Kinetics of Ion-Pair Exchange in Acetic Acid. I. Rate Constants Deduced from Proton Exchange of Anilinium Salts[1a]

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Abstract: A kinetic analysis is made of proton exchange between p-toluidinium p-toluenesulfonate (BHTs, 0.03–0.05 M) and acetic acid in the presence of p-toluenesulfonic acid (10^{-4} to 0.1 M). The solvent is anhydrous acetic acid, where the substrate exists largely in the form of ion pairs ($\mathrm{BH^+Ts^-}$). A reaction mechanism proposed previously[4] is substantiated: $\mathrm{BH^+Ts^-}$ is converted to $\mathrm{BH^+Ac^-}$, which then undergoes proton exchange. One of two processes by which the conversion to $\mathrm{BH^+Ac^-}$ takes place is ion-pair exchange: $\mathit{BH}^+\mathrm{Ts}^- + \mathrm{BH^+Ac^-} \rightarrow \mathit{BH}^+\mathrm{Ac}^- + \mathrm{BH^+Ts^-}$, for which the second-order rate constant, k, can be evaluated by kinetic analysis. Thus k is found to be 8.2×10^8 sec^{-1} M^{-1} at 30° for p-toluidinium p-toluenesulfonate, while values of k for *tert*-anilinium p-toluenesulfonates are only about 6×10^7 sec^{-1} M^{-1}. The large increase in k when $\mathrm{BH^+}$ has more than one NH proton suggests that ion-pair exchange is facilitated by the formation of a cyclic hydrogen-bonded ion quartet as reaction intermediate.

One of the important fast reactions of electrolytes in solvents of low dielectric constant is ion-pair exchange or metathesis. Such reactions are fast enough

$$\mathrm{A^+B^-} + \mathrm{C^+D^-} \rightleftharpoons \mathrm{A^+D^-} + \mathrm{C^+B^-}$$

to affect the fate of short-lived ion-pair intermediates in organic reactions and have been invoked, for example, to explain the special salt effect in solvolysis.[2,3] In that case, it could be shown that ion-pair exchange proceeds with second-order kinetics (first order with respect to each ion-pair reactant),[3] but it was not possible to derive absolute values for the rate constants.

Ion-pair exchange has also been invoked to explain the kinetics of proton exchange between N,N-dialkylanilinium p-toluenesulfonate ion pairs ($\mathrm{BH^+Ts^-}$) and acetic acid molecules in the presence of p-toluenesulfonic acid in glacial acetic acid.[4] The $\mathrm{BH^+Ts^-}$ ion pairs do not undergo proton exchange directly; they are converted to $\mathrm{BH^+Ac^-}$ ion pairs, which then undergo proton exchange with a high rate constant. The conversion of $\mathrm{BH^+Ts^-}$ to $\mathrm{BH^+Ac^-}$ takes place by acid–base reaction (1) in parallel with ion-pair exchange (2); the proton exchange of $\mathrm{BH^+Ac^-}$ with acetic acid is a first-order process (whose mechanism will be discussed later) that may be represented formally by (3). Under

$$\mathit{BH}^+\mathrm{Ts}^- + \mathrm{HAc} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathit{BH}^+\mathrm{Ac}^- + \mathrm{HTs} \qquad (1)$$

$$\mathit{BH}^+\mathrm{Ts}^- + \mathrm{BH^+Ac^-} \underset{k}{\overset{k}{\rightleftharpoons}} \mathit{BH}^+\mathrm{Ac}^- + \mathrm{BH^+Ts^-} \qquad (2)$$

$$\mathit{BH}^+\mathrm{Ac}^- + \mathrm{HAc} \xrightarrow{k_e} \mathrm{BH^+Ac^-} + \mathit{H}\mathrm{Ac} \qquad (3)$$

$$\mathit{B}\mathrm{H^+Ac^-} + \mathrm{HTs} \xrightarrow{k_-} \mathit{B}\mathrm{H^+Ts^-} + \mathrm{HAc} \qquad (4)$$

$$\mathit{B}\mathrm{H^+Ac^-} + \mathrm{BH^+Ts^-} \xrightarrow{k} \mathit{B}\mathrm{H^+Ts^-} + \mathrm{BH^+Ac^-} \qquad (5)$$

the experimental conditions, the ratio $[\mathrm{BH^+Ac^-}]/[\mathrm{BH^+Ts^-}]$ is very small, and $\mathrm{BH^+Ac^-}$ may be treated kinetically as a metastable intermediate. By a combination of kinetic and equilibrium measurements, it is then possible to derive absolute values for all rate constants in eq 1–5.

