Nuclear Magnetic Resonance Study of Salt Effects on the Proton Exchange of Ammonium Salts in *t*-Butyl Alcohol

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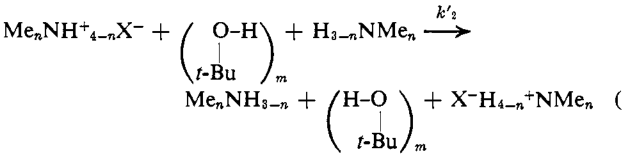
Abstract: The rate of proton exchange (determined by the nmr technique) involving the ion pairs of some methyl-substituted ammonium salts and their conjugate amines in *t*-butyl alcohol has been found to decrease significantly when tetraethylammonium salts are added. The decrease has been explained by the increase in the viscosity of the solution and by the complexing of the tetraethyl salt with the methyl salt to form aggregates that are less reactive than the uncomplexed methyl salt.

In the preceding paper,[1] it was shown that the rate of proton exchange involving methyl-substituted ammonium salts and their conjugate amines in *t*-butyl alcohol followed second-order kinetics. The mechanism shown in eq 1 was found to be consistent with the



$$\mathrm{Me}_n\mathrm{NH}^+_{4-n}\mathrm{X}^- + \left(\begin{array}{c}\mathrm{O{-}H}\\ | \\ t\text{-Bu}\end{array}\right)_m + \mathrm{H}_{3-n}\mathrm{NMe}_n \xrightarrow{k'_2} \mathrm{Me}_n\mathrm{NH}_{3-n} + \left(\begin{array}{c}\mathrm{H{-}O}\\ | \\ t\text{-Bu}\end{array}\right)_m + \mathrm{X}^-\mathrm{H}_{4-n}{}^+\mathrm{NMe}_n \qquad (1)$$

data. According to this mechanism, the ion pair rather than the dissociated ammonium ion takes part in the proton exchange.

In this paper, the results of a study of the effect of tetraethylammonium salts on the rate of this exchange reaction will be presented. Because the exchange does not involve the dissociated ammonium ion, a reduction in rate due to a mass law effect of the type shown in eq 2 is not expected. In fact, for the trimethylammonium salts, the exchange rate is not affected significantly by the presence of tetraethylammonium salts. However, for the mono- and dimethylammonium salts, it was found that addition of tetraethylammonium salts caused a marked decrease in the rate. Since a mechanism involving eq 2 is ruled out,[1] the decrease in rate is attributed to the increase in viscosity of the solution[2] and also to the complexing of the tetraethylammonium salt with the methyl-substituted salt to form mixed aggregates which are less reactive than the uncomplexed methyl-substituted salt. For the trimethylammonium salts, it appears that the complexed salt reacts as fast as the uncomplexed salt. This will be discussed later.

$$\mathrm{Me}_n\mathrm{NH}^+_{4-n}\mathrm{X}^- \rightleftarrows \mathrm{Me}_n\mathrm{NH}^+_{4-n} + \mathrm{X}^- \qquad (2)$$

The qualitative description given above is put in quantitative terms in the following manner. Correcting the second-order rate constants for the increase in viscosity by multiplying by the factor η/η_0 only partially compensates for the decrease caused by the addition of tetraethylammonium chloride. The remaining decrease in rate is attributed to the complexing of the methyl-substituted salt with the tetraethyl salt. From the freezing point depression data, the fraction, α, of uncomplexed methyl salt has been calculated for each solution using an approach similar to that employed by Grunwald and Price.[3] Using these values, the value of the rate constant, k', for exchange involving the complexed methyl salt was calculated using eq 3.

$$k'_2\eta/\eta_0 = k_0\alpha + k'(1 - \alpha) \qquad (3)$$

In this equation, k'_2 is the second-order rate constant obtained experimentally, η is the viscosity coefficient of the solution, η_0 is the viscosity coefficient of pure *t*-butyl alcohol, α is the fraction of the methyl-substituted salt which is not complexed with the tetraethyl salt, and k_0 is the second-order rate constant for reaction of the uncomplexed dimethyl salt. The value of k' obtained in this manner for dimethylammonium chloride is constant over the entire concentration range of tetraethylammonium chloride employed. This constancy of k' indicates that the theory is consistent with the experimental data.

