Spectroscopic, Thermodynamic, and Kinetic Evidence for a Hydrogen-bonded Intermediate in Fast Proton-transfer Reactions in Aprotic Solvents

By J. E. CROOKS and B. H. ROBINSON*
(*University Chemical Laboratory, University of Kent, Canterbury*)

Summary The system Bromophenol Blue + 2,4,6-trimethylpyridine in chlorobenzene shows appreciable quantities of both hydrogen-bonded and ion-pair complex species in protomeric equilibrium; the proton-transfer within the hydrogen bond proceeds at a rate of about 10^5 s^{-1}, which is much slower than has been generally supposed.

IT is usually considered that acids and bases react in aprotic solvents of low dielectric constant to form predominantly hydrogen-bonded complexes ROH $\cdots$ B, ion-pairs RO$^-$ $\cdots$ HB$^+$, or hybrids of the two forms, but the detailed nature of the species in a particular case is still uncertain. It has been suggested that, if ROH is an indicator acid, the formation of ROH $\cdots$ B produces a small bathochromic shift (Δλ *ca.* 30 nm) whereas the formation of RO$^-$ $\cdots$ HB$^+$ produces a large bathochromic shift (Δλ *ca.* 150 nm).[2] There is some evidence from i.r. spectroscopy that, for certain acid–base systems, hydrogen-bonded and ion-pair complexes may co-exist.[3] We have suggested[4] that proton-transfer reactions in aprotic solvents proceed through an intermediate hydrogen-bonded complex, the reaction scheme for which may be written:

$$\underset{(1)}{\mathrm{ROH} + \mathrm{B}} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(2)}{\mathrm{ROH} \cdots \mathrm{B}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{(3)}{\mathrm{RO}^- \cdots \mathrm{HB}^+}$$

We present direct spectroscopic evidence for the coexistence of hydrogen-bonded and ion-pair complexes, which is further confirmed by a kinetic study.

Bromophenol Blue, a dibasic phenolic indicator acid, reacts quantitatively with 1 equiv. of 2,4,6-trimethylpyridine in chlorobenzene solvent at base concentrations below 10^{-3}M (*K ca.* 10^6 l mole^{-1} at 25°). The product, an ion-pair complex, has a u.v. absorption peak at 410 nm, and is itself an acid, denoted by ROH, due to the second free phenolic hydroxy-group. On addition of further amine above 10^{-3}M, a peak grows at 560 nm which may be attributed to the ion-pair complex RO$^-$ $\cdots$ HB$^+$. However, the residual peak at 410 nm not only diminishes, but shifts to the red, so that the solutions do not show an isobestic point. At amine concentration of 0·5M this peak is around 440 nm, and further addition of amine has no effect on the spectrum. On raising the temperature, the peak at 560 nm decreases in height and the peak at 440 nm increases, showing an isosbestic point at 485 nm. We attribute the peak at 440 nm to the hydrogen-bonded complex ROH ... B.

The addition of aliphatic amines to Bromophenol Blue produces the ion-pair complexes ROH ($\lambda_{\max}$ 410 nm) and RO$^-$ $\cdots$ HB$^+$ ($\lambda_{\max}$ 560 nm), but there is no spectroscopic evidence for the presence of ROH $\cdots$ B in finite amounts. Values of the extinction coefficient, $\epsilon^{560}_{\max}$, are found to be $(4{\cdot}3 \pm 0{\cdot}1) \times 10^4$ l mole^{-1} cm^{-1} if B is a tertiary aliphatic amine,[5] so that this value is chosen for 2,4,6-trimethylpyridine as B. The optical density at 560 nm thus gives the concentration of RO$^-$ $\cdots$ HB$^+$. Spectra of solutions at high amine concentration (where there is no free ROH) at various temperatures in the range 6° to 33·5° gives values of K_{23} (*i.e.* [RO$^-$ $\cdots$ HB$^+$]/[ROH $\cdots$ B]) and ΔH^0_{23}. The concentrations of ROH $\cdots$ B in solutions 10^{-3} to 10^{-2}M in base, in which there are appreciable quantities of free ROH, are calculated using these values of K_{23}, and hence values of K_{12} (*i.e.* [ROH $\cdots$ B]/[ROH][B]) and ΔH^0_{12} are found.

Thermodynamic and kinetic parameters for the formation of the second hydrogen-bonded and ion-pair complexes between Bromophenol Blue and 2,4,6-*trimethylpyridine at* 25°.

$K_{12} = 53 \pm 4$ l. mole^{-1} $K_{23} = 1{\cdot}32 \pm 0{\cdot}05$ l. mole^{-1}
$\Delta H^0_{12} = -\ 28{\cdot}6 \pm 1{\cdot}9$ kJ mole^{-1} $\Delta H^0_{23} = -\ 18{\cdot}6 \pm 0{\cdot}5$ kJ mole^{-1}
$\Delta S^0_{12} = -\ 64 \pm 6$ J deg^{-1} mole^{-1} $\Delta S^0_{23} = -\ 60 \pm 1{\cdot}5$ J deg^{-1} mole^{-1}

Errors are standard deviations

$k_{23} = (6 \pm 1) \times 10^5$s^{-1} $k_{32} = (4 \pm 0{\cdot}5) \times 10^5$s^{-1}
$\Delta H^{\ddagger}_{23} = 0 \pm 5$ kJ mole^{-1} $\Delta H^{\ddagger}_{32} = 16 \pm 5$ kJ mole^{-1}
$\Delta S^{\ddagger}_{23} = -\ 134{\cdot}3 \pm 20$ J deg^{-1} mole^{-1} $\Delta S^{\ddagger}_{32} = -\ 84 \pm 20$ J deg^{-1} mole^{-1}

Errors are estimated

To determine rate constants we have used a thermostatted microwave temperature-jump apparatus,[6] of optical detector response time 0·3 μs. The relaxation times of these solutions were found to be around 2 μs, with no marked dependence on temperature or concentration. These results are inconsistent with a one-step mechanism. For the reaction scheme above, there are two relaxation times, given by:[7]

$$\tau_{\mathrm{I}}^{-1} = k_{12}[\mathrm{B}] + k_{21};\ \tau_{\mathrm{II}}^{-1} = \frac{k_{23}K_{12}[\mathrm{B}]}{1 + K_{12}[\mathrm{B}]} + k_{32}$$

where B is in large excess. The formation of ROH $\cdots$ B may be assumed to be diffusion-controlled,[8] in which case τ_{I} would be around 50 ns, so that τ_{II} is the observed relaxation time. A plot of τ^{-1} against K_{12} [B]/(1 + K_{12} [B]) gives values of k_{23} and k_{32}, which were measured in the temperature range 7° to 25°, to give estimates of $\Delta H^{\ddagger}_{23}$ and $\Delta H^{\ddagger}_{32}$. The movement of the proton within the hydrogen bond is subject to a very small activation energy, but the rate is around 10^5 s^{-1} rather than 10^{13} s^{-1} as expected for an OH-stretch. Presumably this is because the rate is controlled by the need for solvent reorganisation.

It is impossible to explain this spectroscopic, thermodynamic, and kinetic evidence on the basis of a one-step mechanism for proton transfer. The two-step mechanism described here is believed to be general for acid–base reactions in aprotic solvents, and a further consideration of kinetic and thermodynamic parameters relating to this mechanism will be given in subsequent papers.

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