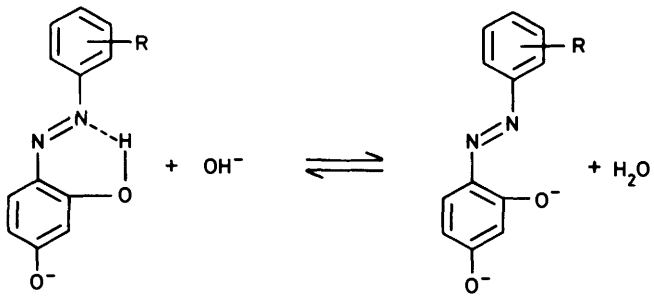
Comparison of the Proton-transfer Behaviour of 4-(2,4-Dihydroxyphenylazo)- and 4-(2-Hydroxy-1-naphthylazo)-benzenesulphonates

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

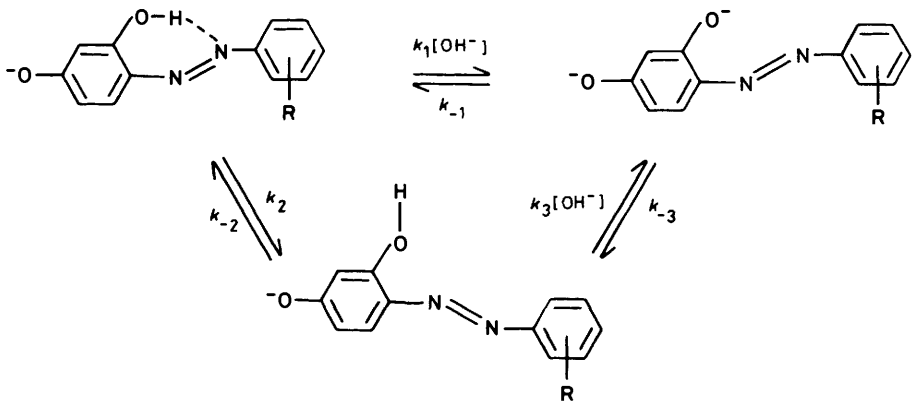
A linear dependence of rate on hydroxide ion concentration has been observed for removal of the intramolecularly hydrogen-bonded proton from 4-(2-hydroxy-1-naphthylazo)benzenesulphonate (**2**), in contrast to the complex rate dependence found for 4-(2,4-dihydroxyphenylazo)benzenesulphonate (**1**). Possible explanations are considered. The magnitude of the kinetic solvent isotope effect and the observation of general base catalysis in proton removal from (**2**) are discussed.

The proton-transfer behaviour of 4-(2,4-dihydroxyphenylazo)benzenesulphonate[1] (**1**) is unusual compared with that of other intramolecularly hydrogen-bonded acids.[2] For proton removal by hydroxide ion as in Scheme 1, the value of the reciprocal relaxation time (τ^{-1}) for the approach to equilibrium following a rapid temperature perturbation shows a complex dependence on hydroxide ion concentration in which τ^{-1} passes through a minimum value.[1] Examples of this behaviour are limited to the monoanions of phenylazoresorcinol[3] (R = H in Scheme 1), substituted phenylazoresorcinols[1,3] (R = 4-SO_3^-, 4-NO_2, or 3-NO_2), and certain bis(phenylazo)resorcinols.[4] In all these cases the phenolic group from which a proton is removed is intramolecularly hydrogen-bonded to a phenylazo group. In addition the molecules possess an ionised hydroxy substituent located in the 4-position of the phenylazo group. The complex rate dependence has been explained[1] by a mechanism with two routes from the hydrogen-bonded phenylazoresorcinol monoanion to its conjugate base as in Scheme 2. One route consists of direct attack by hydroxide ion on the hydrogen-bonded proton (step 1) and the other involves proton loss from an intermediate open form of the phenylazoresorcinol monoanion (steps 2 and 3). An alternative mechanism with the parent acid (phenylazoresorcinol) as a low-concentration intermediate has been proposed[5] but strong evidence in support of the mechanism in Scheme 2 is available.[4] It appeared of interest to discover whether a complex rate dependence could be demonstrated for a species possessing an intramolecular phenol-to-azo hydrogen bond but without an ionised hydroxy group in the phenylazo 4-position. This would eliminate an explanation of the complex rate dependence based on the intermediacy of undissociated phenylazoresorcinol. Accordingly studies with compounds (**2**)—(**4**) in comparison with 4-(2,4-dihydroxyphenylazo)benzenesulphonate (**1**) have been carried out.

