Kinetics of Removal of the Hydrogen-bonded Proton from Substituted 1-Phenylazo-2-naphthols by Hydroxide Ion

Frank Hibbert,* Rowena J. Sellens, and Gareth R. Simpson
Department of Chemistry, King's College London, Strand, London WC2R 2LS

The effect of an intramolecular hydrogen bond on the rate coefficients and equilibrium constants for dissociation of a series of substituted 1-phenylazo-2-naphthols has been studied in basic solution. With an ionized 4-hydroxy substituent, the hydrogen bond is strong and leads to exceptionally low acidity ($pK^0 > 16$) and to a half-life in the millisecond range for proton removal by hydroxide ion in 95% (v/v) Me_2SO–H_2O. The results are compared with those for other species in which hydroxy and azo groups are intramolecularly hydrogen-bonded.

If an acidic proton is held in an intramolecular hydrogen bond the rate of proton removal is reduced below the diffusion-controlled rate normally observed for intermolecular proton transfer between electronegative atoms.[1] The available evidence shows that for various intramolecularly hydrogen-bonded acids, with one exception, proton transfer occurs through an open form of the acid present at low concentration in equilibrium with the hydrogen-bonded acid.[1] However, for substituted phenylazoresorcinol monoanions in which a phenolic proton is hydrogen-bonded to an azo group, it has been concluded that proton removal occurs by direct single-step attack on the hydrogen-bonded proton as well as by the more common route through the non-hydrogen-bonded open form.[2] Further studies[3] have provided information about the rates of opening and closing of the intramolecular hydrogen bonds in phenylazoresorcinol monoanions and the low rates which have been found may be an important factor in determining the unusual proton-transfer behaviour. The occurrence of two simultaneous routes of proton removal is not found for all acids involving a phenol–azo hydrogen bond, however, and for 1-(4-sulphonatophenylazo)-2-naphthol the results can be explained either by direct attack or by two-step proton removal through an open form.[4] In this work we describe kinetic and equilibrium studies of the dissociation of the substituted 1-phenylazo-2-naphthols (**1**)—(**5**) (see Table) as a further investigation of this type of intramolecularly hydrogen-bonded acid.

Experimental and Results

Materials.—Samples of 1-phenylazonaphthalene-2,4-diol (**1**) and 1-(4-sulphonatophenylazo)naphthalene-2,4-diol (**2**) were prepared by stirring 2-hydroxynaphthalene-1,4-dione (3.5 g) with phenylhydrazine (2.2 g) and 4-hydrazinobenzenesulphonic acid (3.8 g) respectively in 60% (v/v) MeOH–H_2O for 6 h at room temperature.[5] Acidification to pH *ca.* 1.0 resulted in the precipitation of the azo derivative (**1**). To bring about precipitation of (**2**), solid sodium chloride was added after acidification. Recrystallization from methanol gave (**1**) as a red solid (90%), m.p. 220 °C (decomp.); $\delta(Me_2SO)$ 16.15 (s, 1 H, 2-OH), 12.00 (s, 1 H, 4-OH), and 8.39—7.19 (m, 10 H, arom.); and (**2**) as a red-brown solid (26%), m.p. 325 °C (decomp.), $\delta(Me_2SO)$ 16.15 (s, 1 H, 2-OH) and 8.40—6.17 (m, 9 H, arom.). The 4-hydroxy resonance of (**2**) was not seen.

Partial methylation of (**2**) to give 1-(4-sulphonatophenylazo)-4-methoxy-2-naphthol (**3**) was accomplished by adding a 40-fold molar excess of dimethyl sulphate to an aqueous solution of (**2**) over 3 h. During this time, aqueous sodium hydroxide was added dropwise to the stirred solution to maintain the pH at *ca.* 9. The pH was lowered to *ca.* 7 with hydrochloric acid and the product was salted-out by addition of sodium chloride. Recrystallization from methanol gave a solid which was shown by n.m.r. to consist of a mixture of (**2**) and (**3**) in roughly equal amounts. In subsequent preparations, the proportion of (**3**) in the product mixture could not be increased. However, the acid-base dissociations of (**2**) and (**3**) in aqueous solution occur at very different pH values and it was possible to study the dissociation of (**3**) without interference from (**2**) using this impure sample.

