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

[HTs]	$1/\tau$	
	Obsd	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: $k_- \approx 10^{10}$ 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

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

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

$$B\cdot \text{HAc} \xrightarrow{k_i} BH^+Ac^- \qquad (19)$$

$K_i = k_i/k_{-i}$. In the present case, the equilibrium constant $K_i = 19.2$ for *p*-toluidine at 30°,[11] and $k_e = 1.04 \times 10^8$ sec^{-1}; hence $k_H = 2.0 \times 10^9$ sec^{-1}. In the earlier work on *N,N*-dialkylanilines, k_H was 1.3×10^9, 6.0×10^8, and 2.7×10^8 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]

---

[11] G. W. Ceska and E. Grunwald, *J. Amer. Chem. Soc.*, **89**, 1371 (1967).

[12] E. Grunwald and E. K. Ralph, *ibid.*, **89**, 4405 (1967).

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

M. R. Crampton[1b] and Ernest Grunwald*

Contribution from the Department of Chemistry,
Brandeis University, Waltham, Massachussetts 02154.

Received August 15, 1970

Abstract: Rate and equilibrium constants have been measured for the ion-pair exchange reaction $BH^+Ts^- + M^+Ac^- \rightleftharpoons BH^+Ac^- + M^+Ts^-$ (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 21×10^8 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.

$$BH^+Ts^- + M^+Ac^- \underset{k_{-M}}{\overset{k_{+M}}{\rightleftharpoons}} BH^+Ac^- + M^+Ts^- \qquad (20)$$

---

[1] (a) Support of this work by the National Science Foundation (under Grant GP 7381X) is gratefully acknowledged. (b) On leave from Durham University, England.

[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.

We find that, although k_{+M} is high (3×10^8 to 2×10^9 sec^{-1} M^{-1}), k_{+M} is quite sensitive to the nature of M^+ and tends to increase as the interaction of M^+ with Ac^- decreases. The values of k_{+M} increase monotonically with those of the equilibrium constant K_M. On the other hand, the values of k_{-M} are relatively insensitive to the nature of M^+. We infer from these facts that the cation–anion interaction is substantially stronger in the M^+Ac^- than in the M^+Ts^- ion pairs. Probable reasons are that acetate ion is a stronger base than *p*-toluenesulfonate ion and that, owing to resonance, the electrical charge of the carboxylate group is polarized more easily.

Experimental Section

Experimental methods described in part I[2] were used also in the present work. We shall give here only the additional experiments and facts.

Materials. Lithium *p*-toluenesulfonate was prepared by the method of Winstein, Klinedinst, and Robinson.[4] To a solution of lithium carbonate (0.35 mol) in acetic acid was added *p*-toluenesulfonic acid monohydrate (0.70 mol) and acetic anhydride (1.0 mol). The mixture was refluxed for 6 hr and left to crystallize. The solid which separated was recrystallized four times from acetic acid and dried *in vacuo* at 60°.

Potassium *p*-toluenesulfonate and cesium *p*-toluenesulfonate were prepared by mixing equivalent quantities of *p*-toluenesulfonic acid monohydrate and potassium or cesium acetate dissolved in methanol. The salts were recrystallized thrice from methanol and dried *in vacuo* at 80°.

Thallous *p*-Toluenesulfonate. To a solution of thallous acetate (Alfa Inorganics, ultrapure) in acetic acid was added a solution of *p*-toluenesulfonic acid monohydrate. The product was recrystallized thrice from acetic acid and dried at 60° *in vacuo*.

The proton nmr spectra of the *p*-toluenesulfonate salts dissolved in dimethyl sulfoxide showed the expected bands and indicated that these salts were free of solvent of crystallization. All salts were stored *in vacuo*.

Cesium acetate was prepared by the addition of cesium carbonate to a slight excess of acetic acid. The solid which separated was recrystallized from acetone–methanol and dried *in vacuo*.