The following rate constants were thus obtained[4] for ion-pair exchange (2) in acetic acid at 26°: when $\mathrm{BH^+} = (\mathrm{C_2H_5})_2\mathrm{NHC_6H_5}^+$, $k = 6.5 \times 10^7$ sec^{-1} M^{-1}; when $\mathrm{BH^+} = (n\text{-}\mathrm{C_3H_7})_2\mathrm{NHC_6H_5}^+$, $k = 5.0 \times 10^7$ sec^{-1} M^{-1}. These values were of a plausible magnitude, representing a reactivity similar to that commonly found for cation transfer and electron transfer of aromatic radical anion–alkali metal ion pairs in aprotic solvents.[5] However, there remained some doubt[4] whether the rate law based on eq 1–5 is uniquely *necessary* (instead of merely sufficient), because the rate of reaction 2 was under no conditions large compared to that of reaction 1.

We now report a further study of proton exchange in acetic acid which establishes the validity of the kinetic scheme shown in eq 1–5 with high probability. For our substrate we chose p-toluidinium p-toluenesulfonate, because we reasoned that kinetic measurements by proton magnetic resonance (pmr) methods would be more accurate for the salt of a primary than of a tertiary amine and could be extended over a wider range of concentrations. We also hoped that the rate constant for ion-pair exchange would be especially high if the cation has more than one NH proton. Ion quartets such as that shown in (6), with a cyclic array of the formal ionic charges, are almost certain to be intermediates in ion-pair exchange. Thus metathesis should be facilitated if the cations can form, and the anions can accept, two hydrogen bonds. Moreover, for the ion quartet shown in (6), molecular models show that the four ions can form a cyclic hydrogen-bonded structure with little angle strain.

As a matter of fact, we find that k for the process shown in (2) is 8.2×10^8 sec^{-1} M^{-1} when $\mathrm{BH^+}$ = p-

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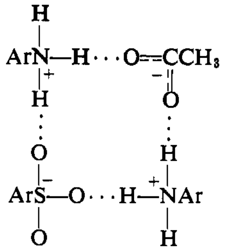

(6)

$CH_3C_6H_4NH_3^+$, *nearly 15 times greater* than the previously reported values[4] of k for the *N,N*-dialkylanilinium salts. On the other hand, the values we find for k_+, k_-, and k_e are consistent with previously reported rate constants for the processes shown in eq 1 and 3.

Experimental Section

Materials. Acetic acid was purified by partial freezing in an ice bath until approximately two-thirds of the material was frozen, and then discarding the mother liquor. This process was carried out three times and yielded a product containing *ca.* 0.004 *M* water (by Karl Fischer titration).

p-Toluenesulfonic acid monohydrate was recrystallized twice from chloroform and dried at 40° *in vacuo.* Nearly anhydrous solutions of the acid in acetic acid were prepared by adding slightly less than 1 equiv of acetic anhydride, taking care to avoid an excess of anhydride. The reaction between water and anhydride is catalyzed by strong acids.[6] Concentrations of *p*-toluenesulfonic acid in acetic acid were checked by titration with standard potassium acid phthalate.

p-Toluidinium *p*-toluenesulfonate was prepared by the addition to a solution of *p*-toluenesulfonic acid in water of an equimolar quantity of *p*-toluidine in methanol. The solid salt was recrystallized thrice from an acetone–benzene mixture, mp 199° (lit. mp 199–200°).[7] Titration of the salt dissolved in methanol with Karl Fischer reagent showed it to be water free.

p-Nitro-*N,N*-dimethylaniline was recrystallized from acetone–water to give yellow needles, mp 164.5°.

Uv-Visible Absorption Spectra. Optical densities were measured with a Beckman Model DU spectrophotometer using matched 1-cm silica cells. The cell compartment was thermostated at 30 ± 0.5°.