The preparations of 1-(4-sulphonatophenylazo)naphthalene-2,6-diol (**4**) and 1-(4-sulphonatophenylazo)naphthalene-2,7-diol (**5**) were carried out by coupling diazotized sulphanilic acid (8.7 g) with naphthalene-2,6-diol (8.1 g) and naphthalene-2,7-diol (8.1 g) respectively under aqueous alkaline conditions. The solids were precipitated from the reaction solution by adjusting the pH to *ca.* 6.0 followed by addition of sodium chloride. The products were dissolved in boiling water and precipitated by adding twice the volume of ethanol. After drying, compound (**4**) was a red-brown solid (45%), m.p. 300 °C (decomp.); $\delta(Me_2SO)$ 15.67 (s, 1 H, 2-OH), 9.81 (s, 1 H, 6-OH), and 8.38—6.78 (m, 9 H, arom.); and (**5**) was a red solid (38%), m.p. 300 °C (decomp.); $\delta(Me_2SO)$ 15.86 (s, 1 H, 2-OH), 10.16 (s, 1 H, 7-OH), and 7.86—6.61 (m, 9 H, arom.).

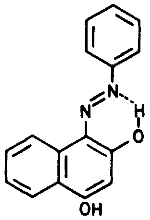
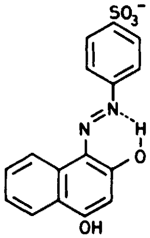
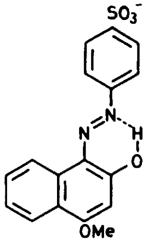
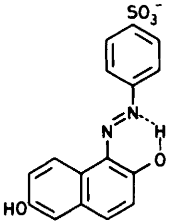
Equilibrium Measurements.—Equilibrium studies of the ionization of (**3**), the second ionization of (**1**), and the first and second ionizations of (**2**), (**4**), and (**5**) were made spectrophotometrically. The second ionizations of (**1**), (**2**), (**4**), and (**5**) correspond to dissociation of the 2-hydroxy groups.

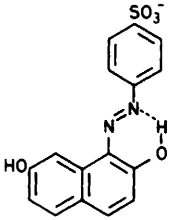
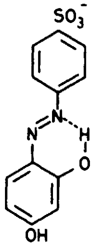
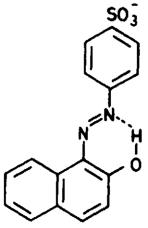
First dissociation. The first dissociation of (**2**) was studied in aqueous acetate buffer solutions; for (**4**) and (**5**), tris(hydroxymethyl)aminomethane and carbonate buffers were used. The ionic strength (I) was kept at 0.1 mol dm^{-3} by addition of potassium chloride. The position of equilibrium in equation (1)

$$R(OH)_2 + H_2O \rightleftharpoons R(OH)O^- + H_3O^+ \qquad (1)$$

for solutions containing *ca.* 1.0×10^{-4} mol dm^{-3} (**2**), (**4**), or (**5**), in the presence of various buffer ratios and thermostatically maintained at 15.0 °C, was determined from absorbance readings at 550 nm, where the undissociated acids, $R(OH)_2$, absorb strongly. Values for the molar absorptivities of $R(OH)_2$ and $R(OH)O^-$ at this wavelength were obtained from measurements in 0.001 mol dm^{-3} hydrochloric acid and in dilute sodium hydroxide solution respectively. The calculated values of $pK_1^{0.1} = -\log[R(OH)O^-][H_3O^+]/[R(OH)_2]$ are given in the Table, together with values of pK_1^0 referring to infinite dilution,

