Kinetic Studies of the Deprotonation of Bis(phenylazo)resorcinol Monoanions by Hydroxide Ion

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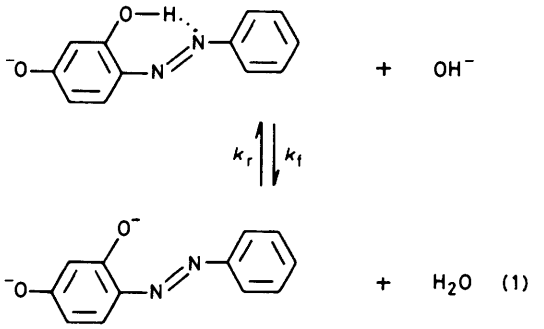
Interconversion of the intramolecularly hydrogen-bonded monoanions of 2,4-bis(phenylazo)resorcinol, 4,6-bis(phenylazo)resorcinol, and 2-methyl-4,6-bis(phenylazo)resorcinol with the corresponding dianions in the presence of hydroxide ion in aqueous solution or in 20% dioxane–water (v/v) gives complex kinetic behaviour in which the reciprocal relaxation time for the process goes through a minimum value as the hydroxide ion concentration is increased. The results are used to provide a choice between two proposed mechanisms for the similar behaviour of monophenylazoresorcinols. It is argued that the behaviour of monophenylazoresorcinols and bis(phenylazo)resorcinols is compatible with a mechanism for the interconversion of the monoanions and dianions by two simultaneous pathways. One path involves direct attack by hydroxide ion on the hydrogen-bonded proton and in the other path the hydrogen-bonded monoanion is converted into a non-hydrogen-bonded open form from which the proton is removed by hydroxide ion. Values of the rate coefficients for some of these steps are deduced from the kinetic results.

Proton removal from intramolecularly hydrogen-bonded acids is usually considered to occur either by direct single-step attack by base on the hydrogen-bonded proton or by a two-step process through a low concentration of a non-hydrogen-bonded species from which the proton is removed by base.[1] Reaction by the two-step mechanism will be of the first order in base provided the rate at which the non-hydrogen-bonded open form reverts back to the hydrogen-bonded species is greater than the rate at which a proton is removed by base from the open form. Definite evidence for the operation of this mechanism has been obtained by studying general base catalysis in proton transfer from salicylate ion[2] and in proton transfer involving diaminonaphthalenes.[3] Many results which in the past have been explained in terms of direct attack on the hydrogen-bonded proton can usually, equally well, be explained by the two-step mechanism[4] and positive results in favour of direct attack have been difficult to obtain. However, quite recently, results for proton removal by hydroxide ion from intramolecularly hydrogen-bonded phenylazoresorcinol monoanions, equation (1), have been explained in terms of a mechanism involving

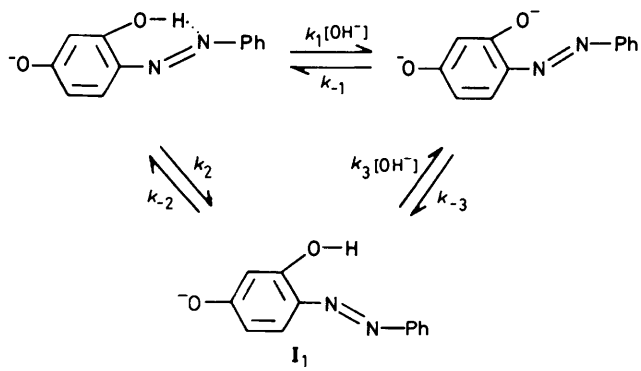


(1)

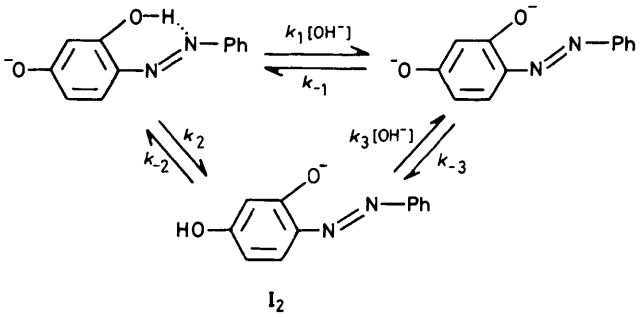
direct attack on a hydrogen-bonded proton.[5,6] The major evidence[5] consisted in the demonstration of a complex dependence of the rate of reaction on the concentration of hydroxide ion. The expected dependence of the reciprocal relaxation time on hydroxide ion concentration for an equilibrium of the type in equation (1) is given in equation (2).

