

Kinetics of Ion-pair Exchange in Acetic Acid

By M. R. CRAMPTON† and ERNEST GRUNWALD*

(Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154)

Summary The rate constants for the ion-pair metatheses p -toluidinium toluene- p -sulphonate + metal acetate \rightleftharpoons p -toluidinium acetate + metal toluene- p -sulphonate have been measured using an n.m.r. technique; the rate constants are *ca.* $10^9 \text{ M}^{-1} \text{ s}^{-1}$ and show that the slow step in the exchange involves cation-acetate cleavage.

THE BINDING of cation to anion in ion-pairs, beyond that described by the model of charged spheres, is largely unknown.¹ We have initiated some kinetic studies of ion-pair exchange, using the n.m.r. technique, which give information as to the ion-pair structure. The solvent used is acetic acid, and a limitation on the ion-pairs that can be studied is that one of the cations must contain an

exchangeable amino-proton. The importance of ion-pairs and their exchange in solvolysis reactions is well documented.²

A suitable substrate in the present work was p -toluidinium toluene- p -sulphonate (BH^+OTs^-) which exists largely in the form of ion-pairs in acetic acid so that the concentration of free ions is small.³ Slow-passage n.m.r. spectra showed that the rate of exchange between carboxyl protons of the solvent and amino-protons, which is fast in the absence of acid, is slowed down by the addition of toluene- p -sulphonic acid. Rates of $\text{NH}-\text{CO}_2\text{H}$ exchange in solutions containing 10^{-4} to 10^{-1} M -acid were accurately determined using spin-echo techniques previously described.^{4,5}

The kinetic analysis follows that previously given⁵ for

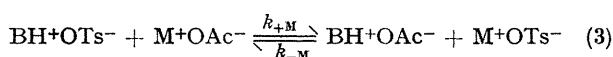
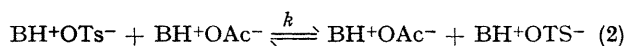
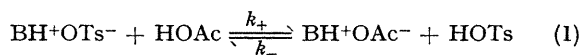
† On leave from Durham University, England.

NN-dialkylanilinium salts. We find that the data can be rationalised only in terms of a fairly complicated mechanism

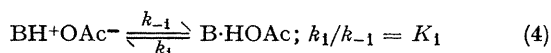
by the good agreement between the experimentally determined values of $1/\tau$ and those calculated with the values

10^2 [HOTs]	0.022	0.0342	0.048	0.069	0.092	0.122	0.151
$1/\tau$ observed	14100	9200	6400	4590	3520	2750	2210
$1/\tau$ calculated	13900	9000	6490	4590	3500	2700	2220
10^2 [HOTs]	0.21	0.42	0.63	1.2	1.87	2.8	4.02
$1/\tau$ observed	1680	928	634	409	289	209	157
$1/\tau$ calculated	1660	922	667	406	289	210	157

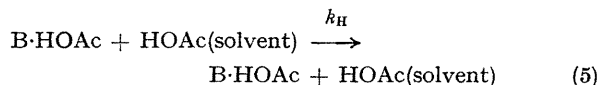
involving formation of the *p*-toluidinium acetate ion-pair by steps 1 or 2 (or 3 in the presence of added M^+OTs^-)



followed by formation of the solvated amine (reaction 4)



and exchange of the solvating acetic acid with bulk solvent (reaction 5).



This mechanism leads⁵ to a rate of exchange R given by:

$$\frac{R}{[BH^+OTs^-]} = \frac{3}{\tau} = \frac{k_e K}{[HOTs]} \times \frac{k_- [HOTs] + k [BH^+OTs^-] + k_{-M} [M^+OTs^-]}{k_e + k_- [HOTs] + k [BH^+OTs^-] + k_{-M} [M^+OTs^-]}$$