Table. Kinetic and equilibrium results for proton removal from hydroxy-azo hydrogen bonds[a,b]

		$pK_1^{0.1}$	$pK_2^{0.1}$	K^d / $dm^3\ mol^{-1}$	$k_{OH}{}^d$ / $dm^3\ mol^{-1}\ s^{-1}$	$k_{H_2O}{}^d$ / s^{-1}	$k_{OH}/k_{H_2O}{}^d$ / $dm^3\ mol^{-1}$	Solvent	T/K
(1)			> 15.6 (> 16)[e]	27.1 ± 1	$1.3 \pm 0.2 \times 10^4$	$7.1 \pm 0.6 \times 10^2$	18 ± 5	95%(v/v)Me_2SO-H_2O	288
(2)		4.73 ± 0.06 (5.21)[e]	> 15.6 (> 16)[e]	56.3 ± 2 26.0 ± 6 2.5 ± 0.3[c]	$6.5 \pm 0.7 \times 10^3$ $8.4 \pm 2 \times 10^3$ $5.1 \pm 0.4 \times 10^3$[c]	$1.6 \pm 0.3 \times 10^2$ $3.3 \pm 0.4 \times 10^2$ $2.0 \pm 0.4 \times 10^3$	41 ± 15 26 ± 5 2.6 ± 0.8[c]	95%(v/v)Me_2SO-H_2O 90%(v/v)Me_2SO-H_2O 85%(v/v)Me_2SO-H_2O	288 298 298
(3)		11.58 ± 0.02 (12.06)[e]		890 ± 40 1 500 ± 200	$4.0 \pm 0.6 \times 10^7$ $7.2 \pm 0.5 \times 10^7$	$7 \pm 2 \times 10^4$	600 ± 300	H_2O 20%(v/v) dioxane-H_2O	278 278
(4)		9.18 ± 0.06 (9.66)[e]	12.49 ± 0.05 (13.21)[e]	44.8 ± 0.8	$1.7 \pm 0.5 \times 10^6$	$3.6 \pm 0.5 \times 10^4$	47 ± 20	H_2O	288

(5)		9.02 ± 0.02 (9.50)[e]	12.37 ± 0.05 (13.09)[e]	59.4 ± 1	1.8 ± 0.3 × 10^6	3.5 ± 0.4 × 10^4	51 ± 20	H_2O	288
(6)		5.87 ± 0.05 (6.35)[e]	12.10 ± 0.05 (12.82)[e]	112 ± 5				H_2O	288
(7)		11.33 ± 0.06 (11.81)[e]		660 ± 90	6.3 ± 0.6 × 10^6	0.9 ± 0.1 × 10^4	700 ± 200	H_2O	288

[a] Results for compounds (**1**)—(**5**) were obtained in the present work and results for (**6**) and (**7**) are taken from ref. 4. [b] Ionic strength 0.1 mol dm^{-3} except where indicated otherwise. [c] Ionic strength 0.5 mol dm^{-3}. [d] For (**3**) and (**7**) values for K, k_{OH}, and k_{H_2O} refer to the first dissociation [equation (2)], and for (**1**), (**2**), (**4**), (**5**), and (**6**) the values refer to dissociation of the second proton [equation (3)]. [e] pK^0 values, referring to infinite dilution. Calculated from $pK^{0.1}$ by means of the Debye–Hückel approximation.

obtained from $pK_1^{0.1}$ using the Debye–Hückel approximation, $\log \gamma_i = -0.50Z^2I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ at ionic strength I.