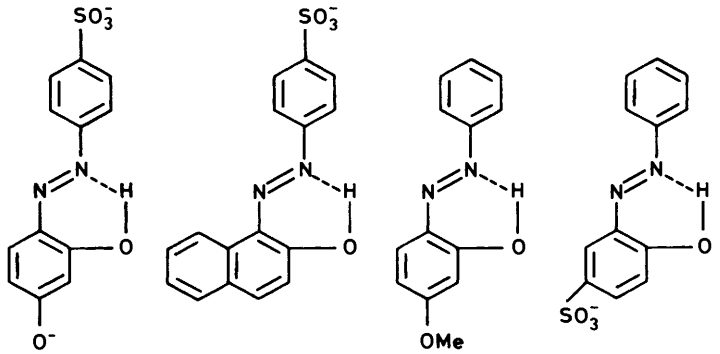
For proton removal from most hydrogen-bonded acids a linear dependence of reciprocal relaxation time on hydroxide ion concentration has been observed, and has been interpreted in terms of a two-step mechanism involving an open form of the acid in low concentration.[2] Proton transfer occurs from the open form at a rate which is lower than the rate at which the open form reverts to the hydrogen-bonded acid.[2] This mechanism is the same as steps 2 and 3 of Scheme 2. However to explain the kinetics observed for phenylazoresorcinol monoanions it is necessary to assume that in Scheme 2 the rate at which a proton is removed from the open form exceeds the rate at which the open form returns to the hydrogen-bonded monoanion. One factor which may be responsible for the complex kinetic behaviour of phenylazoresorcinol monoanions such as (**1**) is the low rate at which the intramolecular hydrogen bonds open and close.[2]



Scheme 1.



Scheme 2.



(1) (2) (3) (4)

Experimental

Materials.—Commercial samples of 4-(2,4-dihydroxyphenylazo)benzenesulphonate (**1**) and 4-(2-hydroxy-1-naphthylazo)-benzenesulphonate (**2**) were used. 2-Phenylazo-5-methoxyphenol (**3**) was prepared by mixing benzenediazonium chloride and 3-methoxyphenol in equimolar amounts under aqueous alkaline conditions. After 30 min, the pH of the solution was adjusted to *ca.* 6 by addition of hydrochloric acid. A mixture of 4-phenylazo-3-methoxyphenol and 2-phenylazo-5-methoxyphenol was precipitated. Separation on an alumina column with chloroform as eluant gave 2-phenylazo-5-methoxyphenol as an orange solid (m.p. 106 °C); δ($CDCl_3$) 13.89 (s, OH), 7.82—6.46 (m, 8 H, arom.), and 3.8 (s, OCH_3). 4-Hydroxy-3-phenylazobenzenesulphonate (**4**) was prepared by mixing equimolar amounts of 4-hydroxybenzenesulphonate and benzenediazonium chloride. After acidification the product was salted out by addition of sodium chloride, dried, and recrystallised from methanol to give a brown solid, m.p. 171 °C (decomp.).

Kinetic Measurements.—Kinetic studies were carried out by use of the temperature-jump technique with Joule heating. A temperature jump of 3.3 °C was obtained within 2 μs in the reaction solution by a discharge of 35 kV from a 0.01 μF capacitor. The aqueous reaction solution was maintained initially by thermostat at 11.7 °C. For reactions in D_2O the magnitude of the temperature jump under the same discharge conditions was 2.9 °C; the reaction solution in this case was therefore maintained initially at 12.1 °C. Following the temperature jump, chemical relaxation to a new equilibrium position at 15.0 °C was followed spectrophotometrically and the output from the instrument was stored in a transient recorder (Physical Data Inc.). The data were transferred to an Apple II microcomputer for rate calculations. The half-lives of the chemical relaxations studied were in the range 9—170 μs.