Proton Magnetic Resonance Measurements. Rates of NH–CO_2H proton exchange were measured between *p*-toluidinium *p*-toluenesulfonate (BH^+Ts^-) and acetic acid at 30.0°, using a pmr spectrometer operating at 56.4 MHz.[4]

In the initial qualitative experiments, pmr spectra of BH^+Ts^- (0.15 *M*) in acetic acid containing various concentrations of *p*-toluenesulfonic acid were recorded in slow passage. In a solution containing 0.08 *M* acid the amino protons gave a broad band about 2 ppm to high field of the carboxyl proton resonance. Increasing the acid concentration caused the amino-proton resonance to sharpen and shift slightly to higher field, the ^{14}N-H spin-spin interaction being averaged to zero by T^I relaxation of the ^{14}N nucleus. In the absence of acid, no separate band due to the amino protons was observable. These results indicated that proton exchange is fast in the absence of acid and slows down as the acid concentration is increased.

To determine the rates of NH-CO_2H proton exchange accurately, the relaxation times T_1 and T_2 of the carboxyl proton resonance (or of the collapsed CO_2H-NH proton resonance) were measured by pulsed pmr techniques.[8] The precision of these measurements was ±2% or better. Since the proton fraction of NH protons was small ($<10^{-2}$), the procedures previously described could be used.[4,8] For the pure solvent it was found consistently that $1/T_2 = 1.07/T_1$. The exchange broadening, Δ, in the presence of BH^+Ts^- was therefore calculated as $\Delta = 1/T_2 - 1.07/T_1$. Solutions of *p*-toluenesulfonic acid in acetic acid caused a small increase in $1/T_1$ and $1/T_2$; however, their ratio (1.07) was unchanged. This indicates that proton exchange between acetic acid and *p*-toluenesulfonic acid is very fast under these conditions.

Rates of proton exchange, R, were calculated from the exchange broadening Δ on the basis of eq 7 and 8.[4] In eq 7, the mean residence time of a proton on an NH site during one cycle of exchange,

$$\Delta/p_{NH} = \delta^2\tau/(1 + \delta^2\tau^2) \qquad (7)$$

$$1/\tau = R/3[BH^+Ts^-] \qquad (8)$$

τ, is calculated from Δ, the proton fraction p_{NH}, and the NH-to-CO_2H chemical shift δ. Equation 7 contains the assumption that ^{14}N-H spin-spin interaction in BH^+ is effectively averaged to zero by T^I relaxation, in agreement with observation; p_{NH} was calculated with respect to all NH + OH protons because OH-proton exchange between HAc and HTs is very fast. Equation 8 relates τ to R; $[BH^+Ts^-]$ denotes the molar concentration of BH^+Ts^-, and the factor 3 accounts for three NH protons per *p*-toluidinium ion. (Brackets will be used throughout this paper to denote molar concentrations.) The NH-to-CO_2H proton chemical shift was obtained from the maximum exchange broadening: $\delta = 2(\Delta/p_{NH})_{max}$. Results were: $[BH^+Ts^-] = 0.05$ *M*, $\delta = 2.26$ ppm; $[BH^+Ts^-] = 0.03$ *M*, $\delta = 2.28$ ppm.

Solutions for each series of pmr measurements were made up from separate stock solutions of pure BH^+Ts^- and nearly anhydrous HTs in pure acetic acid by standard quantitative techniques. Two series of pmr measurements were made. In the first series, $[BH^+Ts^-]$ was constant at 0.0500 *M* and [HTs] was varied from 0.123 to 1.26×10^{-4} *M* in 19 steps. In the second series, $[BH^+Ts^-]$ was constant at 0.0294 *M* and [HTs] was varied from 0.122 to 8.2×10^{-5} *M* in 18 steps.

***p*-Toluenesulfonic Acid Concentrations in the Reaction Mixtures.** HTs concentrations below 0.001 *M* differ significantly from the concentrations of added HTs owing to acetolysis (eq 9 and 10). The

$$BH^+Ts^- + HAc \overset{K}{\rightleftharpoons} BH^+Ac^- + HTs \qquad (9)$$

$$K = [BH^+Ac^-][HTs]/[BH^+Ts^-] \qquad (10)$$

equilibrium constant, K, can be calculated at 26.7° from data for *p*-toluidinium *p*-toluenesulfonate in the literature[9] and is 2.21×10^{-7} *M* at 26.7°. It is expected that K will be slightly greater at 30°. An experimental estimate of K at 30° was obtained in the present study by dissolving pure BH^+Ts^- in pure acetic acid and finding the equilibrium concentration of HTs, using *p*-nitro-*N,N*-dimethylaniline as indicator (see below). The concentration of BH^+Ac^- could then be found from stoichiometry and K thus determined. The results gave $K = 2.32 \times 10^{-7}$ *M* at 30°, a value that will be used throughout this paper. However, this method of measurement is highly vulnerable to the presence of acidic or basic impurities, and the plausible relationship of our value at 30° to the literature value at 26.7° provides an agreeable check on the purity of our reagents. To allow for acetolysis (but neglecting the relatively small concentration of un-ionized B in equilibrium with BH^+Ac^-), the concentration of HTs in the reaction mixtures was then calculated from eq 11.