The dissociation of (3), as in equation (2), was studied at 5 °C

$$\mathrm{ROH} + \mathrm{OH}^- \underset{k_{H_2O}}{\overset{k_{OH^-}}{\rightleftharpoons}} \mathrm{RO}^- + H_2O \qquad (2)$$

and ionic strength 0.1 mol dm^{-3} in the presence of sodium hydroxide in aqueous solution and in 20% dioxane–water. Absorbance measurements were taken at 520 nm where RO$^-$ absorbs strongly, for solutions containing *ca.* 2.0 × 10^{-4} mol dm^{-3} (**3**) in the presence of hydroxide ion concentrations in the range 0.001 to 0.005 mol dm^{-3} and with potassium chloride to maintain constant ionic strength. Values of the molar absorptivity of RO$^-$ and ROH at 520 nm were determined from measurements in the presence of 0.1 mol dm^{-3} NaOH and in the absence of base, respectively. The calculated values of the equilibrium constant for reaction (2) in aqueous solution and in 20% (v/v) dioxane–water are given in the Table. The result in aqueous solution was used to calculate $pK_1^{0.1}$ at ionic strength 0.1 mol dm^{-3} and this was converted into pK_1^0 at infinite dilution. The first dissociation of (**1**) could not be studied because of the low solubility of the undissociated acid.

Second dissociation. Dissociation of the second hydroxy group in (**4**) and (**5**) [equation (3)] was studied in aqueous

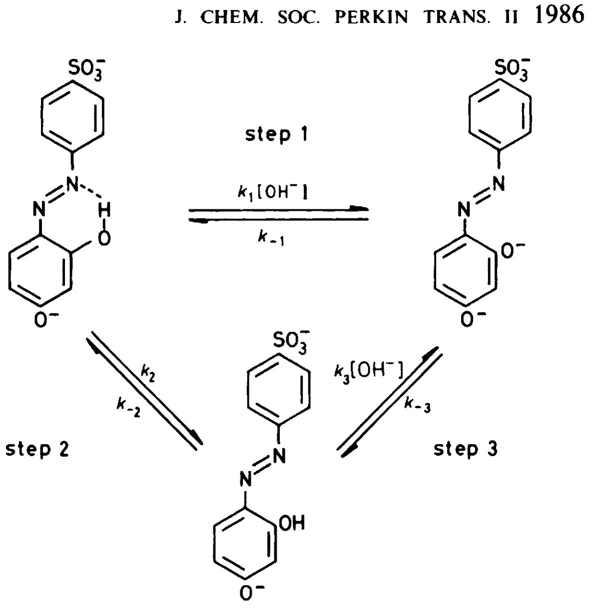
$$\mathrm{R(OH)O}^- + \mathrm{OH}^- \underset{k_{H_2O}}{\overset{k_{OH^-}}{\rightleftharpoons}} \mathrm{R(O^-)_2} + H_2O \qquad (3)$$

sodium hydroxide at 15 °C and ionic strength 0.1 mol dm^{-3}. In the case of (**1**) and (**2**) it was found that the absorbance spectra were unchanged over the range of hydroxide ion concentrations 0.001 to 1.0 mol dm^{-3} from which it was estimated that $pK_2^{0.1} >$ *ca.* 15.6. Studies of the second dissociation of (**1**) and (**2**), as in equation (3), were possible in $Me_2SO–H_2O$ mixtures containing tetramethylammonium hydroxide. The second dissociation of (**1**) was studied in 95% (v/v) $Me_2SO–H_2O$ at 15 °C and ionic strength 0.1 mol dm^{-3}, maintained by addition of tetramethylammonium chloride. For (**2**), measurements were made in 85, 90, and 95% (v/v) $Me_2SO–H_2O$.