Experimental Section

Materials. The preparation and purification of the methyl-substituted ammonium salts, the amines, and *t*-butyl alcohol are described in the preceding paper.[1]

Tetraethylammonium *p*-toluenesulfonate was prepared by neutralizing a 25% solution of $\mathrm{Et_4NOH}$ in $\mathrm{H_2O}$ (Matheson Coleman and Bell) using a methanol solution of *p*-toluenesulfonic acid. After the solvent was stripped off, the salt was recrystallized twice from ethylene dichloride–benzene. The salt was dried *in vacuo* at 70° in an Abderhalden pistol containing $\mathrm{P_2O_5}$ for 36 hr. The salt was found to be neutral. Tetrabutylammonium bromide and tetraethylammonium chloride were Eastman Kodak White Label compounds. Each was recrystallized twice and dried over $\mathrm{P_2O_5}$ at 78° *in vacuo* in an Abderhalden pistol. The equivalent weight as determined by the Volhard method always was within 0.3% of the calculated value. In addition these salts were found to be neutral.

Rate Measurements. The nmr rate measurements are described in the preceding paper.[1]

Cryoscopic Measurements. The freezing points were measured using a Beckmann type apparatus. The thermometer was calibrated in 0.1° unit and could be read to 0.03°. The cooling bath was maintained at about 3° below the freezing point of the solution. In order to obtain consistent measurements, the supercooling of the solutions was minimized by addition of a small crystal of *t*-butyl alcohol to initiate crystallization. Because of the supercooling, the molal concentration of each solution was corrected for the fraction of *t*-butyl alcohol that had solidified. This correction was made in the manner described by Grunwald and Price.[3]

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(1) M. Cocivera, *J. Am. Chem. Soc.*, **88**, 672 (1966).

(2) For the exchange involving methylammonium acetate in acetic acid, Grunwald and Price[3] have shown that the viscosity correction, η/η_0, compensates for the decrease in the first-order rate constant for concentrations of the salt up to about 0.2 *M*. In water for monomethylammonium chloride, Grunwald, *et al.*,[4] have applied this correction to the second-order rate constants for concentrations up to 8 *M* in salt.

(3) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 2965 (1964).

(4) E. Grunwald, P. Karabatsos, R. Kromhout, and E. Purlee, *J. Chem. Phys.*, **33**, 556 (1960).

At least two measurements were made for each solution, and they always agreed to within 0.03°. The freezing point of pure *t*-butyl alcohol used was found to be 25.60°. The reported values range from 25.4[5] to 25.53°.[6]

Viscosity Measurements. The viscosities of the dimethylammonium and tetraethylammonium chloride solutions relative to pure *t*-butyl alcohol were obtained from densities and flow times using an Ostwald modification of the Poiseuille viscometer. The flow measurements which were made at 35.0 ± 0.05° had a precision of ±0.6%.

Results and Discussion

In Table I, the values of the second-order rate constants, k'_2, at 35° are listed for trimethylammonium salts in *t*-butyl alcohol with and without tetraalkylammonium salts. In each case, the value of k'_2 is not altered significantly by the presence of the tetraalkylammonium salt. On the other hand, as shown in Tables II and III, addition of tetraethylammonium salts causes pronounced decreases in the rate for the mono- and dimethylammonium salts studied. For each of these salts, as the concentration of the added salt is increased, the rate decreases.

