Thermodynamics and Kinetics of Ion-pair Formation in Aprotic Solvents

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Summary The thermodynamics and kinetics of ion-pair formation in aprotic solvents exhibit a pronounced solvent dependence, indicating the need for extensive solvent reorganisation around the ion-pair complex; in dichloromethane solvent, dimeric ion-pair species are additionally formed.

THE reaction between the indicator phenolic acid Bromophenol Blue (ROH) and the aromatic amine base pyridine (B) has been investigated in a variety of aprotic organic solvents. The general reaction scheme is thought to be[1] as shown in equation (1).

$$\mathrm{ROH} + \mathrm{B} \underset{\text{Fast}}{\overset{K_{12}}{\rightleftharpoons}} \underset{\substack{\text{H-bonded}\\ \text{complex}}}{\mathrm{ROH}\cdots\cdots\mathrm{B}} \underset{\text{slow}}{\overset{K_{23}}{\rightleftharpoons}}$$

$$\underset{\substack{\text{Ion-pair}\\ \text{complex}}}{\mathrm{RO^-}\cdots\cdots\mathrm{HB^+}} \rightleftharpoons \left\{\begin{matrix}\text{solvent-separated}\\ \text{ion pair, dimers,}\\ \text{free ions, \textit{etc.}}\end{matrix}\right\} \qquad (1)$$

Under the experimental conditions of the present investigation, the concentration of hydrogen-bonded complex was always negligible. The formation of ion pairs was followed by spectrophotometric measurements at 405—410 nm. Thermodynamic and kinetic results are shown in the Table.

TABLE. *Equilibrium and rate constants for ion-pair formation at* 25·0 °C[a]

Solvent	D[b]	E_T(kcal mol^{-1})	$10^{-2}K$(M^{-1})	$10^{-3}k_f$(M^{-1} s^{-1})	k_b(s^{-1})
Toluene	2·38	33·9	11·5 ± 0·4	6·9 ± 0·6	6·0 ± 0·4
Benzene	2·27	34·5	18·2 ± 0·3	13·8 ± 0·2	7·5 ± 0·2
Chlorobenzene[c]	5·62	37·5	21·2 ± 0·8	117 ± 7	55 ± 3
Dichloromethane	8·89	41·1	62·9 ± 4·5	641 ± 15	71 ± 2

[a] Appended error limits are estimated standard deviations; [b] Dielectric constant; [c] Data of Crooks and Robinson;[1] rate constants determined by laser temperature-jump measurements.

The equilibrium constant for hydrogen-bond formation, K_{12}, should not vary significantly with solvent,[2] but the overall equilibrium constant K $(=K_{12}\, K_{23})$ is markedly solvent-dependent, which suggests that the proton transfer step involves a substantial interaction with solvent. Rate constants for overall ion-pair formation, k_f, and for the reverse reaction, k_b (ideally $K = k_f/k_b$), were obtained by a concentration-jump technique using a stopped-flow instrument. The results for k_f indicate an even more pronounced solvent dependence than exhibited by K. The values of k_b^{-1} are measures of the life-times of the ion-pair complex. A good correlation is obtained between log k_f and the solvent polarity parameter E_T,[3] indicating that the rate of formation of the ion-pair complex is determined by the need for solvent reorganisation in the rate-limiting proton-transfer step.

The dichloromethane data could not be analysed solely in terms of K. The observed values of K are concentration dependent in a manner consistent with formation of an additional dimeric species, *i.e.*,

$$2\,\mathrm{RO^-}\cdot\cdot\mathrm{HB^+} \overset{K_D}{\rightleftharpoons} (\mathrm{RO^-}\cdot\cdot\mathrm{HB^+})_2 \qquad (2)$$

The dielectric constant of dichloromethane appears to be high enough to create a relatively large dipole moment in the monomeric ion pair, but not sufficiently high to inhibit the resulting dimer formation. The observation of an additional slow relaxation in the 100 ms region provides confirmatory evidence for the dimerisation mechanism. K_D and K are then given by equation (3), where { } indicates

$$K_{\mathrm{obs}} = 2K^2K_D\{\mathrm{ROH}\}\{\mathrm{B}\} + K \qquad (3)$$

concentrations at equilibrium.

Plots of K_{obs} *vs.* {ROH}{B} are linear, from which we find $K_D = (7{\cdot}5 \pm 2{\cdot}1) \times 10^3$ M^{-1} at 25·0° C, $\Delta H^\circ_D = -60 \pm 20$ kJ mol^{-1}, and $\Delta S^\circ_D = -140 \pm 60$ J mol^{-1} deg^{-1}.

Measurements of K_{obs} in acetonitrile solvent indicate even more complicated behaviour, which does not appear to follow the general reaction scheme given above.

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[1] J. E. Crooks and B. H. Robinson, *Trans. Faraday Soc.*, 1971, **67**, 1707.

[2] G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, London, 1960, Appendix A.

[3] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Annalen*, 1963, **661**, 1.