$$\tau^{-1} = k_f[OH^-] + k_r \qquad (2)$$

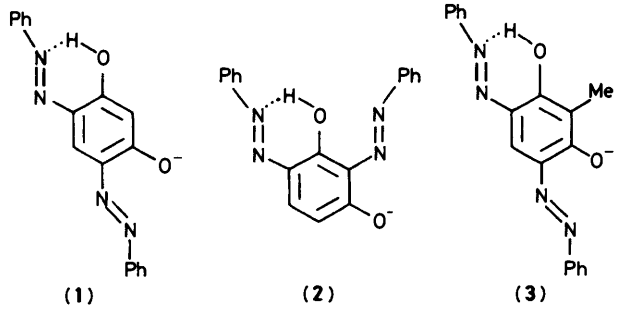
However for the equilibration between the monoanions and dianions of substituted phenylazoresorcinols in the presence of hydroxide ion, the reciprocal relaxation time was found to go through a minimum value[5,7] as the hydroxide ion concentration was varied. In earlier work with substituted phenylazoresorcinol monoanions the minimum in τ^{-1} was not detected and a linear dependence of τ^{-1} on $[OH^-]$ was observed.[8] To explain the minimum in τ^{-1} the mechanism in Scheme 1 was suggested[5,6] in which the upper route involves direct attack and the lower route consists of two-step proton removal. However, an alternative mechanism which does not necessarily involve direct attack on the hydrogen-bonded proton has been suggested[7] to account for the complex rate dependence, Scheme 2. This scheme proposes a tautomeric form of the monoanion in which the hydrogen-bonded proton is relocated at a site where it is unable to participate in intramolecular hydrogen bonding. This species could be formed *via* the conjugate acid and has been postulated as an intermediate in metal ion complex formation.[9] The upper route in Scheme 2 is of the first order in hydroxide ion and either direct attack by hydroxide ion on the hydrogen-bonded proton or two-step proton removal through an open form would give the necessary first-order dependence. In the original publication[7] in which Scheme 2 was proposed, the precise mechanism of the upper route was not specified.



Scheme 1.



Scheme 2.



It is noteworthy that for all the intramolecularly hydrogen-bonded hydroxy-azo compounds for which a complex rate dependence has been observed, an ionised hydroxy group is present in the molecule in a position *para* to the azo group. An ionised hydroxy group is required for the operation of Scheme 2 and an obvious way to eliminate Scheme 2 from consideration is to find a complex rate dependence for a hydroxy-azo compound which does not possess an ionised hydroxy group. Our attempts to find such dependence have been unsuccessful and for hydroxy-azo compounds without an additional ionisable hydroxy group, a linear dependence of rate on hydroxide ion concentration, as in equation (2), has been observed.[10] We have attempted to devise an alternative experiment which will distinguish between Schemes 1 and 2 and we now report studies with the bis(phenylazo)resorcinol monoanions (**1**), (**2**), and (**3**) which do provide some additional evidence. These phenylazoresorcinols are of particular interest because it is not possible to draw tautomeric forms of (**1**), (**2**), and (**3**) in which the proton is relocated in a site where it is unable to participate in an intramolecular hydrogen bond. This means that if Scheme 2 is written for (**1**), for example, the intermediate corresponding to I_2 is either identical with the original monoanion and cannot therefore be considered as an intermediate in the proton-transfer mechanism, or is identical with an open non-hydrogen-bonded form of the original monoanion. In the latter case Schemes 1 and 2 become very similar. In this way it was hoped to provide experimental results which have a bearing on the choice between Schemes 1 and 2. Our initial studies with (**1**) and (**2**) in aqueous solution have been published[11] and we now present a full report of this work. We have extended the studies with (**1**) to 20% dioxane–water (v/v) which proved to be a more suitable solvent and we have also studied 2-methyl-4,6-bis(phenylazo)resorcinol monoanion (**3**). The reasons why it was important to study (**3**) will be made clear.

Experimental

Materials.—4,6-Bis(phenylazo)resorcinol (**1**) and 2,4-bis-(phenylazo)resorcinol (**2**) were prepared[12] by coupling benzenediazonium chloride with resorcinol in a 2:1 molar ratio under alkaline conditions. After a reaction time of 10 min the pH of the solution was lowered to *ca.* 2.0. The solid product mixture which precipitated was separated on an alumina column with chloroform as eluant. 2,4-Bis(phenylazo)resorcinol was contained in the first fraction from the column and was obtained as an orange solid (yield 7%); m.p. 216 °C; $\delta_H(CDCl_3)$ 16.51 (s, OH), 15.61 (s, OH), 7.6—6.3 (m, 12 H, ArH). 4,6-Bis(phenylazo)resorcinol was isolated as a brown solid from the second fraction (yield 3%); m.p. 212 °C; $\delta_H(CDCl_3)$ 13.99 (s, 2 OH), 8.5—6.5 (m, 12 H, ArH). 2-Methyl-4,6-bis(phenylazo)resorcinol (**3**) was prepared from benzenediazonium chloride and 2,6-dihydroxytoluene using a similar procedure. The product was a deep red solid (yield 9%); m.p. 169 °C; $\delta_H(CDCl_3)$ 14.38 (s, 2 OH), 8.4—7.3 (m, 11 H, ArH), 2.2 (s, CH_3).