Table I. Values of k'_2 for Trimethylammonium Salts ($Me_3(NH^+X^-)$) in the Presence of Tetraalkylammonium Salts in *t*-Butyl Alcohol at 35°

X^-	Added salt	Concn of added salt, M	$k'_2 \times 10^{-5}$, M^{-1} sec^{-1}
Cl^-	...	...	1.1 ± 0.12
Cl^-	Et_4NCl	0.192	1.1 ± 0.14
Br^-	...	...	5.3 ± 0.7
Br^-	Bu_4NBr	0.187	5.2
OTs^-	...	...	7.0 ± 0.7
OTs^-	Et_4NOTs	0.266	6.3

Table II. Values of k'_2 for $MeNH_3X$ in the Presence of Et_4NX at 35° in *t*-BuOH

X^-	$[Et_4NX]$, M	$[MeNH_3X]$, M	$k'_2 \times 10^{-6}$, M^{-1} sec^{-1}
Cl^-	...	0.06213	26.1
Cl^-	0.02008	0.03182	16.9
Cl^-	0.04004	0.03203	15.1
Cl^-	0.08032	0.03223	13.5
Cl^-	0.1706	0.03272	9.8
Cl^-	0.2614	0.01799	7.8
Cl^-	0.3260	0.04281	5.5
Cl^-	0.4402	0.04279	4.0
Cl^-	0.5156	0.04276	3.7
Cl^-	0.6868	0.04272	3.0
OTs^-	...	0.08897	29.4
OTs^-	0.05367	0.04548	23.4
OTs^-	0.1068	0.04682	19.0
OTs^-	0.2279	0.04711	15.5
OTs^-	0.4011	0.04768	11.4
OTs^-	0.6335	0.02483	6.1

In the following discussion, a theory which is consistent with the salt effect on the rates for the mono- and dimethyl salts will be presented first. Following this discussion, a possible explanation for the absence of a similar effect for the trimethyl salts will be presented.

Table III. Values of k'_2 for Me_2NH_2Cl in the Presence of Et_4NCl at 35° in *t*-BuOH

Soln	$[Et_4NCl]$, M	$[Me_2NH_2Cl]$, M	$k'_2 \times 10^{-6}$, M^{-1} sec^{-1}	$k'_2(\eta/\eta_0) \times 10^{-6}$, M^{-1} sec^{-1}
1	...	0.08380	31.3	34.4
2	0.03095	0.08368	23.6	27.0
3	0.06401	0.08358	20.6	24.7
4	0.1296	0.08336	15.4	20.4
5	0.2645	0.08291	11.1	16.9
6	0.5541	0.08194	7.4	14.8

The rate reductions observed for the mono- and dimethylammonium salts can be explained adequately by two effects: (1) the increase in the viscosity of the solutions, and (2) the complexing of the methyl-substituted ammonium salt with the tetraethylammonium salt to form mixed aggregates which are less reactive than the uncomplexed methyl salt. Grunwald and Price[3] have shown that a similar explanation accounts for the decrease in the rate of proton exchange between monomethylammonium acetate and solvent acetic acid when monomethylammonium chloride is added. Furthermore, Grunwald and co-workers have shown that the viscosity correction, η/η_0, compensates for the decreasing trend in the rate constant for exchange in solvents such as water or dry acetic acid.[2] In this correction, η and η_0 are the viscosity coefficients of the solution and pure solvent, respectively.

For dimethylammonium chloride, the viscosity correction, η/η_0, has been applied to the observed second-order rate constant k'_2 and the corrected rate constants are given in the fifth column of Table III. Clearly, the viscosity correction compensates only partially for the decrease in k'_2 caused by the addition of tetraethylammonium chloride. The remaining decrease may be attributed to the aggregate formation mentioned above.

A quantitative analysis of the effect of aggregate formation on the rate requires a knowledge of the values of the association constants for the various possible aggregates. First, let us consider a solution containing only one type of salt, *e.g.*, M^+X^-. In this solution aggregates such as M^+X^-, $(M^+X^-)_2$, ..., $(M^+X^-)_n$ may exist. Assuming the amount of dissociated ions to be negligible, the formation of these aggregates can be described by eq 4 and 5. Grunwald and Price[3] have derived eq[7] 6 and 7 by assuming $K_n = K_2^{n-1}$. In

$$2M^+X^- \overset{K_2}{\rightleftarrows} (M^+X^-)_2 \tag{4}$$

$$nM^+X^- \overset{K_n}{\rightleftarrows} (M^+X^-)_n \tag{5}$$

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(5) C. Parks and C. Anderson, *J. Am. Chem. Soc.*, **48**, 1508 (1926).

