Kinetics of Ion-pair Exchange in Acetic Acid

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Summary The rate constants for the ion-pair metatheses *p*-toluidinium toluene-*p*-sulphonate + metal acetate ⇌ *p*-toluidinium acetate + metal toluene-*p*-sulphonate have been measured using an n.m.r. technique; the rate constants are *ca.* 10^9 M^{-1} 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 NH–CO_2H 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 given[5] for

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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	6·20
$1/\tau$ observed	1680	928	634	409	289	209	157	109
$1/\tau$ calculated	1660	922	667	406	289	210	157	109

NN-dialkylanilinium salts. We find that the data can be rationalised only in terms of a fairly complicated mechanism involving formation of the *p*-toluidinium acetate ion-pair by steps 1 or 2 (or 3 in the presence of added $\mathrm{M^+OTs^-}$)

$$\mathrm{BH^+OTs^-} + \mathrm{HOAc} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{BH^+OAc^-} + \mathrm{HOTs} \qquad (1)$$

$$\mathrm{BH^+OTs^-} + \mathrm{BH^+OAc^-} \overset{k}{\rightleftharpoons} \mathrm{BH^+OAc^-} + \mathrm{BH^+OTS^-} \qquad (2)$$

$$\mathrm{BH^+OTs^-} + \mathrm{M^+OAc^-} \underset{k_{-\mathrm{M}}}{\overset{k_{+\mathrm{M}}}{\rightleftharpoons}} \mathrm{BH^+OAc^-} + \mathrm{M^+OTs^-} \qquad (3)$$

followed by formation of the solvated amine (reaction 4)

$$\mathrm{BH^+OAc^-} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{B{\cdot}HOAc};\ k_1/k_{-1} = K_1 \qquad (4)$$

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

$$\mathrm{B{\cdot}HOAc} + \mathrm{HOAc(solvent)} \xrightarrow{k_{\mathrm{H}}} \mathrm{B{\cdot}HOAc} + \mathrm{HOAc(solvent)} \qquad (5)$$

This mechanism leads[5] to a rate of exchange R given by:

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

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; $k_{\mathrm{e}}(=k_{\mathrm{H}}K_1)$ is the probability per second that a $\mathrm{BH^+OAc^-}$ ion-pair exchanges its NH proton and $K = k_+/k_-$. Analysis of the data involving plots of [HOTs]/τ *versus* [HOTs] at low acid concentration and [HOTs]/τ *versus* 1/[HOTs] at high acid concentration allows the determination of the product $k_{\mathrm{e}}K$ and the rate constants k, $k_{-\mathrm{M}}$, k_-, and k_{e}. The results with $\mathrm{BH^+OTs^-}$ in the absence of added metal toluene-*p*-sulphonate ($\mathrm{M^+OTs^-}$) completely confirm this rate law and indicate the importance of step 2 in the formation of the $\mathrm{BH^+OAc^-}$ ion-pair. Results at concentration of $\mathrm{BH^+OTs^-}$ at 0·03 and 0·05 M indicate that k (the rate constant for symmetrical ion-pair exchange) has the value $(8{\cdot}2 \pm 0{\cdot}3) \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ at 30° and is independent of solute concentration.

The rate law remains valid in the presence of added $\mathrm{M^+OTs^-}$. This is demonstrated for the case of solutions containing $\mathrm{BH^+OTs^-}$, 0·05 M and $\mathrm{Cs^+OTs^-}$, 0·038 M at 30° by the good agreement between the experimentally determined values of $1/\tau$ and those calculated with the values $k_{\mathrm{e}}K = 23{\cdot}7$, $k_- = 8{\cdot}5 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$, $k = 8{\cdot}2 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$, $k_{-\mathrm{M}} = 5{\cdot}7 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$, and $k_{\mathrm{e}} = 1{\cdot}02 \times 10^8\ \mathrm{s^{-1}}$.

The rate constants with which we are most concerned here are those involving ion-pair exchange. The values of $k_{-\mathrm{M}}$ 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 $\mathrm{BH^+OTs^-}$, B, $\mathrm{M^+OAc^-}$ and $\mathrm{M^+OTs^-}$. The equilibrium constant K_1 $(=[\mathrm{BH^+OAc^-}]/[\mathrm{B}])$ is known[6] to have the value 19 at 30° so that the concentrations of $\mathrm{BH^+OAc^-}$ followed by the concentrations of other ion-pairs could be found.

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

$\mathrm{M^+}$	$k_{-\mathrm{M}}$ (measured) $(\mathrm{M^{-1}\,s^{-1}})$	$k_{+\mathrm{M}}(=k^-{}_{\mathrm{M}}K_{\mathrm{M}})$ $(\mathrm{M^{-1}\,s^{-1}})$	K_{M} (measured)
$\mathrm{Li^+}$	$5{\cdot}1 \times 10^8$	$3{\cdot}0 \times 10^8$	0·59
$\mathrm{Tl^+}$	$9{\cdot}4 \times 10^8$	$7{\cdot}1 \times 10^8$	0·76
$\mathrm{BH^+}$	$8{\cdot}2 \times 10^8$	$8{\cdot}2 \times 10^8$	1·0
$\mathrm{K^+}$	$5{\cdot}5 \times 10^8$	$8{\cdot}6 \times 10^8$	1·56
$\mathrm{Cs^+}$	$6{\cdot}0 \times 10^8$	14×10^8	2·26
$\mathrm{Bu^n{}_4N^+}$	$7{\cdot}5 \times 10^8$	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 $k_{+\mathrm{M}}$, the rate constants for reaction of metal acetate with $\mathrm{BH^+OTs^-}$, are much more sensitive to the nature of $\mathrm{M^+}$ than are the values of $k_{-\mathrm{M}}$. This is good evidence that the slow step in the exchange reaction involves cleavage of a "bond" between the cation ($\mathrm{M^+}$ or $\mathrm{BH^+}$) 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, $k_{+\mathrm{M}}$, 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.)

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