Dioxane (AnalaR) was refluxed with sodium and distilled under nitrogen. Reaction solutions were made up from standard carbon dioxide-free sodium hydroxide solutions using doubly distilled water and the ionic strength was adjusted by addition of potassium chloride.

Kinetic Measurements.—Relaxation times for the equilibration between the monoanions and dianions were determined using the temperature-jump technique. For reactions in aqueous solution the equilibrium position was disturbed by a temperature jump of 3.3 °C obtained by a 35 kV discharge from a 0.01 μF capacitor. In 20% dioxane–water (v/v) the temperature jump was 4.8 °C. The resulting chemical relaxations were observed spectrophotometrically and the data of absorbance against time were stored using a transient recorder (Physical Data Incorporated). The data were then either plotted using a pen recorder and analysed in the normal way or processed by an on-line Apple II microcomputer.[13] At least five determinations of the relaxation time were made for each solution and the average deviation from the mean was *ca.* 5%.

Results

Equilibrium Measurements.—Values of the equilibrium constants for dissociation of the monoanions (**1**), (**2**), and (**3**) to the dianions in the presence of hydroxide ion, equation (3), were

$$ROH^- + OH^- \rightleftharpoons RO^{2-} + H_2O \qquad (3)$$

determined from spectrophotometric measurements under various conditions (Table). Dissociation of 4,6-bis(phenylazo)resorcinol monoanion (**1**) was studied in aqueous solution in the presence of sodium hydroxide (0.001—0.0025 mol dm^{-3}) and in the presence of carbonate buffers. In 20% dioxane–water (v/v) slightly higher concentrations of hydroxide ion are needed for the ionisation of (**1**) and in this solvent the equilibrium was studied in the presence of sodium hydroxide (0.00075—0.004 mol dm^{-3}). For (**2**) and (**3**) the equilibrium was studied in aqueous solution or in 20% dioxane–water (v/v) containing sodium hydroxide. The bis(phenylazo)resorcinols (**1**) and (**3**) were present at low concentrations in aqueous solution (*ca.* 5×10^{-6} mol dm^{-3}) because of limited solubility, and optical cells of 4 cm path length were used. For (**2**) in aqueous solution and for (**1**) and (**3**) in 20% dioxane–water (v/v) higher concentrations (*ca.* 3×10^{-5} mol dm^{-3}) were used. Under all conditions the equilibrium position was observed spectrophotometrically at a wavelength in the range 510—580 nm where the dianions absorb more strongly than the monoanions. For example with (**2**) in aqueous solution at 15 °C, measurements were made at 510 nm where the molar absorptivities ε_{ROH^-} and $\varepsilon_{RO^{2-}}$ have values of 7.3×10^3 and 2.8×10^4 cm^{-1} mol^{-1} dm^3, respectively. Absorbance readings were taken over a range of hydroxide ion concentrations and values of the

Table. Kinetic and equilibrium studies of the monoanion to dianion equilibrium: $K = [RO^{2-}]/[ROH^{-}][OH^{-}]$; k_1 and k_2 refer to rate coefficients in Scheme 4

					Experimental conditions		
Monoanion	pK_a	K/dm^3 mol^{-1}	$10^{-5}k_1$/dm^3 mol^{-1} s^{-1}	$10^{-4}k_2$/s^{-1}	Ionic strength (mol dm^{-3})	T/°C	Solvent
(1)	11.3 ± 0.1[a]						
		4 600 ± 500	190 ± 20	2.0 ± 0.3	0.1	15	aqueous
		6 500 ± 500	195 ± 20	1.6 ± 0.2	0.2	5	aqueous
		2 300 ± 300	25 ± 3	2.3 ± 0.2	0.1	5	20% (v/v) dioxane–H_2O
(2)	13.6 ± 0.1[a]						
		24.5 ± 1	4.0 ± 0.5	1.6 ± 0.3	0.2	15	aqueous
		32.0 ± 2	4.1 ± 0.2	0.74 ± 0.1	0.2	5	aqueous
(3)	12.2 ± 0.1[a]						
		720 ± 20			0.2	5	aqueous
		209 ± 15	4.5 ± 0.7	1.2 ± 0.2	0.1	5	20% (v/v) dioxane–H_2O

[a] Infinite dilution, 5 °C.

