Mechanism of Proton Transfer from an Intramolecularly Hydrogen-bonded Acid in Aqueous Solution

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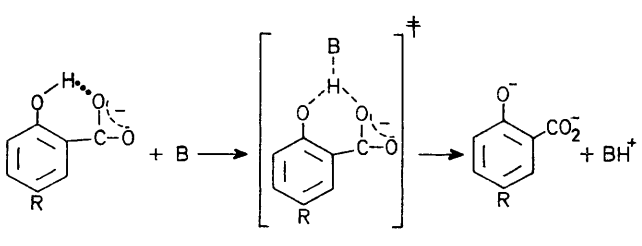
Summary Proton transfer from intramolecularly hydrogen-bonded 4-(*m*-nitrophenylazo)salicylate ion to bases occurs by a two-step mechanism through a low concentration of the non-hydrogen-bonded species from which the proton is removed; a one-step attack by base on the hydrogen-bonded species is ruled out.

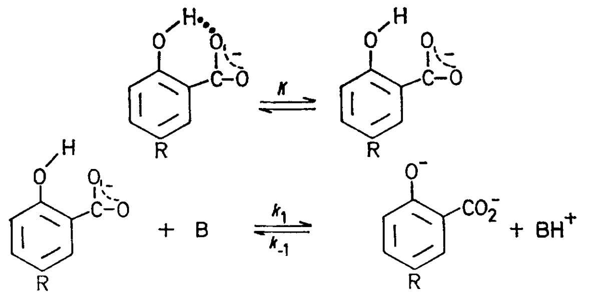
Two mechanisms have been suggested for proton transfer from intramolecularly hydrogen-bonded acids. Direct attack by base on the hydrogen-bonded proton may occur,[1] as shown in Scheme 1 for a substituted salicylate ion. An alternative mechanism[2] (Scheme 2) involves a rapid equilibrium between the hydrogen-bonded acid and a non-hydrogen-bonded species, followed by proton transfer from the latter which is present in low concentration. The choice between these two possibilities is of considerable interest[3] and we now present firm evidence in favour of Scheme 2.

Rate coefficients for the reaction in Scheme 3, with R = $m\text{-}NO_2\cdot C_6H_4\cdot N{=}N\text{-}$, were obtained from temperature-jump measurements on aqueous solutions of 4-(*m*-nitrophenylazo)-salicylate ion (pK 11·13) in the presence of excess of amine



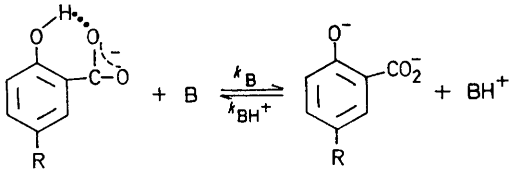
SCHEME 1

buffers (B) at 6·5 °C and an ionic strength of 0·5 M. Equilibrium constants were measured spectrophotometrically under the same conditions.



Scheme 2

For reactions (c)—(f), see Figure, values of both k_B and k_{BH^+} were obtained from the temperature-jump experiments in amine buffers and the ratios k_B/k_{BH^+} are consistent with the measured equilibrium constants for these reactions. For reactions (a) and (b), the measured equilibrium constant was needed to calculate individual values for k_B and k_{BH^+} from the kinetic results. Temperature-jump measurements in sodium hydroxide solutions gave a value $k_{OH^-} = 2{\cdot}4 \pm 0{\cdot}1 \times 10^7$ l mol^{-1} s^{-1} for the reaction in Scheme 3 with $B = OH^-$, and this is in good agreement with a previous measurement.[4]



Scheme 3

The results for proton transfer to amines are shown in the Figure in which $\log_{10}k_B$ and $\log_{10}k_{BH^+}$ are plotted against $\Delta pK = pK$(4-*m*-nitrophenylazosalicylate ion)$-pK(BH^+)$. The values of ΔpK were obtained from the measured equilibrium constants for reaction (3). The plots are linear with least-square slopes $\alpha = 1{\cdot}0 \pm 0{\cdot}1$ (for $\log_{10}k_{BH^+}$) and $\beta = 0{\cdot}0 \pm 0{\cdot}1$ (for $\log_{10}k_B$). The values of k_B which are practically independent of the basic strength of B are about three orders of magnitude below the diffusion limit. These results can be explained by Scheme 2 but are incompatible with Scheme 1.