Absorbance readings (A) for solutions containing *ca.* 3 × 10^{-5} mol dm^{-3} (**1**) and (**2**) in the presence of various concentrations of hydroxide ion were taken at 510 and 520 nm respectively, where the dianions R(O$^-$)$_2$ absorb strongly. The absorbances $A_{R(OH)O^-}$ for solutions with (**1**) and (**2**) in the form R(OH)O$^-$ were obtained from measurements in 0.001 mol dm^{-3} hydroxide ion. It was not possible to find conditions under which (**1**) and (**2**) were fully dissociated into R(O$^-$)$_2$ so that a value for the absorbance $A_{R(O^-)_2}$ could not be measured. A value for the equilibrium constant (K) for reaction (3), involving (**1**) and (**2**), was therefore obtained as the gradient of a plot of $\{A_{R(OH)O^-} - A\}/[OH^-]$ against A, as in equation (4), and the results are given in the Table.

$$\{A_{R(OH)O^-} - A\}/[OH^-] = KA - KA_{R(O^-)_2} \qquad (4)$$

For solutions of (**4**) and (**5**) at concentrations of *ca.* 5 × 10^{-5} mol dm^{-3}, absorbance readings (A) were taken in aqueous solution in the presence of hydroxide ion (0.005 to 0.1 mol dm^{-3}) at 420 and 490 nm, respectively, where the species R(OH)O$^-$ absorb strongly. The absorbances $A_{R(O^-)_2}$ and $A_{R(OH)O^-}$ were obtained from measurements in the presence of 1 mol dm^{-3} sodium hydroxide and at low concentration of sodium hydroxide, respectively. Values of the equilibrium constant for reaction (3) involving (**4**) and (**5**) were calculated at each hydroxide ion concentration and the average values are given in the Table. These results were used to obtain $pK_2^{0.1}$ and pK_2^0.



Scheme.

Kinetic Measurements.—Kinetic studies of proton removal from (**3**) and of removal of the second proton from (**1**), (**2**), (**4**), and (**5**) by hydroxide ion were carried out under the same conditions as the equilibrium measurements. The temperature-jump technique was used. Following a rapid temperature perturbation, relaxation to the new equilibrium position was observed spectrophotometrically at the same wavelengths as those used for the equilibrium studies. The magnitudes of the temperature jumps were typically *ca.* 3 °C and the reaction temperatures are given in the Table. In all cases the reciprocal relaxation time (τ^{-1}) was found to be a linear function of hydroxide ion concentration as in equation (5). The rate

$$\tau^{-1} = k_{OH^-}[OH^-] + k_{H_2O} \qquad (5)$$

coefficients k_{OH^-} and k_{H_2O}, which refer to equilibrium (2) for compound (**3**) and to equilibrium (3) for (**1**), (**2**), (**4**), and (**5**), were determined as the gradient and intercept, respectively, of plots of τ^{-1} against [OH$^-$]. It was found that, within experimental error, the values of k_{OH^-}/k_{H_2O} for each compound were in agreement with the values of the equilibrium constants K determined in separate equilibrium studies. The results are given in the Table.

Discussion

The values of pK_1^0 and pK_2^0 in the Table give an indication of the strengths of the hydroxy–azo hydrogen bonds in these compounds. For 4-(4-sulphonatophenylazo)resorcinol (**6**) the difference $pK_2^0 - pK_1^0 = 6.5$ is much larger than the value (2.1) found for resorcinol.[6] For (**6**), the pK_1^0 value refers to dissociation of the 4-OH. The product of the first dissociation is stabilized by an intramolecular hydrogen bond which is stronger than the hydrogen bond in (**6**) itself because of inductive and conjugative electron release from the ionized 4-OH. This has the effect of decreasing the value of pK_1^0 and increasing the value of pK_2^0. The intramolecular hydrogen bond in the products of the first dissociation of (**1**) and (**2**) is even stronger and leads to $pK_2^0 > 16$. To observe the second dissociation of (**1**) and (**2**) it was necessary to use extremely basic $Me_2SO–H_2O$ mixtures containing hydroxide ion.[7] In the first dissociation product of (**4**) and (**5**) the effect of the ionized hydroxy group on the hydrogen-bond strength is small and the pK_1^0 and pK_2^0 values for (**4**) and (**5**) are less unusual than the