Equilibrium and Kinetic Results

The results were obtained in aqueous solution at 15 °C with 0.1 mol dm^{-3} ionic strength.

4-(2,4-*Dihydroxyphenylazo*)*benzenesulphonate* (**1**).—The kinetics of proton transfer from the sulphonate (**1**) have been studied previously.[1] We have repeated these measurements to provide results for comparison with compounds (**2**)—(**4**) under the same conditions. Dissociation of 4-(2,4-dihydroxyphenylazo)benzenesulphonic acid to give (**1**) was studied spectrophotometrically in phthalate and in phosphate buffers. A pK value of 5.87 ± 0.05 referring to 15 °C and ionic strength 0.1 mol dm^{-3} was determined, in agreement with a previous approximate value, pK *ca.* 5.8.[1] The second dissociation, as in Scheme 1 with R = SO_3^-, was studied in sodium hydroxide solution, and a value for the equilibrium constant (K of 112 ± 5 dm^3 mol^{-1} (184 ± 15 dm^3 mol^{-1} in D_2O) was found. From this value a pK value of 12.10 ± 0.05 at 15 °C and ionic strength 0.1 mol dm^{-3} was calculated for ionisation of the hydroxy proton in (**1**), to be compared with a previous value of 11.82 at 25 °C and ionic strength 0.1 mol dm^{-3}. The value of 12.10 can be corrected to pK_a 12.82 at infinite dilution by using the Debye–Huckel approximation.

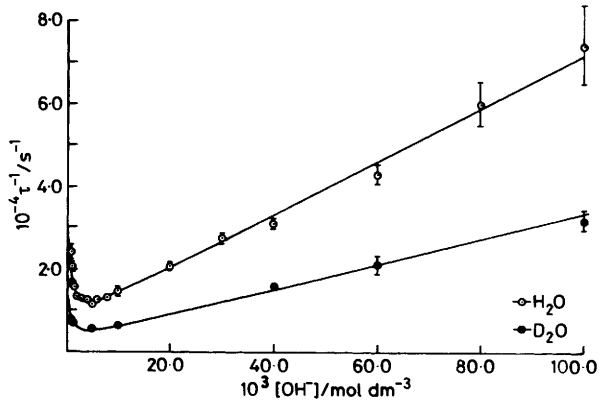
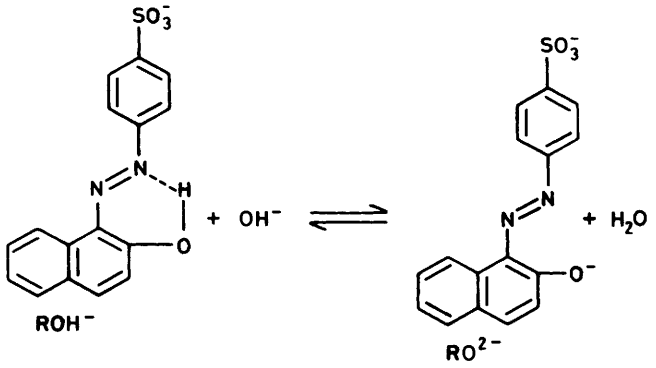


Figure 1. Dependence of reciprocal relaxation time for proton removal from (**1**) on hydroxide ion (or deuteroxide ion) in H_2O and D_2O

Kinetic studies of Scheme 1 with R = SO_3^- were made in sodium hydroxide solutions; the variation of reciprocal relaxation time with hydroxide (and deuteroxide) ion concentration in H_2O (and D_2O) is given in Figure 1.