equilibrium constant for reaction (3) were calculated, where possible, using the expression $K = (A - A_{ROH^-})/(A_{RO^{2-}} - A)[OH^-]$ in which A is the absorbance of a solution containing a particular concentration of sodium hydroxide and A_{ROH^-} and $A_{RO^{2-}}$ are absorbances of solutions in which the bis(phenylazo)resorcinols are completely in the monoanion and dianion forms, respectively. In some cases the values of A_{ROH^-} and $A_{RO^{2-}}$ were obtained from measurements with solutions containing low or high concentrations of sodium hydroxide. In most cases, however, attempts to obtain the spectrum of the monoanion in solutions containing low concentrations of sodium hydroxide resulted in precipitation of the bis(phenylazo)resorcinols. In these cases the value of the equilibrium constant for the monoanion–dianion equilibrium, equation (3), was obtained as the gradient of the linear plot of A against $[OH^-](A_{RO^{2-}} - A)$. The values of the equilibrium constants for equation (3) involving (**1**), (**2**), and (**3**) are given in the Table. The use of dioxane–water as solvent reduces the value of the equilibrium constant obtained in aqueous solution, which means that in dioxane–water the reaction can be studied in a more convenient range of hydroxide ion concentrations. In addition, higher concentrations of the bis(phenylazo)resorcinols could be used in this solvent.

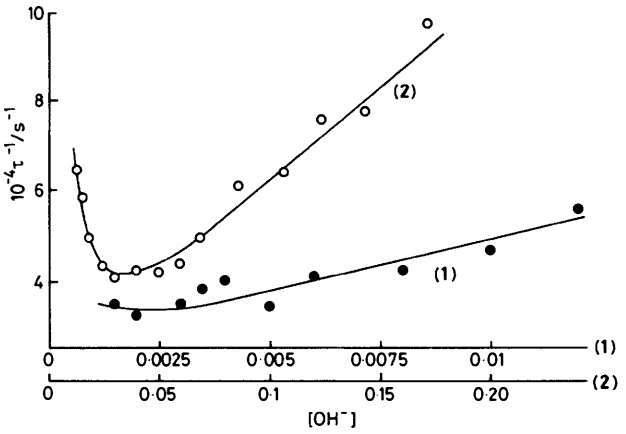


Figure 1. Variation of reciprocal relaxation time with hydroxide ion concentration for the equilibration between the monoanions of 2,4-bis(phenylazo)resorcinol (**2**) and 4,6-bis(phenylazo)resorcinol (**1**) and the corresponding dianions in aqueous solution and 20% dioxane–water (v/v), respectively. The circles are experimental values and the solid lines are best-fits of equation (5)

Kinetic Measurements.—The temperature-jump technique was used to determine chemical relaxation times for the equilibration between the monoanions (**1**), (**2**), and (**3**) and the corresponding dianions in the presence of varying concentrations of sodium hydroxide. The shift in equilibrium position towards the monoanion following a temperature jump was observed spectrophotometrically. The most suitable wavelength was found to coincide with that used for the equilibrium measurements, *ca.* 510—580 nm, where the dianions absorb more strongly. A decrease in absorbance was then observed following the temperature jump. Some relaxations were also monitored by observing the increase in absorbance at a wavelength at which the monoanion absorbs more strongly than the dianion. The bis(phenylazo)resorcinols were present in deficit compared with hydroxide ion; for (**1**) and (**3**) concentrations *ca.* 5×10^{-5} mol dm^{-3} were used, and for (**2**) the concentration was varied in the range 1—5×10^{-4} mol dm^{-3}. The hydroxide ion concentration was varied over the widest possible range for which a measurable relaxation was observed.

The dependence of reciprocal relaxation time on hydroxide ion concentration was investigated under various experimental conditions (Table). With (**2**) in aqueous solution and (**3**) in 20% dioxane–water (v/v) the reciprocal relaxation time was found to pass through a minimum value and data referring to 2,4-bis(phenylazo)resorcinol (**2**) in aqueous solution at 5.0 °C and ionic strength 0.2 mol dm^{-3} and to 2-methyl-4,6-bis(phenylazo)resorcinol (**3**) in 20% dioxane–water (v/v) at 5.0 °C and ionic strength 0.1 mol dm^{-3} are given in Figures 1 and 2, respectively. With 4,6-bis(phenylazo)resorcinol (**1**) in aqueous solution the value of the reciprocal relaxation time was found to increase as the hydroxide ion concentration was increased but in 20% dioxane–water (v/v) at 5 °C and ionic strength 0.1 mol dm^{-3} the results appear to approach a minimum value at the

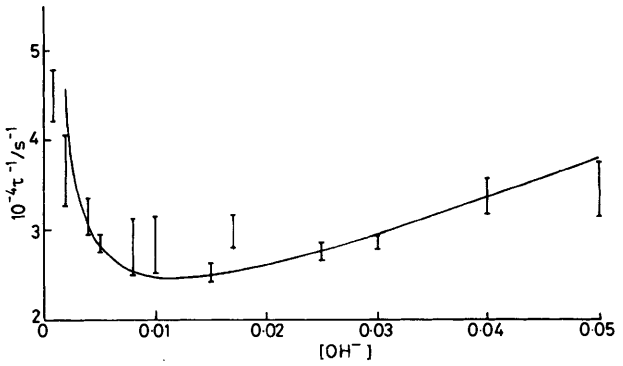


Figure 2. Variation of reciprocal relaxation time with hydroxide ion concentration for the monoanion–dianion equilibrium of 2-methyl-4,6-bis(phenylazo)resorcinol in 20% dioxane–water (v/v). The solid line is a best-fit of equation (5) through the experimental values