$$[HTs]_{equil} = [HTs]_{added} + K[BH^+Ts^-]/[HTs]_{equil} \qquad (11)$$

Because of the importance, for the kinetic analysis, of knowing the HTs concentrations accurately, the values calculated by eq 11 were checked by direct measurement with the indicator, *p*-nitro-*N,N*-dimethylaniline (N).[4,9] The indicator equilibrium is shown in (12). The basic form of the indicator is yellow in acetic acid (λ_{max}

$$N + HTs \rightleftharpoons NH^+Ts^- \qquad (12)$$

$$K_f^{N\cdot HTs} = [NH^+Ts^-]/[N][HTs] \qquad (13)$$

390 mμ, ϵ_{max} 18,300), while the protonated form has negligible absorbance at 390 mμ. The equilibrium constant, $K_f^{N\cdot HTs}$, was determined at 30° and found to be $(1.10 \pm 0.02) \times 10^3$ (M^{-1}).

To measure the actual HTs concentration of a solution, 0.100 ml of standard indicator (*ca.* 2×10^{-3} *M* in acetic acid) was added with a microsyringe to 5.00 ml of solution and the absorbance measured at 390 mμ, using as blank a second sample of solution without added indicator. The equilibrium concentration of HTs before addition of indicator (which uses up some HTs) can then be calculated. The results obtained in this way were in very good agreement with those based on eq 11.

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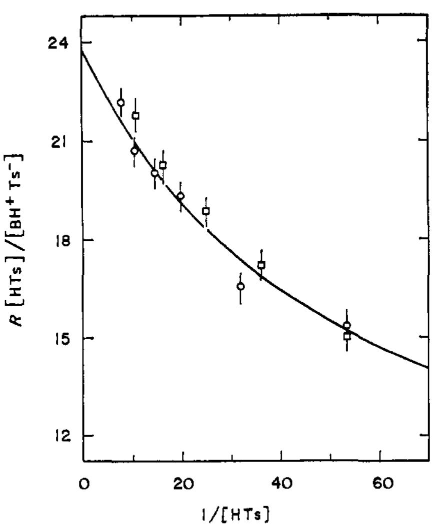

Figure 1. Proton exchange between p-toluidinium p-toluenesulfonate [BH$^+$Ts$^-$] and acetic acid at 30.0°, kinetic plot at high HTs concentrations: circles, [BH$^+$Ts$^-$] = 0.050 M; squares, [BH$^+$Ts$^-$] = 0.0294 M. The solid curve represents the final rate law for [BH$^+$Ts$^-$] = 0.050 M.

A brief study was made of the effect of water on the equilibrium concentrations of HTs. It was found that the equilibrium "constant" for reaction 14 tends to increase with the water concentration,

$$\mathrm{HTs} + \mathrm{H_2O} \rightleftarrows \mathrm{H_3O^+Ts^-} \tag{14}$$

being about 0.9 M^{-1} when [H$_2$O] = 0.2 M and about 2.0 M^{-1} when [H$_2$O] = 0.9 M. At low water concentrations such as those in the kinetic measurements, reaction 14 may be neglected.

Kinetic Analysis. It has been shown[4] that the reaction mechanism shown in eq 1-5 leads (under conditions where BH$^+$Ac$^-$ may be treated as a metastable intermediate) to the rate law given in eq 15. The rate constants k, k_e, and k_- are defined in (1-3), and

$$\frac{R}{[\mathrm{BH^+Ts^-}]} = \frac{k_eK}{[\mathrm{HTs}]}\frac{k[\mathrm{BH^+Ts^-}] + k_-[\mathrm{HTs}]}{(k_e + k[\mathrm{BH^+Ts^-}] + k_-[\mathrm{HTs}])} \tag{15}$$

K is defined in (10). Note that $K = k_+/k_-$. Since K is known (2.32×10^{-7} at 30°), eq 15 involves three unknowns, the rate constants, k, k_e, and k_-.