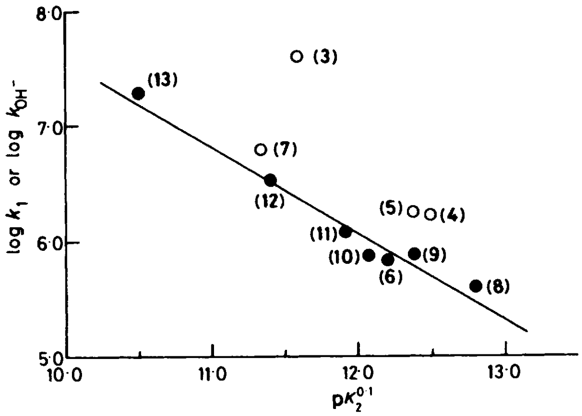


Figure. Plots of log k_1 against $pK_2^{0.1}$ (solid circles) for 4-(4-sulphonatophenylazo)resorcinol (**6**);[2b] 2,4-bis(phenylazo)resorcinol (**8**);[2e] 4-phenylazoresorcinol (**9**);[2b] 4-(4-nitrophenylazo)resorcinol (**10**);[2b] 4-(3-nitrophenylazo)resorcinol (**11**);[2b] 2-methyl-4,6-bis(phenylazo)resorcinol (**12**);[2e] and 4,6-bis(phenylazo)resorcinol (**13**);[2e] and of log k_{OH} against $pK_2^{0.1}$ (open circles) for (**3**), (**4**), (**5**), and (**7**) (see Table)

results for (**1**) and (**2**). The pK_2^0 values are not very different from the pK_1^0 values of (**3**) and (**7**).

The minimum in τ^{-1} against $[OH^-]$ which has been found for the equilibration between the monoanions and dianions of several substituted phenylazoresorcinols, such as (**6**), has been explained[2] by the mechanism in the Scheme. Attack of hydroxide ion on the hydrogen-bonded proton (step 1) occurs in parallel with attack of hydroxide ion on an open form of the monoanion (steps 2 and 3). The mechanism is compatible with the observed minimum in τ^{-1}, providing the open form is present in low concentration and the conditions $k_3[OH^-] > k_{-2}$ and $k_1[OH^-] \sim k_2$ are satisfied. Equation (6), in which K is

$$\tau^{-1} = (k_1[OH^-] + k_2)(1 + 1/K[OH^-]) \qquad (6)$$

the overall equilibrium constant ($K = k_1/k_{-1} = k_2k_3/k_{-2}k_{-3}$) then applies. Seven examples of substituted phenylazoresorcinol monoanions are known for which a minimum in τ^{-1} is observed. In each case proton removal occurs from an intramolecular phenol–azo hydrogen bond which is stabilized by an ionized hydroxy substituent in the phenol ring. In one other example, 1-phenylazo-2-naphthol (**7**), where the ionized hydroxy substituent is absent, a linear dependence of τ^{-1} on hydroxide ion concentration was found.[4]

For species (**1**)—(**5**) a linear dependence of τ^{-1} against $[OH^-]$ was observed for the equilibrium with hydroxide ion involving removal of the hydrogen-bonded proton. In the case of (**1**), (**2**), (**4**), and (**5**) the equilibrium corresponds to the second dissociation, as in equation (3). For (**3**) there is a single ionizable proton and the equilibrium in equation (2) is involved. The observation of a linear dependence of τ^{-1} on $[OH^-]$ for compounds (**1**)—(**5**) means that the conditions $k_3[OH^-] > k_{-2}$ and $k_1[OH^-] \sim k_2$ are not both satisfied in these cases. A linear dependence is predicted if reaction occurs predominantly by step 1 ($k_1[OH^-] > k_2$). Equation (7) is then obtained and the

$$\tau^{-1} = k_1[OH^-] + k_{-1} \qquad (7)$$

measured rate coefficients [see equation (5)] are $k_{OH^-} = k_1$ and $k_{H_2O} = k_{-1}$. Alternately if $k_{-2} > k_3[OH^-]$ and $k_1 < k_2k_3/k_{-2}$, a linear dependence of τ^{-1} on $[OH^-]$ is predicted for reaction by steps 2 and 3, as in equation (8), and

