

Properties of Hydrogen Bonds in Substituted 5,8-Dihydroxy-1,4-naphthoquinones and 1,4-Dihydroxy-9,10-anthraquinones; Kinetics of the Reactions of the Monoanions with Hydroxide Ion and Buffers in Dimethyl Sulphoxide–Water Mixtures

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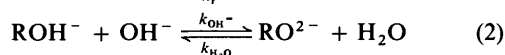
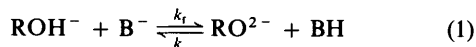
Rate coefficients and equilibrium constants for removal of the hydrogen-bonded protons from the monoanions of two 1,4-dihydroxy-9,10-anthraquinones by hydroxide ion have been measured in 50% (v/v) Me₂SO–H₂O. The values are compared with results from reactions in aqueous solution and with results for the reactions of the monoanions of 5,8-dihydroxy-1,4-naphthoquinone and its 2-methyl derivative with buffers in 50 and 70% (v/v) Me₂SO–H₂O. The similarity between the rate coefficients for proton removal by buffer bases and by hydroxide ion is compatible with a mechanism involving diffusion-controlled proton removal from a low concentration of a non-hydrogen-bonded intermediate in equilibrium with the hydrogen-bonded monoanions. At high buffer concentrations the dependence of rate on buffer concentration is curvilinear, and formation of the non-hydrogen-bonded intermediate may then be rate-limiting.

It has been proposed¹ that differences between the double minimum potential functions of the intramolecular hydrogen bonds in 5,8-dihydroxy-1,4-naphthoquinone (1) and its 2-methyl derivative (2) lead to different rates of proton transfer along the hydrogen bonds. This is supported by n.m.r. data.^{1,2} Kinetic studies of the first dissociation of compounds (1), (2), and (4) in aqueous solution in the presence of buffers, and of the second dissociation of compounds (1)–(4) in aqueous hydroxide solutions, have shown that the undissociated acids possess weak intramolecular hydrogen bonds, whereas moderately strong hydrogen bonds are present in the monoanions.³ Buffer catalysis of the second dissociation could not be studied in aqueous solution because the reaction with hydroxide ion predominates. Recent studies⁴ have shown that information about the rates of opening and closing of an intramolecular hydrogen bond can be deduced from proton-transfer studies in the presence of buffers. We have therefore investigated the reactions of the monoanions of (1) and (2) with buffers in 50 and 70% (v/v) Me₂SO–H₂O where the contribution of hydroxide ion is small. It has also been possible to study the second dissociations of (3) and (4) with hydroxide ion in 50% (v/v) Me₂SO–H₂O for comparison with the results from aqueous solution, and with the results for the reactions of (1) and (2) with buffers.

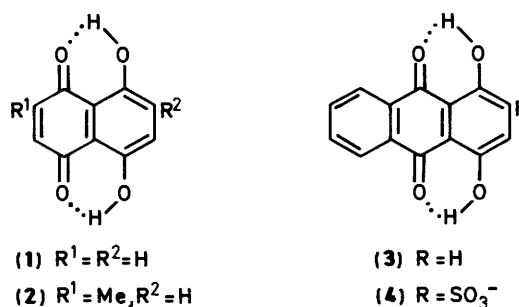
Experimental

Materials.—Samples of compounds (1)–(4) were available from a previous study.³ Benzimidazole was recrystallised from ethanol and 2,6-di-isopropylphenol was distilled. Tetramethylammonium chloride, used to maintain constant ionic strength, was dried under vacuum before use. Solutions were prepared from doubly distilled water and Analar grade Me₂SO.

Equilibrium Measurements.—Equilibrium constants for conversion of the monoanions (ROH[−]) into the dianions (RO^{2−}) [equations (1) and (2)] were obtained spectrophotometrically.



Compounds (1) and (2) were studied in the presence of



benzimidazole and 2,6-di-isopropylphenol buffers (BH) in 50 and 70% (v/v) Me₂SO–H₂O. For (3) and (4), reaction (2) was studied in 50% (v/v) Me₂SO–H₂O containing tetramethylammonium hydroxide. Both reactions were studied at 288 K and ionic strength 0.1 mol dm^{−3}. The species ROH[−] and RO^{2−} were always present in low concentration (*ca.* 5 × 10^{−5} mol dm^{−3}) as compared with hydroxide ion or buffer. Absorbance readings were taken at *ca.* 630 nm, where the dissociated species absorb strongly. The molar absorptivities of the dissociated species (RO^{2−}) were obtained from measurements in the presence of 0.1 mol dm^{−3} hydroxide ion and the molar absorptivities of the undissociated forms (ROH[−]) were obtained in a 1:1 chlorophenol buffer in the appropriate Me₂SO–H₂O mixture. Values of the equilibrium constants *K* for reaction (1) and *K*_{OH[−]} for reaction (2) are given in Table 1.