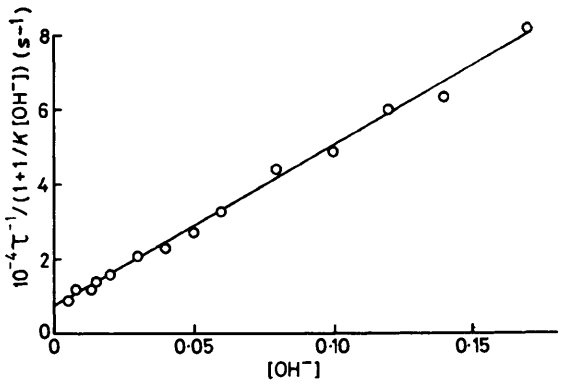


Figure 3. Kinetic data for 2,4-bis(phenylazo)resorcinol in aqueous solution plotted according to equation (5) using the experimental value $K = 32.0\ dm^3\ mol^{-1}$

lowest accessible hydroxide ion concentration and these data are shown in Figure 1.

The total change in absorbance following a temperature jump (relaxation amplitude) was measured at different hydroxide ion concentrations for (**1**), (**2**), and (**3**) under all reaction conditions. For an equilibrium of the type in equation (3) under our experimental conditions the dependence of relaxation amplitude on hydroxide ion concentration is expected to follow equation (4), which predicts that the amplitude passes through a maximum value at $[OH^-] = 1/K$, corresponding to half-dissociation of the monoanion. In all cases the experimental data were well fitted by equation (4) using an experimental value for the equilibrium constant (K) and a fitted value for the constant B.

$$\text{amplitude} = B \times [OH^-]/(1 + K[OH^-])^2 \qquad (4)$$

Discussion

The kinetic and equilibrium results presented in this work refer to the second dissociation of the bis(phenylazo)resorcinols. Under our conditions the first dissociation could not be studied because of the extremely low solubility of the undissociated acids. The pK_a values given in the Table were calculated from the values of the equilibrium constants for equation (3), using the Debye–Hückel approximation to correct to infinite dilution. We have assumed that the first and second dissociations of 2,4-bis(phenylazo)resorcinol correspond to proton loss from the 1- and 3-hydroxy groups, respectively, so that the monoanion has structure (**2**). The 3-hydroxy group is considered to be less acidic because the adjacent phenylazo groups may inhibit solvation of the phenolate ion. This is suggested by analogy with 2,6-di-t-butylpyridinium ion, which is thought to show increased acidity compared with pyridinium ion because of a steric effect to solvation of the protonated amine.[14] The pK_a value of 4,6-bis(phenylazo)resorcinol monoanion is very similar to the second pK value (*ca.* 11.2[15]) of resorcinol and represents a balance between the electron-withdrawing effect of the phenylazo substituents and the effect of the intramolecular hydrogen bond.

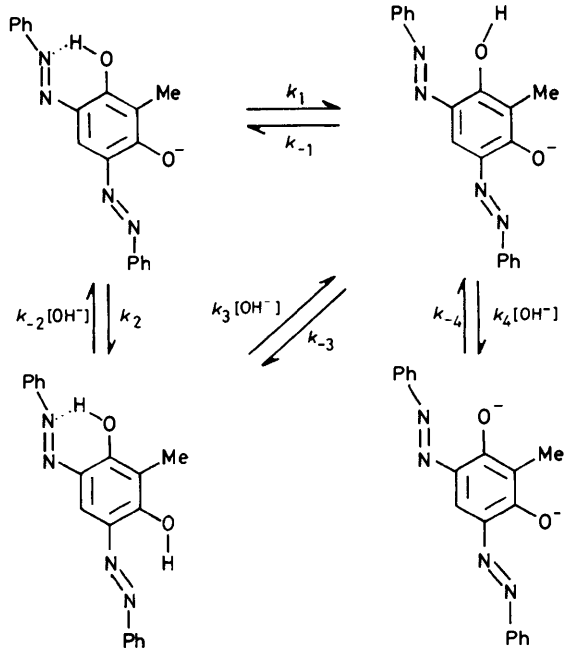
Our studies of the kinetics of proton removal from the bis(phenylazo)resorcinol monoanions (**1**), (**2**), and (**3**) were designed to provide evidence for a choice between Schemes 1 and 2, which have been proposed[5,7] to account for the complex rate dependence for proton removal by hydroxide ion from substituted phenylazoresorcinol monoanions. A similar complex dependence of the reciprocal relaxation time on hydroxide ion concentration is observed for the ionisation of (**2**) and (**3**) and we will consider the additional evidence provided by these results. The dependence of reciprocal relaxation time on hydroxide ion concentration for reaction through Schemes 1 and 2 is given by equation (5) in which K is the value of the equilibrium constant of the reaction. To derive equation (5) it is necessary to assume that the rate of proton removal from the low-concentration intermediates I_1 and I_2 is greater than the rate at which the intermediates revert to the hydrogen-bonded monoanions ($k_3[OH^-] > k_{-2}$). According to equation (5), a