(6) L. de Forcrand, *Compt. Rend.*, **136**, 1034 (1903).

(7) It should be noted that the value of K_2 obtained in this manner is probably lower than the real value since the values of all the association constants are assumed to be approximately the same. For example, for the reaction given by the equation

$$M^+X^- + (M^+X^-)_{m-1} \overset{K'_m}{\rightleftarrows} (M^+X^-)_m$$

the value of K'_m is assumed to be approximately the same as K_2, the association constant for eq 4. Since K'_m is most likely smaller than K_2, the value of K_2 determined from this model is probably lower than the real value.

$$\Sigma m_i = \frac{m}{1 - K_2 m} \tag{6}$$

$$F = \frac{m}{(1 - K_2 m)^2} \tag{7}$$

these equations, m is the equilibrium concentration (molality) of the ion pair (M^+X^-), F is the molality of the salt determined from the weighed amount of salt added to the alcohol, and Σm_i is the sum of the molalities of all the species in solution. The value of Σm_i has been obtained from the freezing point lowering of *t*-butyl alcohol caused by the salt. These data as well as the value of K_2 calculated from eq 6 and 7 for dimethylammonium chloride, trimethylammonium chloride, and tetraethylammonium chloride will be presented later.

For solutions containing two salts, the situation is more complicated. In addition to aggregates such as $(M^+X^-)_n$ and $(N^+X^-)_m$, the solution may contain mixed aggregates such as $(M^+X^-)_n(N^+X^-)_m$. Thus, in addition to equilibria of the type shown in eq 5, one must consider equilibria of the type shown in eq 8.

$$(M^+X^-)_n + (N^+X^-)_m \overset{K_{ab}}{\rightleftharpoons} (M^+X^-)_n(N^+X^-)_m \tag{8}$$

By assuming that K_{ab} is the same regardless of the values of n and m, one can derive eq 9, 10, and 11 using an approach similar to that employed by Grunwald and Price[3] for a slightly simpler system.[8] In these

$$\Sigma m_i = \frac{m_a}{1 - K_{2a}m_a} + \frac{m_b}{1 - K_{2b}m_b} + \frac{K_{ab}m_a m_b}{(1 - K_{2a}m_a)(1 - K_{2b}m_b)} \tag{9}$$

$$F_a = \frac{m_a}{(1 + K_{2a}m_a)^2}\left(1 + \frac{K_{ab}m_b}{1 - K_{2b}m_b}\right) \tag{10}$$

$$F_b = \frac{m_b}{(1 - K_{2b}m_b)^2}\left(1 + \frac{K_{ab}m_a}{1 - K_{2a}m_a}\right) \tag{11}$$

equations, the subscripts a and b denote the two salts; K_{2a} is the association constant K_2 for salt a and is obtained from eq 6 and 7; K_{2b} is the analogous K_2 for salt b; and all of the other terms have been described earlier. From freezing point experiments on solutions containing only salt a or salt b, K_{2a} and K_{2b} can be obtained, and K_{ab} can be obtained from similar experiments on solutions containing both salts a and b.

Let us turn to the freezing point data. As a calibration, measurements were made of the freezing point lowering of *t*-butyl alcohol caused by solutes which do not associate, *i.e.*, naphthalene and toluene. A plot of this freezing point lowering as a function of the molality of these solutes is shown in Figure 1. This plot is linear up to about 0.3 m; above this concentration, it begins to curve downward slightly. Using the data from only the linear part of the plot, the molal freezing point constant calculated by least squares is 8.20. The reported values range from 8.20[9] to 8.37.[10] A value of 8.15 is calculated from the heat of fusion[11] using the van't Hoff equation.

