considered only in the former case and the activation energy associated with this process has been evaluated.

The n.m.r. spectra of ammonium and methylammonium solutions at room temperature and the changes they undergo as a function of pH have been described elsewhere.⁴⁻⁸ The changes in the line shapes of the spectra as the temperature of the solution is raised are similar to those which are observed when the hydrogen ion concentration of

- (1) Supported by a grant from the National Science Foundation.
- (2) The National Physical Laboratory, Teddington, Middlesex, England.
- (3) The Weizmann Institute of Science, Rehovot, Israel.
- (4) (a) R. A. Ogg, *Discussions Faraday Soc.*, **17**, 215 (1954); (b) R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, **26**, 1339 (1957).
- (5) S. Meiboom, A. Loewenstein and S. Alexander, *ibid.*, **29**, 969 (1958).
- (6) M. T. Emerson, E. Grunwald and R. A. Kromhout, *ibid.*, **33**, 547 (1960).
- (7) E. Grunwald, A. Loewenstein and S. Meiboom, *ibid.*, **27**, 630 (1957).
- (8) E. Grunwald, P. J. Karabatos, R. A. Kromhout and E. L. Purlee, *ibid.*, **33**, 556 (1960).
- (9) M. Eigen, *Discussions Faraday Soc.*, **17**, 194 (1954).

the solution is lowered. The only difference noted is that whereas the NH triplet in methylammonium sharpens with increasing temperature,¹⁰ it broadens and coalesces with the water line on increasing the pH at room temperature.⁷ This sharpening of the NH lines has been attributed¹⁰ to the change in the correlation time (τ_c) of the solution which affects the T_1 of the N^{14} nucleus.

The evaluation of the specific rate $R \equiv 1/\tau$ where τ is the mean life-time of the ions between exchanges was performed by the same procedures described previously.⁶⁻⁷ In interpreting the spectra of methylammonium solutions use was made of the changes in the line shapes of the methyl quadruplet (from a sharp quadruplet to a single line).¹¹ This enabled measurements to be made over the temperature range 25 to 70° approximately. The contributions of k_4 and k_5 are small and were neglected, the expression used being

$$R \equiv \frac{1}{\tau} = (k_6 + k_7) \frac{K_A[\text{CH}_3\text{NH}_3^+]}{[\text{H}^+]} \quad (3)$$

The interpretation of the spectra of ammonium solutions was based on the following expression which neglects the small contribution of exchange involving OH^- ions to line broadening (k_6) where

$$\pi\Delta = \frac{1}{T_2} + \frac{1}{\tau} = \frac{1}{T_2} + \frac{k_4}{4} + \left(\frac{k_6}{6} + \frac{k_7}{4}\right) \frac{K_A[\text{NH}_4^+]}{[\text{H}^+]} \quad (4)$$

Δ is the half-width in c./s. of a component of the NH triplet resonances and $1/T_2$ is its half-width in the absence of exchange. The contribution of field inhomogeneity to $1/T_2$ was measured in each experiment by using the decay of the "wiggles" on fast passage in a pure water sample. The contribution of the N^{14} quadrupole relaxation to $1/T_2$ was assumed to be negligible for these reasons: (1) The ammonium ion is symmetrical and no appreciable contribution to the quadrupole relaxation would arise from internal electrical field gradients.^{4b} (2) The quadrupole broadening of the proton resonances is very small at room temperature (< 1 c./s. see ref. 6). By analogy with the methylammonium case¹⁰ it can be soundly assumed that this broadening would decrease with increasing temperature and hence can be neglected when the change of τ_4 with temperature is considered in the following. Equation 4 is valid only for slow exchange rates where no considerable overlap of the NH triplet components occurs, which introduces a limitation in the temperature range over which rate constants can be measured (25 to 55°), as compared with methylammonium solutions.

Results

The experimental procedure was simplified by the fact that the hydrogen ion concentrations of the solutions studied were found to be almost constant over the entire temperature range employed ($< 1\%$ variation).