$$\tau^{-1} = (k_2 + k_1[OH^-])(1 + 1/K[OH^-]) \qquad (5)$$

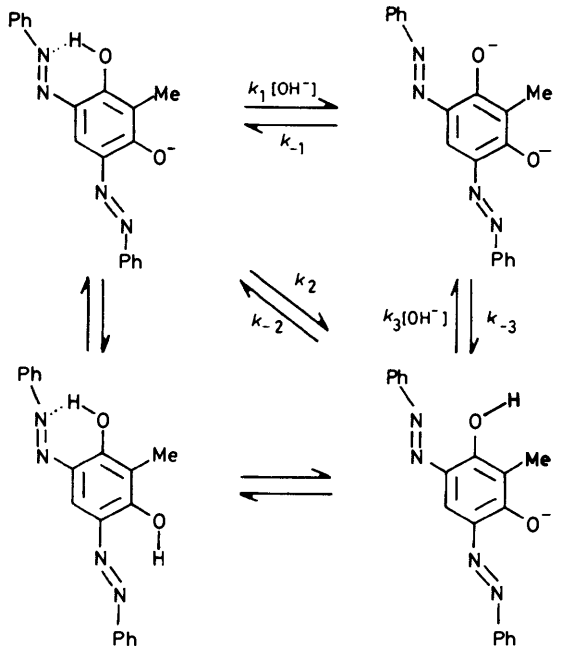
minimum in τ^{-1} is predicted to occur at $[OH^-] = (k_2/Kk_1)^{\frac{1}{2}}$. A linear dependence of τ^{-1} on $[OH^-]$ of the type shown in equation (2) will arise either if $k_2 < k_1[OH^-]$ corresponding to reaction predominantly by the upper route in Scheme 1 or if $k_1[OH^-] < k_2$ and $k_{-2} > k_3[OH^-]$, which corresponds to two-step reaction as in the lower routes of Scheme 1 and 2. Equation (5) predicts that a plot of $\tau^{-1}/(1 + 1/K[OH^-])$ against $[OH^-]$ will be linear with slope k_1 and intercept k_2. The data for 2,4-bis(phenylazo)resorcinol monoanion were plotted in this way (Figure 3) using a value for K determined from separate equilibrium measurements. The data for 2-methyl-4,6-bis-(phenylazo)resorcinol monoanion were treated similarly and the calculated values of k_1 and k_2 for both compounds are given in the Table. The solid lines in Figures 1—3 were constructed using these values of k_1 and k_2 together with values for K determined from separate equilibrium measurements.

Scheme 1 provides a satisfactory explanation of the kinetic results for (**2**) and (**3**). In Scheme 1 the rate coefficient k_1 refers to direct single-step attack by hydroxide on the hydrogen-bonded proton. If Scheme 2 is considered for the ionisation of 2-methyl-4,6-bis(phenylazo)resorcinol monoanion it is seen that the intermediate corresponding to I_2 formed by the protonation-deprotonation steps in Scheme 2 is identical with the open form of 2-methyl-4,6-bis(phenylazo)resorcinol monoanion.* In the original publication in which Scheme 2 was proposed[7] the mechanism of proton removal in the upper route was not specified and may be considered to occur either by direct attack on the hydrogen-bonded proton or by two-step reaction involving reversible formation of a low concentration of the open form from which a proton is removed. If the upper route is

* The protonation–deprotonation sequence could lead to a hydrogen-bonded monoanion but since this species is identical with the reactant it cannot be considered as an intermediate leading to the dianion.



Scheme 3.



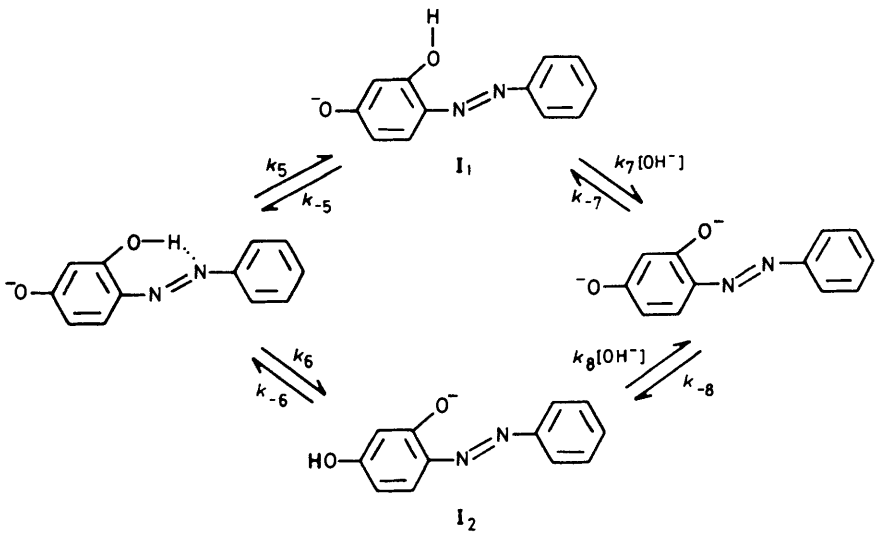
Scheme 4.