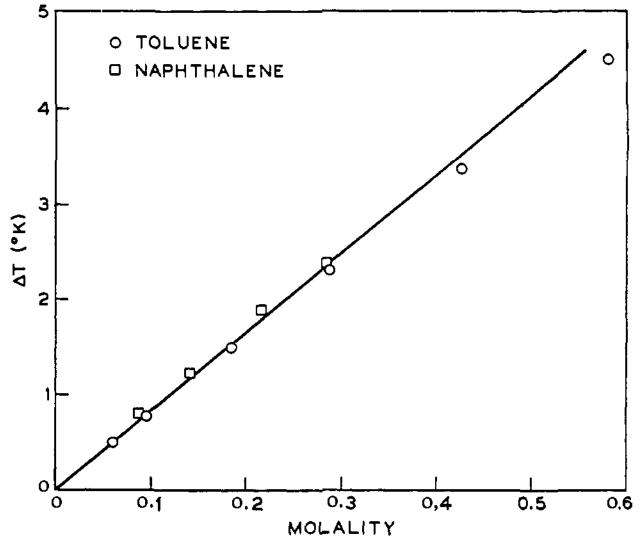

Figure 1. Freezing point lowering of *t*-butyl alcohol as a function of the molality of naphthalene and toluene.

The freezing point depression, ΔT, for solutions containing only one salt are listed in Table IV for Et_4NCl, Me_2NH_2Cl, and Me_3NHCl. The corresponding values of Σm_i which are included in this table were obtained from a large-scale plot of the data shown in Figure 1. Also listed in this table is the value of K_2 calculated from eq 6 and 7 for each salt solution. For each salt, K_2 is constant over the range of concentration studied. The maximum concentration employed was determined by the solubility of the salt. The average value of K_2 is 4.2, 1.7, and 0.88 for Et_4NCl, Me_2NH_2Cl, and Me_3NHCl, respectively.

Table IV. Freezing Point Depression Data and the Average Association Constant, K_2, for Et_4NCl, Me_2NH_2Cl, and Me_3NHCl in *t*-Butyl Alcohol

Salt	F, m	ΔT, °C	Σm_i	K_2, m	K_{di},[a] m
Et_4NCl	0.1125	0.69	0.083	4.2	10
Et_4NCl	0.1669	0.92	0.110	4.7	20
Et_4NCl	0.2189	1.13	0.136	4.5	31
Et_4NCl	0.2790	1.38	0.166	4.1	41
Et_4NCl	0.3411	1.60	0.192	4.0	81
Et_4NCl	0.4075	1.88	0.226	3.6	92
Me_2NH_2Cl	0.07471	0.56	0.067	1.7	2.2
Me_2NH_2Cl	0.09197	0.69	0.0825	1.4	1.8
Me_2NH_2Cl	0.1200	0.85	0.102	1.7	2.5
Me_2NH_2Cl	0.1506	1.02	0.122	1.9	3.3
Me_2NH_2Cl	0.1979	1.29	0.155	1.8	3.6
Me_3NHCl	0.09371	0.72	0.086	1.0	1.3
Me_3NHCl	0.1401	1.06	0.127	0.81	1.0
Me_3NHCl	0.2106	1.52	0.183	0.83	1.1

[a] Assuming formation of dimers only.

For comparison, in Table IV are listed the values for the association constant K_{di}, calculated from the data assuming the existence of only the ion pair and the double ion pair (dimer) in solution. As can be seen from the sharp increase in the value of K_{di} as the concentration is increased, this model cannot fit the data

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[8] Grunwald and Price[3] dealt with equilibria of the type $(M^+X^-) + (M^+Y^-)_m \rightleftharpoons (M^+X^-)(M^+Y^-)_m$.

[9] G. Parks, G. Warren, and E. Greene, *J. Am. Chem. Soc.*, **57**, 616 (1935).

[10] F. Getman, *ibid.*, **62**, 2179 (1940).

[11] C. Parks and C. Anderson, *ibid.*, **48**, 1508 (1926).

for Et_4NCl. For the other two salts, the precision in K_2 is not much better than that for K_{di}, and, because of the magnitude of K_2 for each of these salts, concentrations which exceed their solubility are necessary to distinguish between the two models. However, in view of the results for Et_4NCl, it seems appropriate to reject the dimer model for Me_2NH_2Cl and Me_3NHCl, also.