4-(2-*Hydroxy*-1-*naphthylazo*)*benzenesulphonate* (**2**).—Dissociation of (**2**) as in Scheme 3 was studied over a range of hydroxide ion concentrations. Measurements of the equilibrium position were made spectrophotometrically at 480 nm where the acid (ROH^-) has a high absorbance and at 560 nm where RO^{2-} absorbs strongly. The total concentration of RO^{2-} and ROH^- was *ca.* 1.0 × 10^{-4} mol dm^{-3} and the spectra of ROH^- and RO^{2-} were obtained from measurements in unbuffered aqueous solution and in 0.1 mol dm^{-3} sodium hydroxide, respectively. Values for the equilibrium constant $K = [RO^{2-}]/[ROH^-][OH^-]$ of 660 ± 90 dm^3 mol^{-1} in H_2O and 1.07 ± 0.3 × 10^3 dm^3 mol^{-1} in D_2O were obtained. The result in H_2O gives pK 11.33 ± 0.06 at 15 °C and ionic strength 0.1 mol dm^{-3}, and pK_a 11.81 ± 0.06 at infinite dilution.

Kinetic studies of Scheme 3 were made in sodium hydroxide solutions, and the variation of reciprocal relaxation time with $[OH^-]$ and $[OD^-]$ in H_2O and D_2O for re-equilibration after a temperature jump is given in Figure 2. In order to extend the data to lower hydroxide ion concentrations, measurements were



Scheme 3.

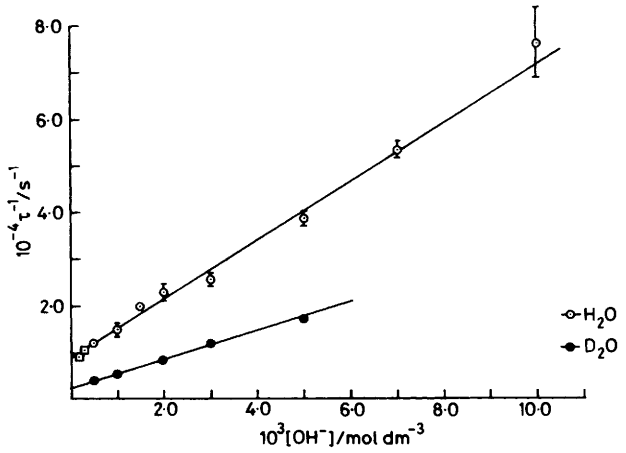


Figure 2. Dependence of reciprocal relaxation time for proton removal from (**2**) on hydroxide ion (or deuteroxide ion) in H_2O and D_2O

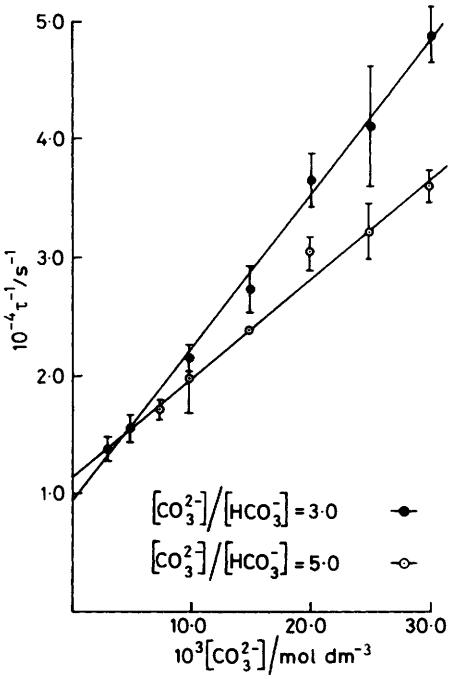


Figure 3. Concentration dependence of reciprocal relaxation times for deprotonation of (**2**) in carbonate buffers

also made in carbonate buffer solutions. Under these conditions the value of the reciprocal relaxation time for equilibration between ROH^- and RO^{2-} depends upon the buffer concentration; see Figure 3. The intercepts of the buffer plots at buffer ratios ($[CO_3^{2-}]:[HCO_3^-]$) of 3.0:1 and 5.0:1 correspond to the value of the reciprocal relaxation time for Scheme 3 at the hydroxide ion concentrations present at each buffer ratio; these results are shown as the square data points in Figure 2.