Table I records the methylammonium and hydrogen ion concentrations and the measured rate constants and temperatures for the solutions studied. The hydrogen ion concentration was so ad-

justed as to give a measurable variation in the methyl resonance line shape over the experimental temperature range. It is seen from Table I that

TABLE I
CONCENTRATIONS, TEMPERATURES AND RATE CONSTANTS
FOR CH_3NH_3^+ SOLUTIONS

$[\text{CH}_3\text{NH}_3^+]$ (M)	$[\text{H}^+]$ ($M \times 10^{-3}$)	T (°C.)	$k = (k_6 + k_7) \times 10^{-3}$ ($\text{sec.}^{-1} M^{-1}$)
0.24	0.89	25.0	1.22
		35.5	1.79
		47.0	1.73
		57.7	1.55
0.50	1.68	26.0	1.79
		34.3	1.42
		39.7	1.65
		51.5	2.27
0.51	1.55	67.3	1.86
		26.5	1.48
		37.5	1.55
		51.5	2.10
1.00	3.14	51.0	2.27
		58.5	1.42
		70.5	1.28
		24.5	2.83
1.94	6.52	38.5	1.82
		65.7	3.19
		73.7	1.22
		26.7	1.68
		39.5	1.77
		55.5	2.08
		67.7	1.58

no systematic variation of rate occurs with change of methylammonium concentration. From a plot of the rate constants as function of the reciprocal of the absolute temperature the activation energy was obtained by a least square calculation. The result for the combined process represented by the rate constants $k_6 + k_7$ is

$$\Delta E = +16 \pm 454 \text{ cal. mole}^{-1}$$

where the deviation is the probable error.¹² Measurements of the ratio k_6/k_7 as a function of the temperature can be accomplished through a separate evaluation of k_7 from the half-widths of the solvent water line. It was found that within experimental accuracy the ratio k_6/k_7 is temperature independent.

Due to the apparent independence of rate and concentration in the case of methylammonium solutions, a similar behavior was assumed for ammonium solutions for which rate constants were thus measured at one concentration (1.0 M) only. The rate constants were obtained by the procedure: a semilogarithmic plot was made of the portion of the half-width due to exchange ($\Delta - 1/\pi T_2$) against the reciprocal of the absolute temperature ($1/T$) for each solution, which resulted in a family of curves corresponding to the values of the pH employed (Fig. 1). Since the half-width is proportional to a rate, one would expect a linear plot in this case, provided the type of processes occurring in solution are not changing over the tempera-

(10) J. D. Roberts, THIS JOURNAL, 78, 4495 (1956).

(11) "Tables of NMR Exchange Broadened Multiplets," The Weizmann Institute of Science, Rehovot, Israel.

(12) H. Margenau and G. M. Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943, p. 502.

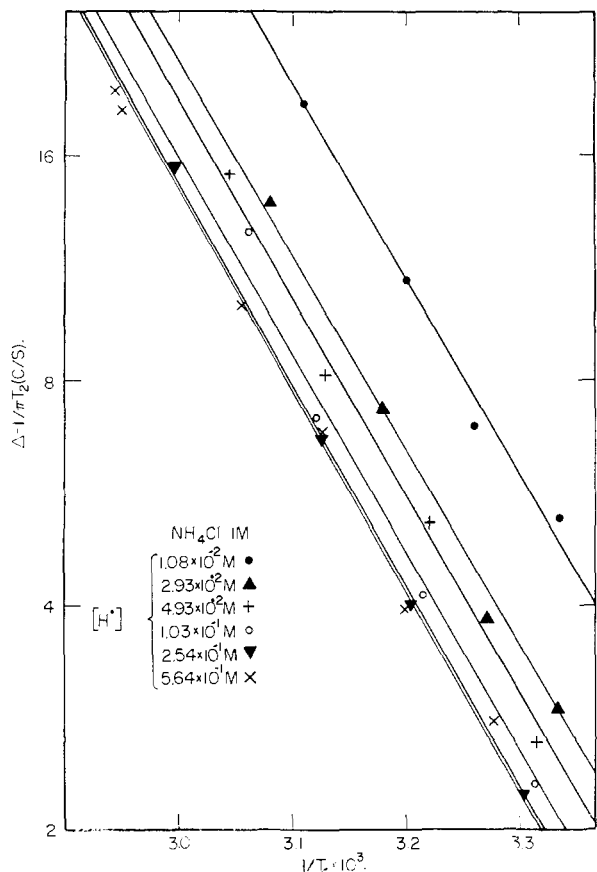


Fig. 1.—Plot of corrected half widths vs. $1/T$ for 1.0 M NH_4Cl solutions of varying pH .