Kinetic Measurements.—Kinetic studies of reactions (1) and (2) were made by the temperature-jump technique. Reaction conditions were similar to those used for the equilibrium measurements. The equilibria were disturbed by a temperature perturbation of 1.7 K. Relaxation times for reaction (2) involving (3) and (4) in 50% (v/v) Me₂SO–H₂O were determined over the widest possible range of concentrations of tetramethylammonium hydroxide for which a measurable amplitude of relaxation was observable. Reaction (1) with 5,8-dihydroxy-1,4-naphthoquinone (1) was studied in 70% (v/v) Me₂SO–H₂O containing 2,6-di-isopropylphenol buffers at buffer ratios ([B[−]]/[BH]) of 0.496, 0.94, and 1.94. The reaction of 5,8-dihydroxy-2-methyl-1,4-naphthoquinone (2) was studied in 50% (v/v) Me₂SO–H₂O containing benzimidazole buffers at buffer ratios of 0.483 and 0.95 and in 70% (v/v) Me₂SO–H₂O

Table 1. Kinetic and equilibrium^a results for reactions (1) and (2)

Comp.	Solvent	Base	$10^{-2}K_{\text{OH}^-}$ $\text{dm}^3 \text{mol}^{-1}$	$10^{-7}k_{\text{OH}^-}$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$10^{-4}k_{\text{H}_2\text{O}}$ s^{-1}	K	$10^{-5}k_f$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$10^{-5}k_r$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
(1)	H ₂ O	OH ⁻	13.6 ± 0.2	1.42 ± 0.1	1.16 ± 0.3			
(2)	70% Me ₂ SO-H ₂ O	2,6-Pr ⁱ ₂ C ₆ H ₃ O ⁻	5.62 ± 0.3	1.45 ± 0.2	2.45 ± 0.2	1.59 ± 0.08	9.5 ± 0.5	5.9 ± 0.3
(3)	70% Me ₂ SO-H ₂ O	OH ⁻	6.12 ± 0.5	0.705 ± 0.05	1.45 ± 0.2	0.27 ± 0.02	4.6 ± 0.5	17.0 ± 2
(3)	50% Me ₂ SO-H ₂ O	BI ^{-b}	2.22 ± 0.1	1.35 ± 0.3	8.0 ± 1	2.07 ± 0.2	28 ± 1	13.3 ± 0.2
(4)	50% Me ₂ SO-H ₂ O	OH ⁻	0.84 ± 0.07	0.41 ± 0.08	7.0 ± 1			
(4)	50% Me ₂ SO-H ₂ O	OH ⁻	2.41 ± 0.06	0.40 ± 0.05	2.6 ± 0.2			

^a The equilibrium constant for reaction (1) is defined as $K = [\text{RO}^{2-}][\text{BH}]/[\text{ROH}^-][\text{B}^-]$; for reaction (2) $K_{\text{OH}^-} = [\text{RO}^{2-}]/[\text{ROH}^-][\text{OH}^-]$.

^b Benzimidazole anion.

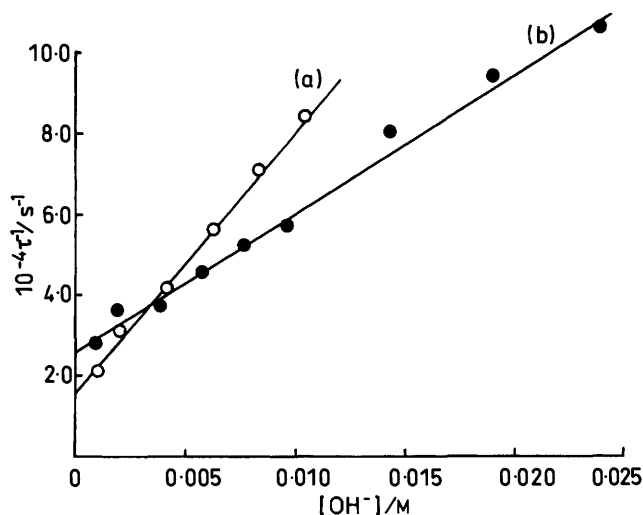


Figure 1. Plots of reciprocal relaxation time against hydroxide ion concentration for reaction (2); (a) with compound (3); (b) with compound (4)