2-Phenylazo-5-methoxyphenol (**3**).—Measurements of the dissociation of (**3**) were made spectrophotometrically in tris(hydroxymethylamino)methane and in carbonate buffers. The absorbances of solutions containing 2×10^{-6} mol dm^{-3} (**3**) with various buffer ratios were taken at 460 nm where the undissociated phenol absorbs strongly. A pK value of 8.99 ± 0.09 at 15 °C and ionic strength 0.1 mol dm^{-3} was obtained. Kinetic measurements were unsuccessful. Because of the low solubility of (**3**), temperature-jump experiments were carried out with concentrations *ca.* 2×10^{-6} mol dm^{-3}; at these low concentrations the amplitudes of the chemical relaxations were undetectable.

4-Hydroxy-3-phenylazobenzenesulphonate (**4**).—The dissociation of (**4**) was studied spectrophotometrically in tris(hydroxymethylamino)methane buffers. Absorbance readings of solutions of (**4**) with various buffer ratios were taken at 436 nm, where the dissociated species absorbs strongly and the result (pK = 7.81 ± 0.03) was determined at ionic strength 0.1 mol dm^{-3}. An attempt was made to study the kinetics of equilibration between (**4**) and the dissociated species under the same conditions. Following a temperature jump, an increase in absorbance at 436 nm of a solution of (**4**) in an aqueous tris(hydroxymethylamino)methane buffer was observed to occur within the instrument heating time. This means that proton transfer from (**4**) is a rapid reaction with a relaxation time of less than 2 μs.

Discussion

The kinetic results obtained for proton removal from (**1**) are compatible with the published data.[1] The points in Figure 1 are experimental results and the curves are best fits of equation (1). For the results in H_2O the best fit was obtained with k_1 6.4×10^5 dm^3 mol^{-1} s^{-1}, k_2 1.2×10^3 s^{-1}, and the experimental value K 112 dm^3 mol^{-1}. In D_2O the values k_1 3.05×10^5 dm^3 mol^{-1} s^{-1}, k_2 1.0×10^3 s^{-1}, and K 184 dm^3 mol^{-1} were found. Equation (1) is derived from the mechanism in Scheme 2 on the

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

assumption that the intermediate open form is present in low concentration and that the rate of proton removal from the open form is greater than the rate at which it reverts to the hydrogen-bonded species ($k_3[OH^-] \gg k_{-2}$). In contrast to the results for (**1**), an accurately linear dependence of τ^{-1} on hydroxide ion concentration was found for (**2**) (Figure 2). For (**4**), proton transfer occurs rapidly. There may exist a rough correlation between hydrogen-bond strength and rate of proton removal,[2] and if this holds in these cases, it follows that the hydrogen bond in (**4**) is weak. Kinetic studies with (**3**) were not possible. Thus the observation still holds that complex kinetic behaviour of the type shown in Figure 1 is restricted to phenylazoresorcinols like (**1**).

To understand the difference in behaviour of (**1**) and (**2**) the assumptions will first be made that proton removal from (**2**) occurs by the mechanism in Scheme 2 and that the same conditions apply as for (**1**), *viz.* $k_3[OH^-] \gg k_{-2}$. According to

Table. Calculated rate coefficients for reaction of (1) and (2) according to Scheme 2

	(1)	(2)
k_1/dm^3 mol^{-1} s^{-1}	6.4×10^5	$< 6.3 \times 10^6$
k_2/s^{-1}	1.2×10^3	$> 6.3 \times 10^4$
k_{-2}/s^{-1}	$< 1.0 \times 10^7$	$> 1.0 \times 10^8$
k_2/k_{-2}	$> 1.2 \times 10^{-4}$	6.3×10^{-4}