The freezing point depression ΔT, along with Σm_i for solutions containing Et_4NCl plus Me_2NH_2Cl or Et_4NCl plus Me_3NHCl, is given in Table V. That mixed aggregates exist in these solutions can be seen by comparing the value of Σm_i for these solutions with the value expected if mixed aggregates were not formed. In Table VI, the salt concentrations, Σm_i, $(\Sigma m_i)_{Me}$, and $(\Sigma m_i)_{Et}$, are listed for Me_2NH_2Cl plus Et_4NCl solutions. $(\Sigma m_i)_{Me}$ and $(\Sigma m_i)_{Et}$ are the contributions to Σm_i made by Me_2NH_2Cl and Et_4NCl, respectively, if no mixed aggregates are formed. They were obtained from plots of the data given in Table IV. In Table VI, the fact that $[(\Sigma m_i)_{Me} + (\Sigma m_i)_{Et}] > \Sigma m_i$ indicates the formation of mixed aggregates.

Table V. Freezing Point Depression, ΔT, and Average Association Constant, K_{ab}, for the Formation of Mixed Aggregates in *t*-BuOH

Salt a	F_a, m	F_b $[Et_4NCl]$, m	ΔT, °C	Σm_1	K_{ab}, m
Me_2NH_2Cl	0.1274	0.1419	1.32	0.158	59
Me_2NH_2Cl	0.1302	0.1867	1.50	0.180	56
Me_2NH_2Cl	0.1187	0.2246	1.60	0.192	51
Me_2NH_2Cl	0.1263	0.2950	1.90	0.228	35
Me_2NH_2Cl	0.1647	0.1635	1.60	0.192	46
Me_3NHCl	0.1396	0.1356	1.53	0.184	15
Me_3NHCl	0.1467	0.1941	1.80	0.217	11
Me_3NHCl	0.1419	0.2059	1.83	0.220	11
Me_3NHCl	0.1438	0.2588	2.03	0.244	10

Table VI. Values of Σm_i, $(\Sigma m_i)_{Me}$, and $(\Sigma m_i)_{Et}$ at Various Salt Concentrations

$[Me_2NH_2Cl]$, m	$[Et_4NCl]$, m	Σm_i	$(\Sigma m_i)_{Me}$[a]	$(\Sigma m_i)_{Et}$[a]
0.1274	0.1419	0.158	0.106	0.097
0.1302	0.1867	0.180	0.108	0.120
0.1187	0.2246	0.192	0.100	0.139
0.1263	0.2950	0.228	0.105	0.172
0.1647	0.1635	0.192	0.132	0.108

[a] Obtained from plots of data given in Table IV.

The average association constant K_{ab} for the formation of mixed aggregates is listed for various salt concentrations in Table V. These values were calculated from eq 9, 10, and 11 using the K_2 value listed for each salt in Table IV. The fairly constant value of K_{ab} obtained for both Me_2NH_2Cl and Me_3NHCl indicates that the proposed mixed aggregate model probably applies for these salts. The average K_{ab} for Me_2NH_2Cl plus Et_4NCl and for Me_3NHCl plus Et_4NCl is 49 and 12, respectively.

Returning to the kinetic data for Me_2NH_2Cl, it has been shown that the increase in viscosity only partially compensates for the decrease in k'_2 caused by addition of Et_4NCl. From the freezing point data, it is clear that mixed aggregates exist in these solutions. Thus, the residual decrease in k'_2 must be due to the complexing of Me_2NH_2Cl with Et_4NCl. For the solutions listed in Table III, the fraction, α, of Me_2NH_2Cl which is not complexed with Et_4NCl was calculated from eq 12 and 13 by successive approximation. In these equations, the subscripts a and b denote Me_2NH_2Cl and Et_4NCl, respectively; the other terms have been defined earlier.

$$\alpha(1 + K_{2a}F_a\alpha) = \frac{1 - K_{2b}m_b}{1 + m_b(K_{ab} - K_{2b})} \qquad (12)$$

$$1 + K_{ab}F_a\alpha = \frac{F_b(1 + K_{2b}m_b)^2}{m_b} \qquad (13)$$

This α is the fraction of F_a which is not complexed with Et_4NCl and, therefore, includes not only the ion pair (Me_2NH_2Cl) but also aggregates such as $(Me_2NH_2Cl)_2$, $(Me_2NH_2Cl)_3$, . . . $(Me_2NH_2Cl)_n$.