with 2,6-di-isopropylphenol buffer at buffer ratios of 1.88 and 3.9. Buffer anion concentrations in the range 0.002–0.1 mol dm⁻³ were used. For the studies of reaction (2) the dependence of reciprocal relaxation time on hydroxide ion concentration was linear within experimental error, but a curvilinear dependence of reciprocal relaxation time on buffer concentration was found for reaction (1). Typical results are given in Figures 1 and 2.

Results and Discussion

Reaction with Hydroxide Ion.—Reaction (2) has previously been studied³ in aqueous solution. The results are given in Table 1 for comparison with the present results for (3) and (4) in 50% (v/v) Me₂SO-H₂O. The values of the equilibrium constants for (3) and (4) are *ca.* 3-fold higher in 50% (v/v) Me₂SO-H₂O than in aqueous solution. Mixtures of Me₂SO-H₂O containing hydroxide ion are much more basic than aqueous solutions containing the same concentration of hydroxide ion;⁵ this is usually attributed to desolvation of hydroxide ion in these mixtures. Thus the equilibrium constant for deprotonation of protonated amines by hydroxide ion in 30% Me₂SO-H₂O is 60-fold higher than in aqueous solution.⁶ The acidity function of 50% (v/v) Me₂SO-H₂O containing hydroxide ion as determined by the dissociation of substituted amines is *ca.* 2.5 units higher than in aqueous solution containing the same concentration of hydroxide ion.⁵

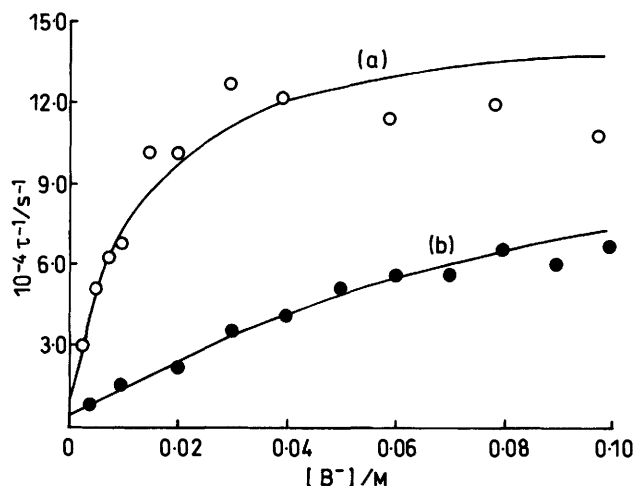


Figure 2. Plots of reciprocal relaxation time against buffer anion concentration for reaction (1); (a) involving (2) in 50% (v/v) Me₂SO-H₂O containing benzimidazole buffers at a buffer ratio $r = 0.48$ and (b) for (2) in 70% (v/v) Me₂SO-H₂O containing 2,6-di-isopropylphenol buffers at buffer ratio $r = 3.9$

The much smaller change in the equilibrium constant for reaction (2) in going to 50% Me₂SO-H₂O arises because the phenolate ions are also desolvated by the addition of Me₂SO.

For a reaction of the type in equation (2) the dependence of reciprocal relaxation time on hydroxide ion concentration is expected to follow equation (3). The observed dependence of