Tetra-*n*-butylammonium acetate was prepared as the acetic acid solvate by the method of Smith.[5] To a solution of tetra-*n*-butylammonium iodide (0.15 mol) in ethanol (200 ml) was added freshly precipitated silver oxide (0.15 mol) and the mixture was stirred for 2 hr, when a test for iodide ion in the supernatant liquid proved negative. The mixture was filtered and centrifuged to remove silver iodide and unreacted silver oxide. Acetic acid (0.3 mol) was added to the solution and the ethanol was removed by distillation. The resulting solid was recrystallized thrice from ethyl acetate containing a few drops of acetic acid and dried *in vacuo* for 1 hr, mp 117° (lit.[5] mp 117–118°). Titration with standard perchloric acid in acetic acid gave an equivalent weight of 366 ± 1 (calcd for $(n\text{-}C_4H_9)_4NAc \cdot HAc$, 361).

Tetra-*n*-butylammonium *p*-toluenesulfonate was prepared as a solution in acetic acid. To a solution of the acetate salt was added an anhydrous solution of *p*-toluenesulfonic acid. The equivalence point was determined by taking small samples, diluting with acetic acid, and adding *p*-nitro-*N*,*N*-dimethylaniline[2] until the indicator showed a small residual concentration (*ca.* 10^{-4} *M*) of *p*-toluenesulfonic acid.

***p*-Dimethylaminoazobenzene** (butter yellow) was a sample recrystallized by Dr. G. W. Ceska, mp 117°.

Proton Magnetic Resonance Measurements

The procedure was similar to that described in part I. The exchange broadening Δ was taken as $1/T_2 - 1.07/T_1$. Rates of exchange were calculated using eq 7 and 8 in part I. High concentrations of *p*-toluenesulfonate salts affected the T_1/T_2 ratio slightly (Table I), but at the salt concentrations used in this work (*ca.* 0.05 *M*) the effect was very small.

Table I. T_1/T_2 Ratio of OH Protons in Acetic Acid at 30°

Solute	$1/T_1$, sec^{-1}	T_1/T_2
	0.310	1.07
HTs, 0.12 *M*	0.334	1.08
HTs, 0.24 *M*	0.364	1.07
LiTs, 0.09 *M*	0.325	1.09
$(n\text{-}C_4H_9)_4NTs$, 0.07 *M*	0.332	1.12
$(n\text{-}C_4H_9)_4NTs$, 0.28 *M*	0.390	1.18

***p*-Toluenesulfonic Acid Concentrations.** Concentrations of HTs in the reaction mixtures were determined by two independent methods, as described in part I (eq 9–13). However, it was found that in the measurements with *p*-nitro-*N*,*N*-dimethylaniline (N), the value of the equilibrium constant $K_f^{N \cdot HTs}$ (eq 13) depended on the concentration of some, but not all, *p*-toluenesulfonate salts. Experimental results are summarized in Table II. In all measurements on reaction mixtures, an equilibrium constant appropriate for the given salt composition was used.

Table II. Salt Effects on $K_f^{N \cdot HTs}$ (Defined in Equation 13, Part I) for *p*-Nitro-*N*,*N*-dimethylaniline in Acetic Acid at 30°

$[BH^+Ts^-]$, *M*	Other salt, *M*	$10^{-3}K_f^{N \cdot HTs}$ M^{-1}
		1.10
0.03		1.12
0.05		1.12
	$(n\text{-}C_4H_9)_4NTs$, 0.07	0.915
	$(n\text{-}C_4H_9)_4NTs$, 0.11	0.80
0.05	$(n\text{-}C_4H_9)_4NTs$, 0.017	1.10
0.05	$(n\text{-}C_4H_9)_4NTs$, 0.028	1.075
0.05	$(n\text{-}C_4H_9)_4NTs$, 0.07	1.00
	KTs, 0.10	1.10
0.05	KTs, 0.031	1.13
0.05	KTs, 0.050	1.12
0.05	KTs, 0.075	1.14
	LiTs, 0.048	1.20
0.05	LiTs, 0.030	1.18
0.05	LiTs, 0.052	1.20
	CsTs, 0.065	1.07
0.05	CsTs, 0.04	1.08
	TlTs, 0.033	1.17
0.05	TlTs, 0.037	1.16

Direct Measurement of K_M. The equilibrium constant K_M for reaction 20 is given in (21) and was found to vary considerably with the nature of the cation M^+.

$$K_M = [M^+Ts^-][BH^+Ac^-]/[BH^+Ts^-][M^+Ac^-] \quad (21)$$

To assure the accuracy of the results, K_M was measured for each M^+ by a direct spectrophotometric method as well as by an alternative indirect method.