Using the values of α obtained in this manner, αk_0, the contribution to the observed rate made by Me_2NH_2Cl not complexed with Et_4NCl, was calculated; k_0 is related by eq 14 to the rate constant, k'_2, for solutions containing no Et_4NCl. In this equation, η/η_0 corrects for the viscosity change, and α^{-1} corrects for the decrease in the concentration of the Me_2NH_2Cl due to the formation of aggregates such as $(Me_2NH_2Cl)_n$.

$$k_0 = \alpha^{-1}k'_2\eta/\eta_0 \qquad (14)$$

The k_0 obtained from eq 14 is an average rate constant for the reaction of all the $(Me_2NH_2Cl)_n$ species in solution.[12]

The values of αk_0 at various salt concentrations are given in column 3 of Table VII. If exchange by the complexed Me_2NH_2Cl were negligible compared with that for the uncomplexed Me_2NH_2Cl, the values given in column 3 would be identical with those in column 2. Clearly, they are not, and the fact that they decrease more rapidly than the values in column 2 indicates that the exchange involving the Me_2NH_2Cl which is complexed with Et_4NCl is not negligible. The difference, Δ, between the values in these two columns is the contribution to the rate made by the complexed Me_2NH_2Cl. The values of k', calculated according to eq 3, are given in the fifth column, and the fact that they are all the same (except for the first one) indicates that the mixed aggregate theory is consistent with the experimental data. The values of k_0 and k' are 4.0×10^7 and 1.3×10^7, respectively. This k' is an average rate constant for reaction involving all of the various mixed aggregates.

As indicated by Table II, monomethylammonium chloride and *p*-toluenesulfonate exhibit salt effects similar to that for dimethylammonium chloride. These salts were not sufficiently soluble to perform the freezing point experiments accurately; as a result, a similar

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[12] Since Me_2NH_2Cl forms aggregates of the type $(Me_2NH_2Cl)_n$, one would expect the rate constant, k'_2, to change as the concentration is changed. The fact that no change occurs[1] indicates that the larger aggregates are reacting about as fast as the ion pair. Thus, k_0 is an average rate constant for the reaction of all the $(Me_2NH_2Cl)_n$ species in solution. However, even after accepting this conclusion, one might expect the value of k'_2 to decrease as the concentration F of Me_2NH_2Cl is increased because $\Sigma m_i/F$ decreases. One reason this concentration effect is not observed is that the change is smaller than the experimental error; the value $\Sigma m_i/F$ decreases by 8% in going from the most dilute to the most concentrated solution, whereas the precision in k'_2 is about ±15%. Another reason may be that $(Me_2NH_2Cl)_n$ reacts n times as fast as Me_2NH_2Cl.

Table VII. Observed and Calculated Rate Constants for Me_2NH_2Cl in the Presence of Et_4NCl

Soln[a]	$10^{-6}\cdot k'_2\eta/\eta_0$	$10^{-6}\cdot \alpha k_0$[b]	$10^{-6}\cdot \Delta$[c]	$10^{-6}k'$
1	34.4[d]	34.4[d]	...	...
2	27.0	24.9	2.1	5.6
3	24.7	17.4	7.3	13.0
4	20.4	9.90	10.2	13.5
5	16.9	5.27	11.6	13.4
6	14.8	2.95	11.9	12.7

[a] For the salt concentrations and the values of k'_2 see Table III. [b] $k_0 = \alpha^{-1}k'_2\eta/\eta_0$; k'_2 is obtained from the solution containing no Et_4NCl; $k'_2 = 3.13 \times 10^7\ M^{-1}\ sec^{-1}$. [c] $\Delta = k'_2\eta/\eta_0 - k_0\alpha$. [d] No Et_4NCl present.

analysis could not be performed on them. However, it seems likely that their salt effects can be explained by the same theory.