$$\tau^{-1} = k_{\text{OH}^-}[\text{OH}^-] + k_{\text{H}_2\text{O}} \quad (3)$$

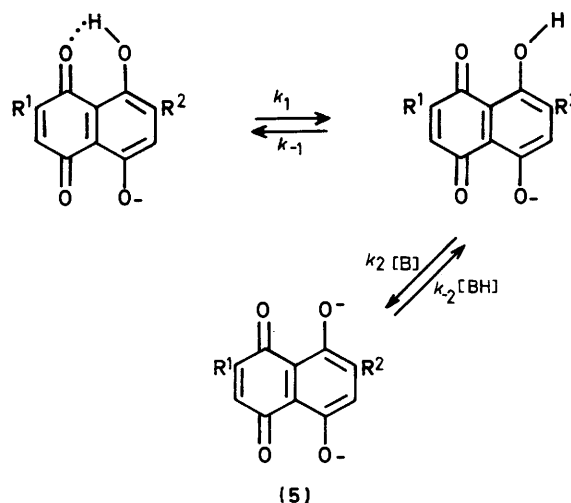
reciprocal relaxation time on hydroxide ion concentration is linear within experimental error (see Figure 1) and the values of k_{OH^-} and $k_{\text{H}_2\text{O}}$ obtained for (3) and (4) are given in Table 1. The agreement between the separately measured values of the equilibrium constants for the reaction [612 ± 50 and 241 ± 6 dm³ mol⁻¹ for (3) and (4) respectively] are in rather poor agreement with the ratios of the values of k_{OH^-} and $k_{\text{H}_2\text{O}}$ [490 ± 50 and 154 ± 30 dm³ mol⁻¹ for (3) and (4), respectively]. This could arise because the studies were carried out at rather low concentrations of hydroxide ion, but an alternative possibility is discussed later. The quite similar values of k_{OH^-} determined for (3) and (4) in aqueous solution and in 50% (v/v) Me₂SO-H₂O show that the strengths of the intramolecular hydrogen bonds are little affected by the change in solvent.

Studies at Low Buffer Concentrations.—The dependence of reciprocal relaxation time on buffer concentration observed for the reactions of (1) and (2) with buffer species [equation (1)] was curvilinear, as shown in Figure 2. At low buffer concentrations a linear dependence was observed; this region will be discussed first and compared with the results for the reactions of (3) and (4) with hydroxide ion. For a reaction of the type in equation (1) the dependence of reciprocal relaxation time on buffer concentration is expected to follow equation (4), provided

$$\tau^{-1} = k_f(1 + 1/Kr)[B^-] \quad (4)$$

that hydroxide ion makes a negligible contribution to the rate. In equation (4), the buffer ratio r is $[B^-]/[BH]$ and K is the equilibrium constant for the reaction. The data for the reactions of (1) and (2) in buffer solutions at low buffer concentrations were treated according to equation (4) using linear regression analysis. A small positive intercept was observed in the plots of τ^{-1} against buffer concentration; this may mean that hydroxide ion makes a small contribution to the rate. The intercepts were not analysed further since the hydroxide ion concentration in these solutions is not known. The gradients of the plots at several buffer ratios were used to calculate values for k_f and k_r and the results are given in Table 1. The data at different buffer ratios gave consistent values for the rate coefficients. It was not possible to study the reaction of any single substrate with buffer and with hydroxide ion. However in 50% (v/v) $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ the value of k_f for the reaction of (2) with benzimidazole anion is only a factor of 2.5 below the value of k_{OH^-} for reaction of (3) with hydroxide ion. In aqueous solution the values of k_{OH^-} for (2) and (3) are very similar (see Table 1), so that it seems likely that the reactions of (2) with buffer and with hydroxide ion occur at very similar rates. This is surprising in view of the much greater basic strength of hydroxide ion, but can be explained by assuming that the mechanism of proton removal involves formation of a low concentration of a non-hydrogen-bonded species from which the proton is removed in a diffusion-controlled reaction with base. Further discussion of this point is given in the following section.

Studies at High Buffer Concentrations.—At high buffer concentrations the reciprocal relaxation time for reaction (1) involving (1) and (2) gives a curved dependence on buffer concentration (see Figure 2). The same behaviour has been observed previously in the reaction of an intramolecularly hydrogen-bonded phenylazoresorcinol with buffer⁴ and has been explained by a mechanism similar to that shown as reaction (5). The dependence of reciprocal relaxation time on buffer concentration given in equation (6) is obtained on the assumption that the open non-hydrogen-bonded intermediate is present in low concentration and that the contribution of hydroxide ion to the rate is small.