The direct method makes use of the fact that *p*-toluidinium acetate (BH^+Ac^-) is always in equilibrium with un-ionized *p*-toluidine (B). The concentration of the latter in the equilibrium mixtures can be measured by its strong optical absorption between 280 and 290 mμ, where the other solute species absorb only weakly. The molar extinction coefficient of *p*-toluidine in acetic acid was determined by the method of Ceska and Grunwald:[6] it was assumed that in a series of hy-

---

[4] S. Winstein, P. F. Klinedinst, Jr., and G. C. Robinson, *J. Amer. Chem. Soc.*, **83**, 895 (1961).

[5] Stanley Smith, private communication (April 1, 1968). We are grateful to Professor Smith for sending us helpful instructions.

droxylic solvents, $\epsilon_{\max}$ for the first uv absorption band of *p*-toluidine varies linearly with $\lambda_{\max}$. Results at 30° were [solvent, $\lambda_{\max}$ (mμ), $\epsilon_{\max}$] methanol, 290, 1490; 95/5 (v/v) water-methanol, 286, 1440; acetic acid, 283, 1400 (by linear extrapolation). Given $\epsilon_{\max}$ at $\lambda_{\max}$, we could then evaluate the ionization constant $K_i{}^{\mathrm{B}}$ = [BH$^+$Ac$^-$]/[B] and ϵ at other wavelengths near $\lambda_{\max}$. We thus found $K_i{}^{\mathrm{B}}$ to be 18.8 at 30°, in good agreement with the previously reported[6] value of 19.2.

A typical measurement of K_{M} is illustrated in Table III. Formal concentrations (which do not allow for metathesis) in this experiment were: K$^+$Ts$^-$, 0.00534 F; K$^+$Ac$^-$, 0.00432 F; BH$^+$Ts$^-$, 0.00326; (B + BH$^+$Ac$^-$), 0.00365 *F*. The equilibrium concentration of B was found to be (0.193 ± 0.002) m*M*—see Table III. Hence [BH$^+$Ac$^-$] = 18.8 × 0.193 = 3.63 m*M*, and thus, by stoichiometry from the formal concentrations, [BH$^+$Ts$^-$] = 3.09 m*M*, [K$^+$Ts$^-$] = 5.51 m*M*, and [K$^+$Ac$^-$] = 4.15 m*M*. On substituting these molar concentrations in (21), we obtain K_{M} = 1.56.

Table III. A Typical K_{M} Measurement: K$^+$Ac$^-$ + *p*-$CH_3C_6H_4NH_3{}^+$Ts$^-$ in Acetic Acid at 30°

Wave-length, mμ	Absorbance of soln[a] 1	2	3	4	[B],[b] m*M*
280	0.343	0.032	0.041	0.270	0.195
283	0.314	0.010	0.033	0.271	0.193
284	0.308	0.007	0.031	0.270	0.195
286	0.290	0.004	0.027	0.259	0.193
288	0.268	0.003	0.025	0.240	0.191
290	0.240	0.003	0.022	0.215	0.190
292	0.207	0.002	0.018	0.187	0.191

[a] 1, equilibrium mixture; 2, due to Ts$^-$ (absorbance of a solution of K$^+$Ts$^-$ whose formal *p*-toluenesulfonate concentration is equivalent to that in 1; 3, due to BH$^+$ (absorbance of a solution of BH$^+$ClO$_4{}^-$ whose formal *p*-toluidinium concentration is equivalent to that in 1; 4, due to un-ionized *p*-toluidine in the equilibrium mixture (by difference from 1 − (2 + 3)). [b] Molar extinction coefficients of *p*-toluidine were measured by the method of ref 6 and can be obtained by simple division of data in the last two columns.