equation (1), the minimum in τ^{-1} occurs at a hydroxide ion concentration given by $[OH^-]_{min.} = (k_2/k_1K)^{\frac{1}{2}}$. For (1), the result K 112 dm^3 mol^{-1} is obtained and the best-fit values of k_1 and k_2 predict that $[OH^-]_{min.} = 0.004$ mol dm^{-3}, in good agreement with the data in Figure 1. For (2), no minimum in τ^{-1} is apparent at $[OH^-] > 1.0 \times 10^{-4}$ (Figure 2). It follows, therefore, that for (2) $(k_2/k_1K)^{\frac{1}{2}} < 1.0 \times 10^{-4}$, and using K 660 dm^3 mol^{-1} leads to $k_2/k_1 < 6.6 \times 10^{-6}$. The proportion of reaction that occurs by the upper and lower routes in Scheme 2 is determined by the relative values of $k_1[OH^-]$ and k_2. If $k_2/k_1 < 6.6 \times 10^{-6}$ the condition $k_1[OH^-] \gg k_2$ applies, and then equation (1) reduces to (2), which corresponds to proton removal only by the upper route in Scheme 2. The experimental results for (2) are fitted by equation (2), and give k_1

$$\tau^{-1} = k_1[OH^-] + k_{-1} \quad (2)$$

$6.3 \pm 0.6 \times 10^6$ dm^3 mol^{-1} s^{-1}, k_{-1} $0.9 \pm 0.1 \times 10^4$ s^{-1}, and $k_2 < 42$ s^{-1}. Thus if the mechanism in Scheme 2 is assumed to apply for (2) with $k_3[OH^-] > k_{-2}$, the value deduced for k_1 is ten-fold higher for (2) than for (1) and the value deduced for k_2 is at least thirty-fold lower for (2) than for (1). It would have been expected in going from (1) to (2) that the values of k_1 and k_2 would change in the same direction if, for example, the strengths of the intramolecular hydrogen bonds in the two compounds differed.

An alternative explanation for the difference in behaviour of (1) and (2) is provided by making the assumption that for (2) reaction occurs predominantly by the lower route in Scheme 2 and the condition $k_3[OH^-] < k_{-2}$ applies. This is the mechanism previously found to operate for proton removal from salicylate ion[2,6] and other intramolecularly hydrogen-bonded acids.[7] Making the assumption $k_3[OH^-] < k_{-2}$ leads to equation (3) and the results for (2) are fitted using k_2k_3/k_{-2}

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

$6.3 \pm 0.6 \times 10^6$ dm^3 mol^{-1} s^{-1} and k_{-3} $0.9 \pm 0.1 \times 10^4$ s^{-1}. If reaction of (2) occurs predominantly by the lower route in Scheme 2, it follows that $k_1 < k_2k_3/k_{-2}$, *i.e.* $k_1 < 6.3 \times 10^6$ dm^3 mol^{-1} s^{-1}. It is likely that proton removal from the intermediate open form in step 3 is diffusion limited, so that for (1) and (2) the value for k_3 of 1.0×10^{10} dm^3 mol^{-1} s^{-1} will be assumed. Since for (2) the condition $k_3[OH^-] < k_{-2}$ must be satisfied to explain the observed kinetics, the result $k_{-2} > 1.0 \times 10^8$ s^{-1} is deduced. The value for k_2k_3/k_{-2} of 6.3×10^6 dm^3 mol^{-1} s^{-1} then leads to k_2/k_{-2} 6.3×10^{-4} and $k_2 > 6.3 \times 10^4$ s^{-1}. The results of this analysis are given in the Table. For (2) it has been assumed that proton transfer occurs by the lower route in Scheme 2 ($k_1 < 6.3 \times 10^6$ dm^3 mol^{-1} s^{-1}), that $k_{-2} > k_3[OH^-]$, and that $k_3 = 1.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. The results from a similar analysis for (1) based on the assumptions that reaction occurs by the mechanism in Scheme 2 with $k_{-2} < k_3[OH^-]$ and $k_3 = 1.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1} are also given in the Table. From the Table it is seen that the value of k_2 is at least 50-fold greater for (2) than for (1). This would be expected if the hydrogen bond in (2) is much weaker, but the calculated values $k_2/k_{-2} > 1.2 \times 10^{-4}$ for (1) and $k_2/k_{-2} = 6.3 \times 10^{-4}$ for (2) indicate that this is not the case. However if an additional activation energy for opening and closing of the hydrogen bond in (1) is required in excess of that for (2), the values of k_2 and k_{-2} for (1) would be lower even though the strengths of the hydrogen bonds, as indicated by the values of k_2/k_{-2}, may not be very different. One possible source of additional activation energy for opening of the hydrogen bond in (1) arises from conjugation between the azo and ionised hydroxy group. This may lead to some stabilisation of the hydrogen bond and to restricted rotation about the C–N bond between the resorcinol ring and the azo group. The precise effect of restricted rotation about the C–N bond on the values of k_2 and k_{-2} is difficult to assess because the values may also be determined by the rates of rotation about the bond between the resorcinol ring and the hydrogen-bonded hydroxy group.