As shown in Table I, the value of k'_2 for trimethylammonium salts does not decrease significantly when tetraethylammonium salts are added. The freezing point data given in Table V for trimethylammonium chloride clearly indicate that this salt is complexing with tetraethylammonium chloride. Therefore, one may conclude that the complexed and uncomplexed trimethylammonium chloride undergo proton exchange at about the same rate.

The fact that added Et_4NCl does not affect the value of k'_2 for Me_3NHCl and decreases it for Me_2NH_2Cl is not unreasonable. Since the sole NH proton of Me_3NHCl is already strongly interacting with the chloride ion,[1] complexing with Et_4NCl need not affect significantly the reactivity of this proton. On the other hand, in addition to an NH proton hydrogen bonded to the anion, Me_2NH_2Cl has one which is hydrogen bonded to solvent and is much more reactive.[1] Consequently, complexing with Et_4NCl can reduce the reactivity of this "free" NH proton.

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The Crystal and Molecular Structure of 1-Methyl-6-[5-(1-methyl-1H-1-pyrindinyl)]-1-azoniaindan Iodide

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Abstract: The crystal structure of an unknown material has been solved by the heavy-atom method using three-dimensional X-ray diffraction data. The compound consists of 1-methyl-1H-1-pyrindine and 1-methyl-1-azoniaindan iodide groups joined by their respective 5- and 6-positions. Location of the two nitrogen atoms within the carbon skeleton was not possible using limited Cu data. This difficulty was subsequently resolved with a larger set of Mo data. Structural parameters, including those describing thermal anisotropy, were refined by the technique of least squares. The 1,5-disubstituted 1H-1-pyrindine half of the molecule is iso-π-electronic with azulene. Bond lengths, angles, and planarity are in agreement with postulated aromatic character for such a moiety. The structure is layered with the organic residues forming well-defined rectangular "rods" parallel to *a*. The iodide ions are located in spaces between the "rods."

Demonstrations of aromatic character in azulene[2] have stimulated study of similar iso-π-electronic structures in which heteroatoms have replaced one or more carbon atoms. These compounds can be classified as either (1) π-equivalent, in which one or more heteroatoms (=X–; X = N, S^+, O^+) replace an equal number of carbon atoms (=C–) in the 5- and 7-rings or (2) π-excessive,[3] in which a heteroatom (–X–; X = NR, S, O) replaces an ethylenic group (–C=C–) in the 7-ring. Early examples of the π-excessive heterocycles were either highly substituted, fused to other benzenoid nuclei, or both, and as such were too complex to permit significant comparisons with the azulenes. Only very recently have certain of the parent heterocycles been synthesized (cyclopenta[*c*]thiapyran,[4,5] cyclopenta[*b*]thiapyran[6]).

The compound 5H- and 7H-pyrindine (**1**; these two isomers are probably in tautomeric equilibrium), first prepared by Robison,[7] provides a ready entry (see Figure 1) into the 1H-1-pyrindine system. Anderson, *et al.*,[4] had even postulated that the slight orange color of **1** was due to the presence of a small amount of a

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(2) A review of azulene aromaticity is given by E. Heilbronner, "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter V.

(3) The terms "π-equivalent" and "π-excessive"[4] are used to denote relative numbers of π-electrons and ring atoms. Examples of π-equivalent and π-excessive derivatives of benzene are pyridine and pyrrole, respectively.

(4) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson, and A. G. Osborne, *J. Am. Chem. Soc.*, **81**, 1255 (1959).

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(6) R. Mayer, J. Franke, V. Horák, I. Hanker, and R. Zahradník, *Tetrahedron Letters*, 289 (1961).

(7) M. M. Robison, *J. Am. Chem. Soc.*, **80**, 6255 (1958).