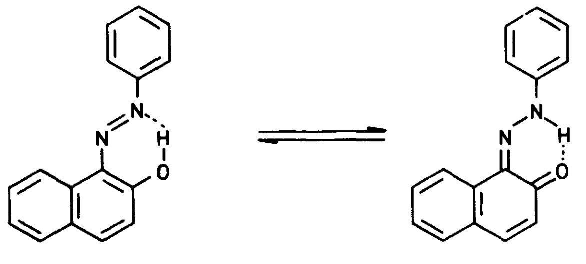
$$\tau^{-1} = k_2k_3[OH^-]/k_{-2} + k_{-3} \qquad (8)$$

the measured rate coefficients are then $k_{OH^-} = k_2k_3/k_{-2}$ and $k_{H_2O} = k_{-3}$. Equations (7) and (8) both provide satisfactory explanations for the kinetic behaviour of compounds (**1**)—(**5**) and on the basis of the present results these two possibilities cannot be distinguished.

The lowest rates of proton removal are observed for (**1**) and (**2**). The exceptionally high values of pK_2^0 suggest that the intramolecular hydrogen bonds in the first dissociation products of (**1**) and (**2**) are exceptionally strong and this is confirmed by the low rates of proton removal. The hydrogen bond is strengthened by the inductive and conjugative effects of the ionized 4-hydroxy substituent and when these effects are absent, as in (**3**), the hydrogen-bonded proton is much more reactive. The results for (**3**), (**4**), and (**5**) are quite similar to those for (**7**). In (**5**), conjugation of the ionized hydroxy group with the phenylazo group is possible but appears to have little effect on the strength of the hydrogen bond since the rate coefficient and pK_2^0 value for (**5**) are almost identical with those for (**4**), in which conjugation cannot occur.

Values have been obtained[2] for the rate coefficient (k_1) for direct attack of hydroxide ion on the hydrogen-bonded proton in seven phenylazoresorcinols which gave kinetic data described by equation (6). In the Figure the values of log k_1 and $pK_2^{0.1}$ for these phenylazoresorcinols are shown as the solid data points. The results were mostly obtained in aqueous solution at ionic strength 0.1 mol dm^{-3} and 15 °C. In some cases it was necessary to make small adjustments to correct the experimental results to these conditions. It would be expected that as the hydrogen-bond strength increases along this series the value of log k_1 would decrease and the value of $pK_2^{0.1}$ would increase. The value of the gradient (-0.75) of the line through the points indicates that a given substituent has an effect on log k_1 which is $\frac{3}{4}$ of the effect on the value of $pK_2^{0.1}$. The values of log k_{OH^-} for compounds (**3**), (**4**), (**5**), and (**7**) are plotted in the Figure as open circles. The data for (**1**) and (**2**) cannot be included because of the different reaction conditions which were needed. However, the results for (**1**) and (**2**) fit in qualitatively with those for (**3**), (**4**), (**5**), and (**7**), since (**1**) and (**2**) give the lowest values of log k_{OH^-} and the largest values of $pK_2^{0.1}$. According to equations (7) and (8), k_{OH} for (**3**), (**4**), (**5**), and (**7**) may correspond with the rate coefficient k_1 or with k_2k_3/k_{-2}. If k_{OH^-} for (**3**), (**4**), (**5**), and (**7**) refers to the rate coefficient k_1 for direct attack by hydroxide ion on the hydrogen-bonded proton, it might be expected that the points for (**3**), (**4**), (**5**), and (**7**) in the Figure (open circles) would fit the same correlation of rate with pK as the seven phenylazoresorcinols (solid circles) for which values of k_1 were obtained from the kinetic data. If k_{OH^-} for (**3**), (**4**), (**5**), and (**7**) corresponds to k_2k_3/k_{-2}, some deviation between the two sets of data might be anticipated. However, the results do not deviate sufficiently to permit a firm conclusion to be reached. The decreasing values of k_{OH^-} along the series (**3**) > (**7**) > (**5**) ~ (**4**) > (**1**) > (**2**) roughly correlate with the order of increasing pK values and this can be accounted for by equation (7) or (8) in terms of increasing strength of the intramolecular hydrogen bond.