The observation of catalysis by general base in proton transfer from (2) (see Figure 3), and the magnitude of the kinetic solvent isotope effect on proton removal by hydroxide ion, can be understood in terms of either of the mechanisms used to explain the difference in behaviour of (1) and (2). In using equation (3) to account for general base catalysis, the equation needs to be extended to (4), where k_3' and k_{-3}' are the forward and reverse rate coefficients for proton removal from the non-hydrogen-bonded intermediate by carbonate ion, and $[OH^-]$ is the concentration of hydroxide ion present at a particular buffer ratio ($R = [CO_3^{2-}]/[HCO_3^-]$). The first two terms in equation (4) refer to the hydroxide-ion-catalysed reaction and

$$\tau^{-1} = (k_2k_3/k_{-2})[OH^-] + k_{-3} + (k_2k_3'/k_{-2} + k_{-3}'/R)[CO_3^{2-}] \quad (4)$$

correspond to the intercepts of the plots in Figure 3. The intercepts are shown as the square data points in Figure 2. The slopes of the plots in Figure 3 were used to calculate the values k_2k_3'/k_{-2} $1.7 \pm 0.1 \times 10^5$ dm^3 mol^{-1} s^{-1} and k_{-3}' $3.4 \pm 0.2 \times 10^6$ dm^3 mol^{-1} s^{-1}. The difference between the value of k_2k_3/k_{-2} for hydroxide ion catalysis and k_2k_3'/k_{-2} for catalysis by carbonate ion is similar to the difference observed between the corresponding terms in proton transfer from salicylate ion,[6,8] and this difference arises because of different rate coefficients (k_3 and k_3') for diffusion-controlled proton transfer from the non-hydrogen-bonded intermediates to hydroxide and carbonate ions.

The best fits of equation (1) to the kinetic data for (1) in H_2O and D_2O give $k_2(H_2O)/k_2(D_2O)$ *ca.* 1.2 and $k_1(H_2O)/k_1(D_2O)$ *ca.* 2.1. At low hydroxide ion concentrations the larger contribution to the reciprocal relaxation time is made by the lower route in Scheme 2, whereas at high hydroxide ion concentrations the upper route becomes more important. However, the isotope effect $\tau^{-1}(H_2O)/\tau^{-1}(D_2O)$ does not reflect this shift in mechanism. The values of τ^{-1} contain contributions from forward and reverse reactions and the value of $\tau^{-1}(H_2O)/\tau^{-1}(D_2O)$ remains roughly constant within the range 3.0 to 1.9 as the hydroxide ion concentration is changed. Application of equation (3) to the data for proton removal by hydroxide ion from (2) in H_2O and D_2O leads to the result $(k_2k_3/k_{-2})_{H_2O}/(k_2k_3/k_{-2})_{D_2O} = 2.0 \pm 0.3$. Again, the isotope effect $\tau^{-1}(H_2O)/\tau^{-1}(D_2O)$ is roughly independent of hydroxide ion concentration and values between 3.0 and 2.1 were measured. These values of the kinetic solvent isotope effects on reaction of (1) and (2) are similar to those observed for proton transfer from most oxygen and nitrogen acids; it is only in rare cases that larger isotope effects are observed.[9]

Acknowledgements

The S.E.R.C. and the Royal Society are thanked for their support of this work.

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Received 30*th July* 1985; *Paper* 5/1314