It is convenient to test eq 15 in three steps, as follows. (a) At high concentrations of HTs, R/[BH$^+$Ts$^-$] approaches k_eK/[HTs]. This permits evaluation of k_e. (b) At low concentrations of HTs R/[BH$^+$Ts$^-$] approaches k_eKk[BH$^+$Ts$^-$]/[HTs](k_e + k[BH$^+$Ts$^-$]). This permits evaluation of k. (c) Finally, k_- is obtained by fitting of the data at intermediate HTs concentrations and the rate law is tested over the entire concentration range.

High HTs Concentrations. When [HTs] > (k_e + k[BH$^+$Ts$^-$])/k_-, it is convenient to represent the rate law as a power-series expansion in 1/[HTs]. According to (16), the plot of [HTs]R/[BH$^+$Ts$^-$] $vs.$ 1/[HTs] at high [HTs] becomes linear and independent of [BH$^+$Ts$^-$].

$$\frac{R}{[\mathrm{BH^+Ts^-}]} = \frac{k_eK}{[\mathrm{HTs}]}\left(1 - \frac{k_e}{k_-[\mathrm{HTs}]} + \frac{k_e(k_e + k[\mathrm{BH^+Ts^-}])}{k_-^2[\mathrm{HTs}]^2} + \cdots\right) \tag{16}$$

The intercept is k_eK. Our experimental data for [HTs] > 0.015 M are plotted in Figure 1. (The solid curve represents the final rate law for [BH$^+$Ts$^-$] = 0.05 M.) The data conform to the expected limiting relationship with negative slope, and the intercept, k_eK, is defined with a precision of 2%. On introducing the experimental value of K, we obtained k_e. Results are summarized in Table I.

Low HTs Concentrations. When [HTs] < k[BH$^+$Ts$^-$]/k_-, it is convenient to represent the rate law (15) as a power-series expansion in [HTs]. We define a parameter g according to (17) and write the power-series expansion as in (18). According to (18), the plot of [HTs]R/[BH$^+$Ts] $vs.$ [HTs] at low [HTs] becomes linear, with positive slope. Both intercept and slope vary with [BH$^+$Ts$^-$]. These predictions are consistent with the experimental data. Figure 2 shows a typical plot for [BH$^+$Ts$^-$] = 0.050 M. The intercept, k_eK/g, is defined with a precision of about 2%. On introducing the previously obtained value for k_e/K, we obtain g; and on introducing values for k_e and [BH$^+$Ts$^-$], we calculate k according to (17). Results are shown in Table I. The close agreement of values obtained for k at two different BH$^+$Ts$^-$ concentrations is strong evidence in support of the rate law.

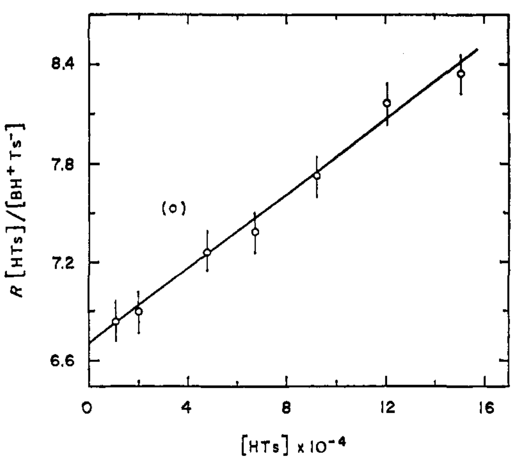

Figure 2. Proton exchange between 0.050 M p-toluidinium p-toluenesulfonate and acetic acid at 30.0°, kinetic plot at low HTs concentrations. The experimental point far from the straight line was rejected in the final calculations.

$$g = (k[\mathrm{BH^+Ts^-}] + k_e)/k[\mathrm{BH^+Ts^-}] \tag{17}$$

$$R\frac{[\mathrm{HTs}]}{[\mathrm{BH^+Ts^-}]} = \frac{k_eK}{g}\left\{1 + \frac{(g-1)k_-[\mathrm{HTs}]}{gk[\mathrm{BH^+Ts^-}]} - \frac{(g-1)}{g^2}\left(\frac{k_-[\mathrm{HTs}]}{k[\mathrm{BH^+Ts^-}]}\right)^2 + \cdots\right\} \tag{18}$$