For a reaction with the mechanism in Scheme 1, it would be expected that when the salicylate ion and BH⁺ have similar acidities ($\Delta pK = 0$) the proton in the transition state will be roughly half-transferred. In this case plots of $\log_{10}k_{BH^+}$ and $\log_{10}k_B$ against ΔpK would have slopes around $\Delta pK = 0$ of α and $\beta = ca.$ 0·5.[2a] The results are not compatible with this expectation. If the mechanism in Scheme 2 holds, the measured rate coefficients are $k_B = Kk_1$ and $k_{BH^+} = k_{-1}$. Assuming normal proton transfer behaviour[2a] for the second step in Scheme 2, k_1 will be diffusion-limited with values[2] $k_1 = ca.\ 2 \times 10^{10}$ and 2×10^9 l mol^{-1} s^{-1} for $B = OH^-$ and B = amine respectively. Hence the equilibrium constant for breakage of the intramolecular hydrogen-bond has the value $K = ca.\ 1 \times 10^{-3}$. This result is compatible with a difference in pK of three units between the hydroxy groups in phenol and salicyclic acid.[2b] If $K = 10^{-3}$ this means that the second step in Scheme 2 is strongly thermodynamically favourable in the forward direction for all our reactions even though $\Delta pK = ca.$ 0. Hence k_1 and therefore k_B will be independent of the base strength of B and independent of ΔpK in this region. Plots of $\log_{10}k_{BH^+}$ and $\log_{10}k_B$ against ΔpK should therefore have slopes $\alpha = 1{\cdot}0$ and $\beta = 0$. Within experimental error, this is what is observed in the Figure. In a previous study,[5] rate coefficients for proton transfer to bases from an intramolecularly hydrogen-bonded ammonium ion in 70% Me_2SO–H_2O were also found to be independent of the pK of the base. The results were explained in terms of the mechanism in Scheme 2 but since the reactions were in the range $\Delta pK < -1{\cdot}8$, the mechanism in Scheme 1 was not definitely ruled out. This mechanism is excluded by the present study referring to reactions around $\Delta pK = 0$ and both sets of data are consistent with the mechanism shown in Scheme 2.

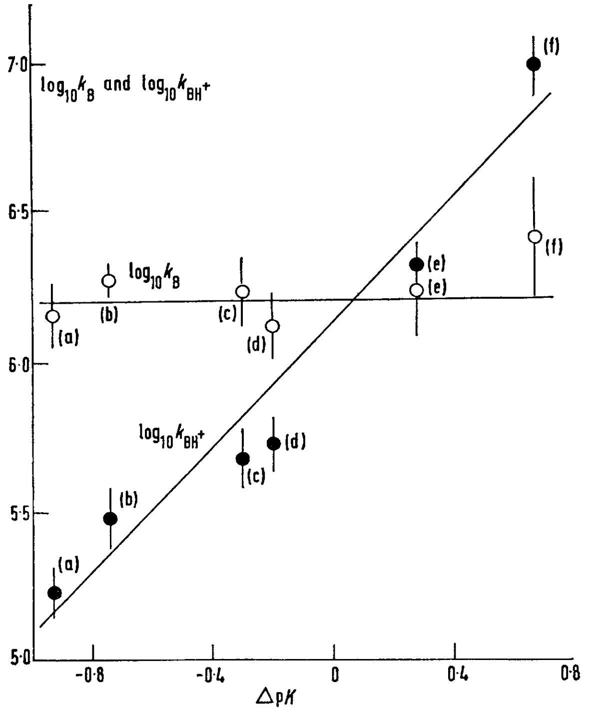


Figure. Plots of $\log_{10}k_{BH^+}$ and $\log_{10}k_B$ against ΔpK for reaction (3) where the points refer to B = (a) 1,2,2,6,6-pentamethylpiperidine, (b) 2,6-dimethylpiperidine, (c) triethylamine, (d) *cis*-1,2,6-trimethylpiperidine, (e) *N*-methylpiperidine, and (f) trimethylamine.

Proton transfer to the bulky base 1,2,2,6,6-pentamethylpiperidine is not sterically hindered. This result can be explained by Scheme 2 involving a normal proton-transfer step since normal proton transfers between oxygen and nitrogen acids in aqueous solution show almost negligible steric effects.[2a]

We thank the Royal Society for an equipment grant.

(*Received*, 13*th September* 1976; *Com.* 1049.)

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