assumed to occur by two-step reaction the mechanism in Scheme 3 is obtained for 2-methyl-4,6-bis(phenylazo)resorcinol. However, the dependence of reciprocal relaxation time on hydroxide ion concentration predicted for this mechanism, equation (6), is incompatible with the observed minimum in τ^{-1}.

$$\tau^{-1} = \frac{k_4[OH^-](k_1k_{-2} + k_1k_3 + k_2k_3) + k_{-4}(k_{-1}k_{-2} + k_{-1}k_3 + k_{-2}k_{-3})}{k_{-1}k_{-2} + k_{-1}k_3 + k_{-2}k_{-3} + (k_{-2}k_4 + k_3k_4)[OH^-]} \quad (6)$$

We therefore conclude that the upper route in Scheme 2 must involve direct attack on the hydrogen-bonded proton. In that case Schemes 1 and 2 become quite similar and can be combined as in Scheme 4. Thus for (**2**) and (**3**), reaction from the monoanion to the dianion involves direct attack on the hydrogen-bonded proton in addition to a route through an open form of the monoanion which may arise by unimolecular or solvent-assisted opening of the hydrogen bond or by a protonation–deprotonation pathway through the conjugate acid.

For 4,6-bis(phenylazo)resorcinol monoanion (**1**) in 20% dioxane–water (v/v) a minimum in τ^{-1} was not clearly demonstrated (Figure 1). However, the kinetic data cannot be fitted to equation (2) since the results obtained for k_f and k_r from the roughly linear plot of τ^{-1} against $[OH^-]$ are incompatible with the value of the equilibrium constant for the reaction determined in separate experiments. The ratio of the gradient to the intercept of the plot of τ^{-1} against $[OH^-]$ has a value of 60 ± 10 dm^3 mol^{-1} compared with the result $K = 2\,300 \pm 300$ dm^3 mol^{-1} obtained from equilibrium measurements. In aqueous solution at 15 °C the equilibrium constant for ionisation of the monoanion has a value of $4\,600 \pm 500$ whereas the ratio of the gradient to the intercept of the approximately linear plot of τ^{-1} against $[OH^-]$ has a value of 600 ± 150 dm^3 mol^{-1}. Equation (2) requires that the value of the ratio of the gradient (k_f) to the intercept (k_r) of a plot of τ^{-1} against $[OH^-]$ should be identical with the value of the equilibrium constant of the reaction. Since equation (2) is incompatible with the experimental results for 4,6-bis(phenylazo)resorcinol monoanion, the data were treated according to equation (5). Linear plots of $\tau^{-1}/(1 + 1/K[OH^-])$ against $[OH^-]$ were obtained from which the values for k_1 and k_2 shown in the Table were calculated. The solid line in Figure 1 was constructed using the appropriate values of k_1 and k_2 referring to 20% dioxane–water (v/v) at ionic strength 0.1 mol dm^{-3} and 5 °C together with the experimental value $K = 2\,300$ dm^3 mol^{-1} and a minimum in τ^{-1} is predicted to occur at $[OH^-]$ *ca.* 0.002 mol dm^{-3}. In aqueous solution at 5 °C and ionic strength 0.2 mol dm^{-3} a minimum is predicted to occur at $[OH^-]$ *ca.* 0.0004 mol dm^{-3}. Thus the kinetic results for the bis(phenylazo)resorcinol monoanions (**1**), (**2**), and (**3**) provide evidence that reaction to the dianion occurs by the mechanism in Scheme 4. To reach this conclusion it was necessary to extend our preliminary work[11] with monoanions (**1**) and (**2**) to include (**3**) because for (**1**) a minimum in τ^{-1} was not directly observed and because for (**2**) it is possible to draw intermediates I_1 and I_2 which differ in the location of a proton. For (**3**) a minimum in τ^{-1} is clearly demonstrated and the intermediate open forms corresponding to I_1 and I_2 are identical. Essentially the data for the bis(phenylazo)resorcinols permit us to conclude that the upper route in Scheme 2 occurs by direct single-step proton transfer (as opposed to two-step reaction through a non-hydrogen-bonded monoanion) so that Schemes 1 and 2 can be combined to Scheme 4. Actually by making various assumptions it is possible to reach the same conclusion from the data for monophenylazoresorcinol monoanions, although this was not done in the original publication.[7] If the upper route in Scheme 2 is considered to occur by two-step reaction the mechanism in Scheme 5 is obtained. To satisfy the kinetic behaviour it is necessary that one set of the following conditions should apply; either (*i*) $k_{-5} > k_7[OH^-]$, $k_{-6} < k_8[OH^-]$, and k_6 *ca.* $(k_5/k_{-5})k_7[OH^-]$ or (*ii*) $k_{-5} < k_7[OH^-]$, $k_{-6} > k_8[OH^-]$, and k_5 *ca.* $(k_6/k_{-6})k_8[OH^-]$. The intermediates I_1 and I_2 in Scheme 5 are closely related and it will be assumed that the free energies of formation of I_1 and I_2 from the hydrogen-bonded monoanion are similar (*i.e.*, k_5/k_{-5} *ca.* $k_6/$