Solutions used in these measurements were always freshly prepared, because *p*-toluidine was slightly unstable in acetic acid and the absorbance at 280–290 mμ increased noticeably over the course of several days. K_{M} measurements for each set of reactants were repeated with at least six independent solutions. Final results and their standard deviation are listed in Table IV.

Table IV. Equilibrium Constants for Ion-Pair Reactions in Acetic Acid at 30°

Cation M$^+$	K_{M} for metathesis (eq 20) Direct	Indirect	Wt av	$10^7K_{\mathrm{B}}{}^{\mathrm{M^+Ts^-}}$, *M*
Li$^+$	0.59 ± 0.04	0.56 ± 0.07[a]	0.58	4.1 ± 0.4
Tl$^+$	0.76 ± 0.06	1.0 ± 0.2[a]	0.80	2.2 ± 0.3
BH$^+$	Unity	Unity	Unity	(2.32 ± 0.2)[b]
K$^+$	1.56 ± 0.16	1.71 ± 0.20[a]	1.60	1.36 ± 0.08
Cs$^+$	2.26 ± 0.19	2.13 ± 0.3[a]	2.20	1.09 ± 0.13
(*n*-Bu)$_4$N$^+$	2.71 ± 0.26	2.80 ± 0.15[c]	2.75	

[a] Method based on eq 24. [b] This equilibrium constant is identical with *K* (part I, eq 9 and 10). [c] Method based on eq 26. K_{IM} for (*n*–Bu)$_4$N$^+$Ac$^-$ = 1.12; K_{IM} for BH$^+$Ac$^-$ = 0.400 (ref 8).

Indirect Measurement of K_{M}. Two different methods were used. For all M$^+$ except (*n*-Bu)$_4$N$^+$, K_{M} was calculated from the basicity constants of M$^+$Ts$^-$ and BH$^+$Ts$^-$. The basicity constant for BH$^+$Ts$^-$ is, of

$$\mathrm{M^+Ts^- + HAc \rightleftharpoons M^+Ac^- + HTs} \tag{22}$$

$$K_{\mathrm{B}}{}^{\mathrm{M^+Ts^-}} = [\mathrm{M^+Ac^-}][\mathrm{HTs}]/[\mathrm{M^+Ts^-}] \tag{23}$$

course, identical with the equilibrium constant *K* obtained in part I (eq 9 and 10). Comparison of (23) and (10) with (21) leads to eq 24 for K_{M}. $K_{\mathrm{B}}{}^{\mathrm{M^+Ts^-}}$ was

$$K_{\mathrm{M}} = K_{\mathrm{B}}{}^{\mathrm{BH^+Ts^-}}/K_{\mathrm{B}}{}^{\mathrm{M^+Ts^-}} \equiv K/K_{\mathrm{B}}{}^{\mathrm{M^+Ts^-}} \tag{24}$$

measured by dissolving pure M$^+$Ts$^-$ in pure acetic acid and using *p*-nitro-*N*,*N*-dimethylaniline as indicator (with equilibrium constants as listed in Table II) to measure the HTs concentrations in the resulting solutions. This method has been described in part I in connection with the measurement of *K*. Although the method is quite vulnerable to the presence of acidic or basic impurities, results of useful precision could be obtained (see Table IV), and the values of K_{M} calculated by eq 24 are in quite reasonable agreement with those measured directly.

For M$^+$ = (N-Bu)$_4$N$^+$, K_{M} was measured indirectly by a previously described method[7,8] employing butter yellow (I, *p*-dimethylaminoazobenzene) at indicator concentrations. Briefly, one obtains the equilibrium constant for ion-pair exchange of M$^+$Ac$^-$ with IH$^+$Ts$^-$ (eq 25) by spectrophotometric measurement of the concentration of un-ionized I at equilibrium in a solution containing known amounts of M$^+$Ac$^-$, M$^+$Ts$^-$, and total indicator. (The principle used here is the same as

$$\mathrm{M^+Ac^- + IH^+Ts^-} \overset{K_{\mathrm{IM}}}{\rightleftharpoons} \mathrm{M^+Ts^- + IH^+Ac^-} \tag{25}$$

in the direct method for K_{M}.) If K_{IM} is measured for both M$^+$Ac$^-$ and BH$^+$Ac$^-$, K_{M} for M$^+$ can be calculated by eq 26. The result for (*n*-Bu)$_4$N$^+$, listed in Table IV,

$$K_{\mathrm{M}}\ (\text{for M}^+) = K_{\mathrm{IM}}\ (\text{for M}^+\text{Ac}^-)/K_{\mathrm{IM}}\ (\text{for BH}^+\text{Ac}^-) \tag{26}$$

is accurate to better than 5% and is in good agreement with the value found by the direct method.