where τ is the mean residence time of a proton on an NH site in one cycle of exchange and the factor 3 results from the three NH protons; $k_e (=k_H K_1)$ is the probability per second that a BH^+OAc^- ion-pair exchanges its NH proton and $K = k_+/k_-$. Analysis of the data involving plots of $[HOTs]/\tau$ versus $[HOTs]$ at low acid concentration and $[HOTs]/\tau$ versus $1/[HOTs]$ at high acid concentration allows the determination of the product $k_e K$ and the rate constants k , k_{-M} , k_- , and k_e . The results with BH^+OTs^- in the absence of added metal toluene-*p*-sulphonate (M^+OTs^-) completely confirm this rate law and indicate the importance of step 2 in the formation of the BH^+OAc^- ion-pair. Results at concentration of BH^+OTs^- at 0.03 and 0.05 M indicate that k (the rate constant for symmetrical ion-pair exchange) has the value $(8.2 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 30° and is independent of solute concentration.

The rate law remains valid in the presence of added M^+OTs^- . This is demonstrated for the case of solutions containing BH^+OTs^- , 0.05 M and Cs^+OTs^- , 0.038 M at 30°

$k_e K = 23.7$, $k_- = 8.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k = 8.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-M} = 5.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and $k_e = 1.02 \times 10^8 \text{ s}^{-1}$.

The rate constants with which we are most concerned here are those involving ion-pair exchange. The values of k_{-M} were determined at 30° for a series of metal toluene-*p*-sulphonate salts to an accuracy of $\pm 10\%$. The values of K_M , the equilibrium constants for ion-pair exchange, were measured by determining spectrophotometrically the equilibrium concentrations of free *p*-toluidine (B) in mixtures made up from stock solutions of BH^+OTs^- , B, M^+OAc^- and M^+OTs^- . The equilibrium constant $K_1 (= [BH^+OAc^-]/[B])$ is known⁶ to have the value 19 at 30° so that the concentrations of BH^+OAc^- followed by the concentrations of other ion-pairs could be found.

Rate and equilibrium constants for ion-pair exchange at 30°

M^+	k_{-M} (measured) ($\text{M}^{-1} \text{ s}^{-1}$)	$k_{+M} (= k_{-M} K_M)$ ($\text{M}^{-1} \text{ s}^{-1}$)	K_M (measured)
Li ⁺	5.1×10^8	3.0×10^8	0.59
Tl ⁺	9.4×10^8	7.1×10^8	0.76
BH ⁺	8.2×10^8	8.2×10^8	1.0
K ⁺	5.5×10^8	8.6×10^8	1.56
Cs ⁺	6.0×10^8	14×10^8	2.26
Bu ₄ N ⁺	7.5×10^8	21×10^8	2.75

The rates of ion-pair exchange are high but are significantly lower than expected for diffusion control. The results show that the values of k_{+M} , the rate constants for reaction of metal acetate with BH^+OTs^- , are much more sensitive to the nature of M^+ than are the values of k_{-M} . This is good evidence that the slow step in the exchange reaction involves cleavage of a "bond" between the cation (M^+ or BH^+) and acetate ion. It implies also a stronger interaction in the acetate ion-pairs than in the toluene-*p*-sulphonate ion-pairs, a result which is in accord with the greater basicity of the acetate ion than that of the toluene-*p*-sulphonate ion. The general trend to a faster rate constant, k_{+M} , with larger size of the cation is to be expected, because the small lithium ion will co-ordinate more strongly than the larger ions. This effect is seen also in the trend in values for the equilibrium constants K_M . We conclude that these ion-pairs have definite structure and that the ion-pair exchange reactions are more like chemical reactions than like the exchange of independent ionic partners.

This work was supported by a grant from the National Science Foundation of the U.S.A.

(Received, June 9th, 1970; Com. 890.)

¹ M. Szwarc, *Accounts Chem. Res.*, 1969, 2, 87.

² S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc. Special Publ.*, No. 19, 1965, 109.

³ C. S. Leung and E. Grunwald, *J. Phys. Chem.*, 1969, 73, 1822.

⁴ E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, 1964, 86, 2965, 2970.

⁵ E. Grunwald and M. Puar, *J. Amer. Chem. Soc.*, 1967, 89, 6842.

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