$$\tau^{-1} = k_1(1 + 1/Kr)[B^-]/(k_{-1}/k_2 + [B^-]) \quad (6)$$

$$\tau = k_{-1}/k_1 k_2(1 + 1/Kr)[B^-] + 1/k_1(1 + 1/Kr) \quad (7)$$

The data for (1) in 70% (v/v) $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ with 2,6-di-isopropylphenol buffers at three buffer ratios and for (2) in 70% (v/v) $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ at two di-isopropylphenol buffer ratios and in 50% (v/v) $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ containing benzimidazole at two buffer ratios were treated by linear regression analysis according to equation (7). Values of K obtained from the equilibrium measurements were used and it was necessary to estimate an intercept from each plot of τ^{-1} against $[B^-]$ corresponding to a small contribution from hydroxide ion and to subtract this value from the value of τ^{-1} . At each buffer ratio the values of k_1 and k_{-1}/k_2 obtained from the linear regression analysis are given in Table 2. The solid lines in Figure 2 were constructed using the appropriate values of k_1 and k_{-1}/k_2 . The values of k_1 and k_{-1}/k_2 can only be regarded as very approximate since different values are obtained at different buffer ratios. The reasons for this are not clear. At high buffer concentrations a decrease in the value of τ^{-1} with buffer concentration is apparent from the data in Figure 2. Unusual electrolyte effects on reactions in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ mixtures have been observed previously.⁷ In the reaction of an intramolecularly hydrogen-bonded bis(phenylazo)-resorcinol monoanion with buffer in 70% (v/v) $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ for which curvilinear plots were obtained,⁴ the derived values of k_1 and k_{-1}/k_2 also showed some variation with buffer ratio but the effects were much smaller than observed here. The present results were obtained at higher buffer concentrations and this may account for the larger variation. At present the variation in the values of k_1 and k_{-1}/k_2 is attributed to an electrolyte effect brought about by the change in electrolyte from tetramethylammonium chloride at low buffer concentra-

Table 2. Analysis of kinetic data at high buffer concentration

Compd.	Solvent	Buffer	r	$10^{-5}k_1/\text{s}^{-1}$	$(k_{-1}/k_2)/\text{mol dm}^{-3}$
(1)	70% $\text{Me}_2\text{SO}-\text{H}_2\text{O}$	2,6-Pr ⁱ ₂ C ₆ H ₃ OH	0.496	0.7	0.08
			0.94	1.1	0.13
			1.94	1.7	0.18
(2)	70% $\text{Me}_2\text{SO}-\text{H}_2\text{O}$	2,6-Pr ⁱ ₂ C ₆ H ₃ OH	1.88	0.36	0.09
			3.9	1.1	0.20
	50% $\text{Me}_2\text{SO}-\text{H}_2\text{O}$	BI ^{-a}	0.48	0.74	0.014
			0.95	0.96	0.024

^a Benzimidazole anion.

tions to the tetramethylammonium salt of the buffer anion which is present at high buffer concentration.

For the reaction of the monoanions of (3) and (4) with hydroxide ion in 50% (v/v) Me₂SO-H₂O the dependence of reciprocal relaxation time on concentration was linear within experimental error, as shown in Figure 1. This contrasts with the behaviour of (1) and (2) with buffer. If a mechanism similar to that in equation (5) is assumed to apply for the reactions of (3) and (4) with hydroxide ion the linear dependence on hydroxide ion concentration would only be observed if the inequality $k_{-1} > k_2[\text{OH}^-]$ is satisfied at all concentrations. It follows for (3) that $k_{-1}/k_2 > 0.02$. Although the value of k_2 would be expected to be slightly higher for a diffusion-controlled reaction with hydroxide ion as compared with buffer, the result $k_{-1}/k_2 > 0.02$ for the reaction of (3) with hydroxide ion is not incompatible with the values found for k_{-1}/k_2 in the reaction of (2) with benzimidazole. Further, the poor agreement between $k_{\text{OH}^-}/k_{\text{H}_2\text{O}}$ found from the gradient and intercept of the plot in Figure 1 and the separately measured value of the equilibrium constant for the reaction may mean that at $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$ the onset of curvature has begun. Unfortunately, because of the low amplitude of the relaxation the reaction could not be studied at higher concentrations of hydroxide ion.

It is interesting that curvilinear plots of τ^{-1} against buffer concentration have been observed for removal of the hydrogen-bonded protons from the monoanions of 5,8-dihydroxy-1,4-

naphthoquinone and 4,6-bisphenylazoresorcinol⁴ in Me₂SO-H₂O, but in aqueous solution no evidence for this behaviour has been found for reactions with buffer or with hydroxide ion. It is possible that in the mixed solvent the value of k_{-1} is reduced as compared with the value in aqueous solution so that the inequality $k_2[\text{B}^-] > k_{-1}$ is satisfied at accessible buffer concentrations.

Acknowledgements

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