Kinetic Analysis. To allow for ion-pair exchange between BH$^+$Ts$^-$ and M$^+$Ac$^-$, we enlarge the kinetic scheme of eq 1–5 (part I) by adding eq 2a and 5a. The resulting rate law is (27).

$$B\mathrm{H^+Ts^-} + \mathrm{M^+Ac^-} \underset{k_{-\mathrm{M}}}{\overset{k_{+\mathrm{M}}}{\rightleftharpoons}} B\mathrm{H^+Ac^-} + \mathrm{M^+Ts^-} \tag{2a}$$

$$B\mathrm{H^+Ac^-} + \mathrm{M^+Ts^-} \xrightarrow{k_{-\mathrm{M}}} B\mathrm{H^+Ts^-} + \mathrm{M^+Ac^-} \tag{5a}$$

$$\frac{R}{[\mathrm{BH^+Ts^-}]} = \frac{k_{\mathrm{e}}K}{[\mathrm{HTs}]} \times \frac{k_-[\mathrm{HTs}] + k[\mathrm{BH^+Ts^-}] + k_{-\mathrm{M}}[\mathrm{M^+Ts^-}]}{k_{\mathrm{e}} + k_-[\mathrm{HTs}] + k[\mathrm{BH^+Ts^-}] + k_{-\mathrm{M}}[\mathrm{M^+Ts^-}]} \tag{27}$$

Evaluation of the rate constants follows the method described in part I: (a) the intercept of the plot of $R\cdot$[HTs]/[BH$^+$Ts$^-$] *vs.* 1/[HTs] at high (0.1–0.01 *M*) HTS concentrations is equal to $k_{\mathrm{e}}K$. (b) The intercept of the plot of *R*[HTs]/[BH$^+$Ts$^-$] *vs.* [HTs] at low (<10^{-3} *M*)

---

(6) G. W. Ceska and E. Grunwald, *J. Amer. Chem. Soc.*, **89**, 1371 (1967).

(7) E. Grunwald and M. S. Puar, *ibid.*, **89**, 6842 (1967).

(8) C. S. Leung and E. Grunwald, *J. Phys. Chem.*, **73**, 1822 (1969).

HTs concentrations is equal to k_eK/g', where g' is defined in (28). Experimentally, g' is simply the ratio of

$$g' = \frac{k[\mathrm{BH^+Ts^-}] + k_{-\mathrm{M}}[\mathrm{M^+Ts^-}] + k_e}{k[\mathrm{BH^+Ts^-}] + k_{-\mathrm{M}}[\mathrm{M^+Ts^-}]} \tag{28}$$

the intercepts obtained in (a) and (b). Since k_e and k are known (part I), $k_{-\mathrm{M}}$ can be calculated. (c) Finally, k_- is obtained by fitting the data at intermediate HTs concentrations.

Results of the kinetic analysis are summarized in Table V. The validity of the rate law is evident from the following. (a) The intercepts of the plots *vs.* 1/[HTs] at high HTs concentrations are constant (within a few per cent) and independent of the added salt, as expected if these intercepts measure k_eK. (b) The intercepts of the plots at low HTs concentrations vary with [$\mathrm{M^+Ts^-}$] in the expected manner. The values obtained for $k_{-\mathrm{M}}$ are specific for the given salt but independent of its concentration. (c) With one exception (noted below), the values obtained for k_- are sensibly constant and independent of the added salt, as expected if these numbers measure the rate constant for reaction of $\mathrm{BH^+Ac^-}$ with HTs.