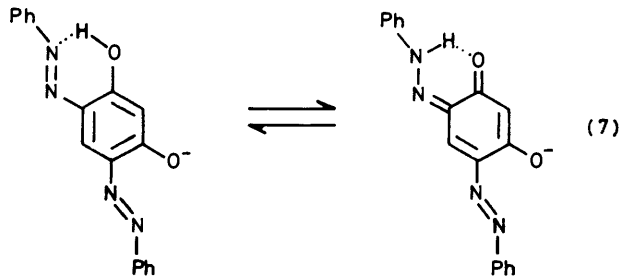


Scheme 5.

k_{-6}). It is required by condition (*i*) that k_6 *ca.* $(k_5/k_{-5})k_7$ [OH^-] which reduces to k_{-6} *ca.* k_7[OH^-] if k_5/k_{-5} *ca.* k_6/k_{-6}. It is unlikely that the conditions k_{-6} *ca.* k_7[OH^-] and $k_{-6} < k_8$[OH^-] required by condition (*i*) can be met simultaneously since k_7 and k_8 refer to thermodynamically favourable proton transfers from a phenol to hydroxide ion. Similar arguments for condition (*ii*) require that k_{-5} *ca.* k_8[OH^-] and $k_{-5} < k_7$[OH^-] are satisfied simultaneously and this again seems unlikely. It is therefore difficult to explain the kinetic behaviour satisfactorily in terms of Scheme 5 and it is concluded that if Scheme 2 is operating for phenylazoresorcinols, the upper route involves direct proton removal by hydroxide ion. This is the conclusion which is reached in the present work with 2-methyl-4,6-bis(phenylazo)resorcinol monoanion although in this case it is not necessary to assume that the intermediates I_1 and I_2 are of similar energy since for 2-methyl-4,6-bis(phenylazo)resorcinol the corresponding intermediates are identical.

It is useful to consider whether the complex kinetic behaviour observed for bis(phenylazo)resorcinol monoanions can be explained by Schemes other than 4. One possibility which has not been considered previously for these systems involves the tautomerisation in equation (7) which is equivalent to a description of the intramolecular hydrogen bond as of the type with a double potential-energy minimum. Various mechanisms can be written which involve two routes from the monoanion to the dianion and incorporate the tautomerisation in equation (7) as a rapidly established equilibrium. For example, one route may consist of slow isomerisation of one of the species in equation (7) to give a non-hydrogen-bonded open form from which a proton is removed rapidly and a second route may involve rapid isomerisation of the other tautomer to give an open form from which a proton is removed slowly. Although this Scheme is compatible with the observed kinetics, quite different behaviour for the two tautomers in equation (7) is required and for this reason the Scheme is not considered further.

The kinetic data for the bis(phenylazo)resorcinol monoanions can be analysed in greater detail in terms of Scheme 4. For 2,4-bis(phenylazo)resorcinol in aqueous solution the result k_2 *ca.* 7.4×10^3 s^{-1} is obtained for unimolecular or solvent-assisted opening of the intramolecular hydrogen bond. If bond opening actually occurs by the alternative protonation–deprotonation sequence in Scheme 4, it means that the unimolecular route must be even slower. A reasonable estimate of *ca.* 1×10^{10} dm^3 mol^{-1} s^{-1} for the value of k_3 can be made and since the condition k_3[OH^-] > k_{-2} must be satisfied over the range of hydroxide ion concentrations 0.01 to 0.17 mol dm^{-3} it follows that $k_{-2} <$ *ca.* 5.0×10^7 dm^3 mol^{-1} s^{-1}. If the value k_2 *ca.* 7.4×10^3 s^{-1} is taken to refer to unimolecular opening of the hydrogen bond, a minimum value of 1.5×10^{-4} is calculated for the equilibrium constant for opening of the intramolecular hydrogen bond. This analysis shows that a delicate balance between the various rate coefficients and equilibrium constants is necessary for the operation of both routes of proton removal from these intramolecularly hydrogen-bonded acids.



(7)

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