Table I. Kinetic Summary of Proton Exchange between p-Toluidinium p-Toluenesulfonate and Acetic Acid at 30°

[BH$^+$Ts$^-$], M	0.0294	0.050
k_eK, sec^{-1} M[a]	24.3 ± 0.6	23.7 ± 0.6
k_e, sec^{-1} [b]	1.06×10^8	1.02×10^8
g[c]	5.3 ± 0.2	3.52 ± 0.10
k, sec^{-1} M^{-1}	$(8.4 \pm 0.4) \times 10^8$	$(8.1 \pm 0.3) \times 10^8$
k_-, sec^{-1} M^{-1}	$(7.2 \pm 1.5) \times 10^9$	$(7.8 \pm 1.5) \times 10^9$

[a] Intercept of plot of R[HTs]/[BH$^+$Ts$^-$] $vs.$ 1/[HTs]; see eq 16. [b] $K = 2.32 \times 10^{-7}$ M. [c] k_e/K divided by the intercept of the plot of R[HTs]/[BH$^+$Ts$^-$] $vs.$ [HTs]. See eq 17 and 18.

Fit of All Data. Given K, k_e, and k, the only parameter remaining unknown in (15) is k_-. This rate constant was calculated from the experimental rate of proton exchange at each HTs concentration (except at the very highest and lowest HTs concentrations where R is practically independent of k_-), and mean values for each BH$^+$Ts$^-$ concentration are listed in Table I. The agreement of the values is satisfactory.

Table II illustrates the fit of the kinetic data to eq 15. For the data shown, [HTs] varies by more than a 1000-fold, and $1/\tau$ varies by more than 300-fold. The standard error of fit of $1/\tau$ is 3.0%. The corresponding error of fit of Δ is 2.8%. This is the worst fit obtained in 13 kinetic series reported in this and the subsequent paper.[10] The mean error of fit for all series is about 2% and is easily consistent with the experimental precision. Thus there is little doubt that the rate law given in (15) is correct. In view of the

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[10] M. R. Crampton and E. Grunwald, *J. Amer. Chem. Soc.*, **93**, 2991 (1971).

Table II. Kinetic Data for Proton Exchange of 0.050 *M* BH^+Ts^- in Acetic Acid at 30.0°

[HTs]	$1/\tau$ Obsd	$1/\tau$ Calcd[a]
1.06×10^{-4}	21,500	21,500
2.0×10^{-4}	11,520	11,500
3.4×10^{-4}	7,390	6,900
4.75×10^{-4}	5,090	5,020
6.7×10^{-4}	3,660	3,640
9.2×10^{-4}	2,780	2,740
1.21×10^{-3}	2,230	2,150
1.51×10^{-3}	1,820	1,780
2.1×10^{-3}	1,355	1,350
3.9×10^{-3}	800	830
4.8×10^{-3}	720	713
9.0×10^{-3}	446	458
1.2×10^{-2}	363	374
1.87×10^{-2}	273	273
3.12×10^{-2}	176	186
5.0×10^{-2}	129	128
6.8×10^{-2}	98	99
9.27×10^{-2}	74	75
0.123	60	58

[a] Using rate constants given in Table I. $1/\tau$ defined in eq 8.

characteristic complexity of that rate law, it is then highly probable that the reaction mechanism of eq 1-5 is also correct.

Brief Discussion of Rate Constants. By confirming the reaction mechanism in eq 1-5, the present work reaffirms the validity of the previously reported[4] rate constants for proton exchange of *N*,*N*-dialkylanilinium salts in acetic acid. We now wish to compare the rate constants.

Rate constants for ion-pair exchange (eq 2) have already been discussed: k is much greater for *p*-toluidinium salts than for the tertiary anilinium salts, probably because of the greater number of NH protons. Ion quartets such as (6) with stable cyclic hydrogen-bonded structures, which are impossible of formation from *tert*-anilinium cations, appear to be reaction intermediates and to facilitate ion-pair exchange.

Rate constants for the reaction of BH^+Ac^- with HTs (eq 1 or 4) are very similar for the primary and tertiary anilinium acetates: $k_- \approx 10^{10}\ \mathrm{sec^{-1}}\ M^{-1}$ in each case. It is probable that reaction is diffusion controlled.