Table V. Kinetic Analysis of Proton Exchange between 0.0500 *M* *p*-Toluidinium *p*-Toluenesulfonate and Acetic Acid at 30.0° [a]

Added salt	Concn, M	k_eK	g'	$10^{-8}k_{-\mathrm{M}}$, $\mathrm{sec^{-1}}\ M^{-1}$	$10^{-9}k_-$, $\mathrm{sec^{-1}}\ M^{-1}$
$\mathrm{Li^+Ts^-}$	0.0296	23.4	2.87	4.8	7.5 ± 1.2
	0.0500	23.4	2.50	5.3	6.6 ± 1.5
			av	5.1	
$\mathrm{K^+Ts^-}$	0.0308	(23.7)[b]	2.82	5.1	
	0.0505	23.1	2.47	5.8	9.0 ± 1.5
	0.0746	(23.1)[b]	2.22	5.8	
			av	5.5	
$\mathrm{Cs^+Ts^-}$	0.0380	23.7	2.63	5.8	8.4 ± 1.2
	0.0558	(23.7)[b]	2.35	6.3	
			av	6.0	
$\mathrm{Tl^+Ts^-}$	0.0343	23.7	2.40	9.4	8.4 ± 1.5
$(n\text{-Bu})_4\mathrm{N^+Ts^-}$	0.0168	23.7	2.95	7.1	9.6 ± 2.0
	0.0280	24.3	2.65	7.6	9.9 ± 2.0
	0.0700	24.6	2.08	7.8	13.5 ± 3.0
			av	7.5	

[a] Based on eq 27 and 28. $k_e = 1.02 \times 10^8\ \mathrm{sec^{-1}}$; $k = 8.1 \times 10^8\ \mathrm{sec^{-1}}\ M^{-1}$; except where noted, the HTs concentration was varied between 10^{-1} and 10^{-4} *M* in 15–20 steps. [b] Estimated. Rates were measured at low HTs concentrations only.

At HTs concentrations above 0.1 *M*, the rate of exchange decreases, slightly but significantly, below that predicted from eq 27. This effect is specific for each added salt and appears to be due to specific solute–solute interaction involving the added salt and HTs. The apparent exaltation of k_- in the presence of 0.0700 *M* $(n\text{-Bu})_4\mathrm{N^+Ts^-}$ can also, plausibly, be attributed to solute–solute interaction.

Table VI presents a summary of our results for the effect of the cation in ion-pair exchange. Values of $k_{+\mathrm{M}}$ are equal to $K_\mathrm{M}k_{-\mathrm{M}}$.

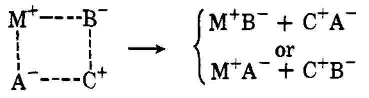
Discussion

Table VI lists rate constants for two series of ion-pair exchange reactions: *p*-toluidinium *p*-toluenesulfonate with a series of acetate salts ($k_{+\mathrm{M}}$), and *p*-toluidinium acetate with a series of *p*-toluenesulfonate salts ($k_{-\mathrm{M}}$). While $k_{-\mathrm{M}}$ varies by less than a factor of 2, $k_{+\mathrm{M}}$ (with the same series of cations) varies by a factor of 7. Evidently, the reactivity of the acetate ion pairs is considerably more sensitive to the nature of the cation.

Table VI. Effect of the Cation in Ion-Pair Exchange, According to Equation 20, in Acetic Acid at 30.0°

$\mathrm{M^+}$	$10^{-8}k_{+\mathrm{M}}$, $\mathrm{sec^{-1}}$	$10^{-8}k_{-\mathrm{M}}$, $\mathrm{sec^{-1}}$	K_M
$\mathrm{Li^+}$	3.0	5.1	0.58
$\mathrm{Tl^+}$	7.5	9.4	0.80
$\mathrm{BH^+}$	8.2	8.2	1.00
$\mathrm{K^+}$	8.8	5.5	1.60
$\mathrm{Cs^+}$	13.2	6.0	2.20
$(n\text{-Bu})_4\mathrm{N^+}$	21	7.5	2.75