The potential-energy function of the intramolecular hydrogen bond in 1-phenylazo-2-naphthols is almost certainly of the double-minimum type, with the minima corresponding to the species (A) and (B). Many techniques[8] have been used to investigate the relative contributions of (A) and (B), as this provides information about the shape of the potential function. For example,[9] the occurrence of a band in the visible spectrum at *ca.* 420 nm has been taken as evidence for (A), whereas an absorbance at *ca.* 460 nm is thought to be characteristic of (B). We have examined the possibility that the differences in proton-transfer behaviour of the various phenylazoresorcinols may be correlated with information about the shape of the potential function of the hydrogen bond. It is interesting that of the



(A) (B)

1-phenylazo-2-naphthols for which we have obtained kinetic and spectral data, (**3**) shows an absorbance at $\lambda_{max.}$ *ca.* 440 nm, whereas (**4**), (**5**), and (**7**) have $\lambda_{max.}$ *ca.* 485 nm. This suggests that the contribution from (A) may be greater in the case of (**3**) than for (**4**), (**5**), and (**7**) and, as seen in the Figure, the rates of proton transfer for (**3**) are anomalously high as compared with those for (**4**), (**5**), and (**7**). However, it is likely that the phenylazo-resorcinols (**6**) and (**8**)—(**13**) (see Figure) exist largely in the hydroxy-azo form but the rates of proton transfer for these species are more similar to the data for (**4**), (**5**), and (**7**) than for (**3**). A possible correlation of proton-transfer behaviour with other probes of the potential function will be considered in future work.

Acknowledgements

We thank Dr. P. J. Taylor (I.C.I. Pharmaceuticals Division) for discussions.

References

1 A. J. Kresge, *Acc. Chem. Res.*, 1975, **8**, 354; F. Hibbert, *ibid.*, 1984, **17**, 115.
2 (*a*) B. Perlmutter-Hayman and R. Shinar, *Int. J. Chem. Kinet.*, 1975, 7, 453; (*b*) B. Perlmutter-Hayman, R. Sarfaty, and R. Shinar, *ibid.*, 1976, **8**, 741; (*c*) B. Perlmutter-Hayman and R. Shinar, *ibid.*, 1977, **9**, 1; (*d*) N. Yoshida and M. Fujimoto, *Chem. Lett.*, 1977, 1301; (*e*) F. Hibbert and G. R. Simpson, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1247.
3 N. E. Briffett, F. Hibbert, and R. J. Sellens, *J. Chem. Soc.*, 1985, **107**, 6712.
4 F. Hibbert and G. R. Simpson, *J. Chem. Soc., Perkin Trans. 2*, 1986, 985.
5 A. Inoue, N. Kuroki, and K. Konishi, *Yûki Gôsei Kagaku Kyôkaishi*, 1959, **17**, 714 (*Chem. Abstr.*, 1960, **54**, 4504h).
6 E. P. Serjeant and B. Dempsey, 'Ionisation Constants of Organic Acids in Aqueous Solution,' Pergamon, Oxford, 1979.
7 D. Dolman and R. Stewart, *Can. J. Chem.*, 1967, **45**, 911; C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.
8 A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, *J. Chem. Soc. B*, 1968, 1308.
9 A. Buraway, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 1952, 4793.

Received 3*rd January* 1986; *Paper* 6/023