Regarding k_e (eq 3), there is good evidence that proton exchange of BH^+Ac^- with acetic acid takes place by the mechanism shown in (19), with $k_H << k_i$.[4,8] It then follows that $k_e = k_H/K_i$, where

$$\mathrm{B}H^+Ac^- \underset{k_i}{\overset{k_{-i}}{\rightleftharpoons}} \mathrm{B}\cdot HAc$$

$$\mathrm{HAc(solvent)} + \mathrm{B}\cdot HAc \xrightarrow{k_H} \mathrm{B\cdot HAc} + HAc\mathrm{(solvent)}$$

$$\mathrm{B\cdot HAc} \xrightarrow{k_i} \mathrm{BH^+Ac^-} \tag{19}$$

$K_i = k_i/k_{-i}$. In the present case, the equilibrium constant $K_i = 19.2$ for *p*-toluidine at 30°,[11] and $k_e = 1.04 \times 10^8\ \mathrm{sec^{-1}}$; hence $k_H = 2.0 \times 10^9\ \mathrm{sec^{-1}}$. In the earlier work on *N*,*N*-dialkylanilines, k_H was 1.3×10^9, 6.0×10^8, and $2.7 \times 10^8\ \mathrm{sec^{-1}}$, respectively, for N,N-$(CH_3)_2$, $(C_2H_5)_2$, and $(n\text{-}C_3H_7)_2$. Evidently, the introduction of *N*-alkyl groups on nitrogen causes k_H to decrease when acetic acid is the solvent, in close analogy to the behavior of k_H when water is the solvent.[12]

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Kinetics of Ion-Pair Exchange in Acetic Acid. II. Effect of the Cation on Reaction Rate[1a]

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Abstract: Rate and equilibrium constants have been measured for the ion-pair exchange reaction $BH^+Ts^- + M^+Ac^- \rightleftarrows BH^+Ac^- + M^+Ts^-$ (where BH^+ = *p*-toluidinium ion and Ts^- = *p*-toluenesulfonate ion) in acetic acid at 30°. The rate constants for forward reaction (k_{+M}) vary from 3.0×10^8 to $21 \times 10^8\ \mathrm{sec^{-1}}\ M^{-1}$, depending on M^+, while the equilibrium constants (K_M) vary from 0.58 to 2.75. Both constants vary with M^+ in the identical sequence: $Li^+ < Tl^+ < BH^+ < K^+ < Cs^+ < (n\text{-}C_4H_9)_4N^+$. On the other hand, the rate constants for reverse reaction (k_{-M}) are considerably less sensitive to the nature of M^+ and show no correlation with either k_{+M} or K_M. The results indicate that the binding of cation to anion is more sensitive to specific properties of the cation in acetate than in *p*-toluenesulfonate ion pairs and that, in acetate ion pairs, it increases with the strength of the cation as a Lewis acid.

In the preceding paper (part I)[2] we have shown that rate constants for ion-pair exchange (metathesis) of anilinium salts in acetic acid can be derived from rates of proton exchange. We now report equilibrium and rate constants for the ion-pair exchange of *p*-toluidinium *p*-toluenesulfonate (BH^+Ts^-) with a series of acetate salts (M^+Ac^-, eq 20; equations are numbered consecutively with those in part I).[3] The cations M^+ included in this study are Li^+, Tl^+, BH^+, K^+, Cs^+, and $(n\text{-}C_4H_9)_4N^+$. Equilibrium constants ($K_M = k_{+M}/k_{-M}$) were measured spectrophotometrically. All measurements were made in acetic acid at 30.0° at such concentrations that the electrolytic reactants existed largely in the form of ion pairs. As far as we know, this is the first kinetic study of ion-pair exchange for a wide variety of cations.

$$\mathrm{BH^+Ts^-} + \mathrm{M^+Ac^-} \underset{k_{-M}}{\overset{k_{+M}}{\rightleftharpoons}} \mathrm{BH^+Ac^-} + \mathrm{M^+Ts^-} \tag{20}$$

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[2] M. R. Crampton and E. Grunwald, *J. Amer. Chem. Soc.*, **93**, 2987 (1971).

[3] Equations will be numbered beginning with eq 20 to facilitate reference to eq 1-19 in part I.