In previous discussions of ion-pair exchange,[2,7] we found it helpful to assume that reaction proceeds by way of a cyclic ion quartet, shown schematically in (29), in which each ion "binds" (interacts at short range with) *two* ions of opposite charge. Such an ion quartet has

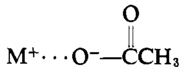


(29)

more explicit molecular structure than is normally assumed for an electrostatic ion-pair association complex, and it retains no vestige of the specific combination of ion pairs from which it was formed. When the formation of such an ion quartet is energetically unfavorable, ion-pair exchange will be relatively slow. Thus it was found in part I that ion-pair exchange is much slower for *tert*-anilinium salts (where the cations have only one NH proton for hydrogen bonding) than for *p*-toluidinium salts.[2]

In the present study we are concerned, not with absolute reactivity, but with the sensitivity of the rate constant to the nature of the cation, and why that sensitivity is so different in the two reaction series. Since we are dealing with reversible reactions at dynamic equilibrium, the transition states in the two reaction series must be identical, and our explanation must therefore involve the reactant states, that is, the original ion pairs.

We believe that the high sensitivity in the acetate series can be linked to the high mobility of the electric charge in the carboxylate group. The symmetrical charge distribution over both oxygen atoms in the free acetate ion is perturbed, more or less, by the cation, and the ion pair is more or less like a Lewis acid–base complex, depending on the size and Lewis acidity of the cation (eq 30). When such an ion pair reacts with *p*-



$$\mathrm{M^+\cdots O^-{-}\overset{\overset{\displaystyle O}{\|}}{C}CH_3} \tag{30}$$

toluidinium *p*-toluenesulfonate to form the cyclic ion quartet (29), the charge in the carboxylate group becomes distributed more evenly over the two oxygen atoms. Hence the "bond" to the cation in the original ion pair is weakened, and this will raise the energy of activation. As a matter of fact, the values of $k_{+\mathrm{M}}$ in Table VI are essentially in the sequence of Lewis acidity of the cations, with $k_{+\mathrm{M}}$ being lowest for $\mathrm{Li^+}$ (an active "hard" acid) and $\mathrm{Tl^+}$ (an active "soft" acid), and highest for $(n\text{-Bu})_4\mathrm{N^+}$ (which is negligible as an acid.) The contribution of Lewis acid–base character is expected to be much smaller in the *p*-toluenesulfonate ion pairs, and this provides a consistent explanation for the relatively low sensitivity of k_{-M} to the nature of the cation.

There are several instances for aprotic solvents,[9] and one for acetic acid,[10] in which the existence of ion pairs with the formula $M^+Ac^- \cdot HAc$ has been indicated. Furthermore, dissociated acetate ion is exceptionally stable in acetic acid and should probably be formulated as $Ac^- \cdot HAc$[8] (which might be stabilized further by ultrafast proton transfer, $Ac^- \cdot HAc \rightleftarrows AcH \cdot Ac^-$). In the solid state, the existence of stable compounds such as $(n\text{-}Bu_4N^+)Ac^- \cdot HAc$ is well known. We nevertheless feel that the acetate ion pairs studied in the present work are best formulated as shown in (30), with the acetate ions in the ion pairs being solvated only by loosely attached acetic acid molecules. Otherwise we would need a far more complicated theory to account for our kinetic results.

Relationship to Ion-Pair Exchange in Solvolysis. It can be shown that K_M is related to ion-pair dissociation constants K_d according to

$$K_M = (K_d^{M^+Ac^-}/K_d^{M^+Ts^-})(K_d^{BH^+Ts^-}/K_d^{BH^+Ac^-}) \quad (31)$$

$K_d^{BH^+Ts^-}/K_d^{BH^+Ac^-}$ for the *p*-toluidinium salts has been reported to be 0.248 ± 0.003 in acetic acid at 26.7°.[8] On using that value in conjuction with K_M, we find that for tetra-*n*-butylammonium salts, $K_d^{M^+Ac^-}/K_d^{M^+Ts^-} = 11.3$, with a confidence limit estimated conservatively at ±20%.