ture range investigated. To within experimental accuracy Fig. 1 confirms this expectation. By interpolating at specific values of $1/T$, several series of exchange half-widths were obtained, each half-width corresponding to a particular pH value. This interpolation procedure was necessary owing to the difficulty of accurately reproducing a given sample temperature in separate experiments. A second family of curves then was constructed by plotting the half-widths thus obtained against the reciprocal of the hydrogen ion concentration which again resulted in a series of straight lines, each line corresponding to a particular value of $1/T$. From eq. 4 each resulting line has a slope $(k_6/6 + k_7/4)K_A[\text{NH}_4^+]$ and an intercept of $k_4/4$ on the y axis. Therefore, values of $k_6/6 + k_7/4$ and $k_4/4$ at a variety of temperatures could be determined. In ammonium solutions the contribution of k_7 at room temperature is very small ($<8\%$ of k_6) and by analogy with the methylammonium case, the ratio k_6/k_7 was assumed to be temperature independent. The value given by Grunwald, *et al.*,^{6,8} for k_6/k_7 was therefore used throughout this work.

The values of $k_6/6 + k_7/4$ and k_4 at different values of the interpolated temperatures are shown in Table II. From a plot of $k_6/6 + k_7/4$ as function of the reciprocal of the absolute temperature, the activation energy for the combined processes was obtained. The result is

$$\Delta E = -370 \pm 500 \text{ cal. mole}^{-1}$$

TABLE II

INTERPOLATION TEMPERATURES AND RATE CONSTANTS FOR 1.0 M NH_4^+ SOLUTIONS

T ($^{\circ}\text{C}$.)	$k = (k_6/6 + k_7/4) \times 10^{-8}$ ($\text{sec.}^{-1} M^{-1}$)	k_4 (sec.^{-1})
30.0	2.25	27.6
36.2	2.26	41.5
42.7	2.23	61.5
49.3	2.18	94.2
56.6	2.13	138.1

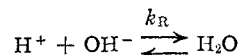
A similar plot for k_4 gives the activation energy for this process. The result is

$$\Delta E = +12,200 \pm 500 \text{ cal. mole}^{-1}$$

Discussion

The activation energies for the reactions which involve the rate constants k_6 and k_7 are surprisingly low. Previously, rates of reactions of this type have been interpreted in terms of diffusion control.^{6,8,13} However, activation energies of diffusion are normally of the order of 4 kcal. mole⁻¹ and in hydrogen bonded liquids show a marked temperature dependence.¹⁴ Thus, for the diffusion of mannitol in water, the activation energy of diffusion varies from 6,600 cal. mole⁻¹ in the range 0 to 10 $^{\circ}$ to 3,800 cal. mole⁻¹ between 60 and 70 $^{\circ}$. This decrease in the activation energy has been attributed to the breakdown of the hydrogen bonded structure of water at high temperatures.

An activation energy for the reaction



has been determined by Eigen and De Maeyer,¹⁵ who found a value of 2 to 3 kcal. mole⁻¹ for the temperature range 25 to 40 $^{\circ}$. The existence of an appreciable activation energy for this very fast reaction ($k_R = (1.4 \pm 0.2) \times 10^{11} M^{-1} \text{sec.}^{-1}$ at 25 $^{\circ}$) between oppositely charged ions is surprising in view of the virtually zero activation energies found in this investigation for slower ion-dipole reactions ($k_6 = 1.32 \times 10^9 M^{-1} \text{sec.}^{-1}$ for NH_4^+). As Eigen and De Maeyer point out, their figure represents an "apparent" activation energy for an over-all molecular process where there is a considerable change in solvation in passing from the reactants to the transition state of the reaction, which is electrically neutral. Possibly proton transfer to the OH^- ions becomes more efficient as the temperature is raised, because of the decrease in size of the solvation spheres of the H^+ and OH^- ions. However, whatever the detailed mechanism of the increase in rate for this reaction, it is evident for the fast reactions studied here, where reactants and products are equivalent, that the solvation change in forming the symmetrical transition state from the reactants will be small. Solvation effects will therefore be unimportant in determining the behavior of the reaction rate with temperature.

It is possible to calculate values of the heats, free energies and entropies of activation for these

(13) M. Eigen and L. De Maeyer, *Proc. Roy. Soc. (London)*, **A247**, 505 (1958).

(14) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 523.