In a recent review, Winstein, Appel, Baker, and Diaz[11] have presented a theory of ion-pair exchange in solvolysis which makes the assumptions that (a) the equilibrium constant for (32) is equal to $K_d^{M^+Y^-}/K_d^{M^+X^-}$, and (b) that the rate constant for acetolysis (33) is approximately the same for all X^- and Y^-. ($R^+||X^-$ and $R^+||Y^-$ denote solvent-separated ion-pair reaction intermediates.) The theory requires that certain parameters in the rate law for acetolysis be predictable from ion-pair dissociation constants.

$$R^+||X^- + M^+Y^- \rightleftarrows R^+||Y^- + M^+X^- \quad (32)$$

$$HAc + (R^+||X^- \text{ or } R^+||Y^-) \longrightarrow RAc + (HX \text{ or } HY) \quad (33)$$

The theory seems to fit the data well for $X^- = Ts^-$ and $Y^- = ClO_4^-$.[11] However, in the case of tetra-*n*-butylammonium salts, the value of 11.3 obtained above for $K_d^{M^+Ac^-}/K_d^{M^+Ts^-}$ is in serious discrepancy with the theoretical prediction of 2.8.[11] Thus, in solvolysis as well, the reactions of acetate ion pairs display a greater specificity than do those of *p*-toluenesulfonate or (presumably) perchlorate ion pairs.

(9) M. M. Davis, "Acid-Base Behavior in Aprotic Organic Solvents," National Bureau of Standards Monograph 105, Washington, D. C., 1968, Chapter 4.

(10) A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 4484 (1964).

(11) S. Winstein, B. Appel, R. Baker, and R. Diaz, *Chem. Soc., Spec. Publ.*, No. **19**, 115 (1965).

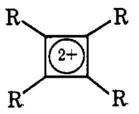
Evidence Concerning the Bishomocyclobutenium Dication as a Solvolytic Intermediate

Joseph B. Lambert[*1a] and **Allen G. Holcomb**[1b]

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201.
Received September 8, 1970

Abstract: *cis-exo*-2,3-Norborn-5-enyl ditosylate (IV) acetolyzes 500 times more rapidly than the related saturated *cis-exo*-ditosylate XI. Since a double bond is generally rate retarding in a homoallylic situation, *e.g.*, comparison of the saturated and unsaturated *exo*-monotosylates XII and XIII in the norbornyl series, a special effect must be operative. One such possibility is loss of both tosylate groups to form a bishomocyclobutenium ion. As demanded of this mechanism, acetolysis of IV for one half-life produces no acetoxy tosylate intermediate, whereas XI does produce a mixed ester. If a dication mechanism were operative, the cis relationship of the leaving groups must bring about a rate enhancement. *trans*-2,3-Norborn-5-enyl ditosylate (XIV), however, solvolyzes at a rate comparable to that of IV. Furthermore, the mixed ester *cis-exo*-2-acetoxy-3-tosyloxynorborn-5-ene (XV), for which a dication mechanism is impossible, reacts slightly more rapidly than IV. If a single explanation is to be found for the rapid reactions of IV, XIV, and XV compared to saturated models, a double ionization is excluded. Consistent with all the data for the diesters is a greatly enhanced homoallylic assistance compared to that in the monoesters. To diminish the rate-retarding effect of the electronegative substituent adjacent to the leaving group, the double bond becomes a much more effective participator than it is in monotosylates such as XII.

Experiments in highly acidic media have recently placed cyclobutenium dications (I) on firm ground.[2,3] Such molecules are isoelectronic with the



I, $R = CH_3, C_6H_5$

---

[1] (a) Alfred P. Sloan Foundation Fellow, 1968–1970. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-A4,5), and by the National Science Foundation (Grant No. GP-9257). (b) National Science Foundation Predoctoral Fellow, 1966–1970.

[2] G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969); G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970).

[3] Earlier work was less successful in confirming a dication; see D. G. Farnum, M. A. T. Heybey, and B. Webster, *ibid.*, **86**, 673 (1964); H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962); H. H. Freedman and A. E. Young, *ibid.*, **86**, 734 (1964); R. F. Bryan, *ibid.*, **86**, 733 (1964).