(15) M. Eigen and L. De Maeyer, *Z. Elektrochem.*, **59**, 986 (1955).

processes (ΔH^* , ΔF^* and ΔS^* , respectively) using the results of the theory of absolute reaction rates.¹⁴ The figures obtained are recorded in Table III, which also includes the experimental activation

TABLE III
VALUES OF ΔE , ΔH^* , ΔF^* , ΔS^* FOR PROTON TRANSFER PROCESSES

Reaction	ΔE	ΔH^* (cal. mole ⁻¹)	ΔF^*	ΔS^* (e.u.)
$\text{NH}_4^+ + \text{NH}_3$	-370	-970	+5010	-20.1
$\text{NH}_4^+ + \text{H}_2\text{O}$	+12200	+11600	+15740	-13.9
$\text{MeNH}_3^+ + \text{MeNH}_2$	+16	-580	+5310	-19.8
$\text{MeNH}_3^+ + \text{H}_2\text{O} + \text{MeNH}_2$	+16	-580	+5150	-19.2

energies measured for the various processes. It can be seen that for all the processes involving rate constants k_6 and k_7 , the free energies of activation are positive and ~ 5 kcal. mole⁻¹ in magnitude. This seems to indicate that in these reactions the most important factor in determining the rates is the entropy factor, or the mutual orientation of the molecules taking part in the reaction (the "steric" factor). In comparison the reaction involving direct proton exchange between NH_4^+ and H_2O (k_4), the change in the profile of the reaction coordinate caused by considering the entropy term is very much smaller than in the case of the fast reactions involving the rate constants k_6 and k_7 .

It may also be interesting to point out that the enthalpy change ΔH involved in the equilibrium $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ is about 12,400 cal. as obtained from the change of K_A with the temperature.¹⁶ In view of the results for r_4 this would imply that the activation energy for the reaction $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$ is nearly zero. This conclusion seems to indicate that similar roles are played by the proton donors NH_4^+ and H_3O^+ ions in these transfer processes whereas the acceptors, NH_3 and H_2O , are of different nature. The activation energy for the process $\text{H}_3\text{O}^+ + \text{H}_2\text{O}$ is now being measured and would be interesting in comparison.

Experimental

N.m.r. measurements were made with a Varian model V4300 spectrometer operating at a proton frequency of 60

(16) D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, **A169**, 190 (1938); *ibid.*, **A177**, 499 (1941).

Mc. The probe was equipped with a Varian VHT Insert for measurements at elevated temperatures. The temperature was measured with a copper-constantan thermocouple and a Type K potentiometer. Frequency calibration was obtained by the side-band technique. Solutions of A.R. ammonium and methylammonium chlorides were prepared according to the procedure described previously.⁷ A Beckman model G pH-meter was used. It was found, by potentiometric titrations at different temperatures, that the hydrogen ion concentration in the solutions is almost unaffected by changing the temperature from 25 to 75°.

The K_A 's, defined in concentration terms, were determined by the differential potentiometric method,¹⁷ using a Beckman Model G pH-meter with glass and calomel electrodes to measure the e.m.f. of the solutions.

The dissociation constants are represented by

$$\log K_A = -A/T + B \quad (5)$$

The values of the constants A and B are given in Table IV.

TABLE IV
VALUES OF THE CONSTANTS A AND B AND THE PROBABLE ERROR IN K_A FOR DIFFERENT NH_4Cl AND $\text{CH}_3\text{NH}_3\text{Cl}$ CONCENTRATIONS

NH_4Cl (30-50°)			
Concn. (M)	$A \times 10^{-3}$	$B \times 10$	Probable error ¹² in $K_A \times 10^3$
0.97	+2.810	+0.085	± 6.7
.49	+2.756	-1.076	± 10.3
.26	+2.697	-2.819	± 7.0
$\text{CH}_3\text{NH}_3\text{Cl}$ (30-65°)			
Concn. (M)	$A \times 10^{-2}$	$B \times 10$	Probable error ¹² in $K_A \times 10^3$
3.80	+3.072	-8.459	± 7.8
1.95	+3.136	-4.764	± 20.0
0.97	+3.027	-7.155	± 9.2
.50	+2.951	-8.841	± 7.7
.25	+2.912	-9.492	± 5.4

The dependence of the K_A values on the temperature and their calculated values at room temperature are in fair agreement with the results given by Everett and Wynne-Jones,¹⁶ Bates and Pinching¹⁸ and by Grunwald and co-workers.^{6,8}

The ammonium ion concentration of the solutions was determined by the Volhard method.

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(17) A. L. Bacarella, E. Grunwald, H. P. Marshall and E. L. Purlee, *J. Org. Chem.*, **20**, 747 (1955).

(18) R. G. Bates and G. D. Pinching, *THIS JOURNAL*, **72**, 1393 (1950).