Kinetics of Hydrolysis of 1-Acetoxy-, 1-Acetoxy-8-hydroxy-, and 1,8-Diacetoxynaphthalenes; Intramolecular Participation by a Hydroxy Group

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Consecutive hydrolysis of the acetoxy groups in 1,8-diacetoxynaphthalene in aqueous alkaline solution can be studied kinetically because hydrolysis occurs more rapidly for the diacetate than for 1-acetoxy-8-hydroxynaphthalene which is mostly present in the ionised form. The dependence of the rate coefficient (k_2) for hydrolysis of 1-acetoxy-8-hydroxynaphthalene on the concentration of hydroxide ion is complex because of the equilibrium between the ionised and un-ionised forms and their different reactivities. The equilibrium between the ionised and un-ionised forms has been measured separately and the data are combined with the kinetic results to show that the linear dependence of k_2 on $[OH^-]$ at high concentrations is due to reaction of the ionised form with OH^-. At low concentrations, the curved dependence of k_2 on $[OH^-]$ can be explained by reaction of ionised 1-acetoxy-8-hydroxynaphthalene with solvent. The value of the rate coefficient (k_4) for this reaction, in comparison with the value for the reaction of 1-acetoxynaphthalene with water, shows that the hydroxy group assists the attack of water by intramolecular general base catalysis. A kinetic solvent isotope effect $k_4(H_2O)/k_4(D_2O)$ 2.2 ± 0.5 is observed.

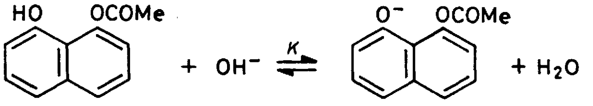
We have previously found that 1-acetylamino-8-hydroxynaphthalene is stable to hydrolysis in neutral and alkaline solution.[1] In the present work, the hydrolysis of 1-acetoxy-8-hydroxynaphthalene has been studied to investigate whether the hydroxy group can take part as an intramolecular catalyst. Examples of intramolecular catalysis by phenolic groups in the hydrolysis of esters are known, and various mechanisms have been proposed.[2,3] High effective molarities are found when the phenolate ion is involved in intramolecular nucleophilic attack to give a cyclised product. For example, the anion of 2-hydroxyphenylacetic acid phenyl ester cyclises to a lactone by a mechanism in which intramolecular nucleophilic attack of the phenolate ion on the ester carbonyl occurs.[4] The ratio of the rate coefficient for this process to the rate coefficient for the intermolecular reaction of phenolate ion with phenyl acetate has a value of 2.5×10^5 mol dm^{-3}. Effective molarities as high as 10^{12} mol dm^{-3} have been estimated[3] from the values of the equilibrium constants for lactonisation of hydroxycarboxylic acids.[5] Lower effective molarities, less than *ca.* 80 mol dm^{-3}, are found for reactions in which phenolate ions behave as intramolecular base catalysts.[3] The rate coefficient for hydrolysis of ionised 2-hydroxyphenyl benzoate in aqueous solution is several hundred-fold larger than the rate coefficient for hydrolysis of 2-methoxyphenyl benzoate. This is interpreted in terms of base catalysis of the attack of water by the ionised hydroxy group[6] and an effective molarity of 19 mol dm^{-3} is calculated.[3] For 2-hydroxyphenyl acetate, the rate coefficient for reaction of the anion with the aqueous solvent[7] is 6.5×10^4-fold greater than the rate coefficient for spontaneous hydrolysis of phenyl actate.[8] The effective molarity of the phenolate anion is estimated[3] as *ca.* 80 mol dm^{-3}. Reactions of the anions of 2-hydroxyphenyl benzoate and 2-hydroxyphenyl acetate with water are kinetically equivalent to the reactions of the undissociated species with hydroxide ion. If the kinetic data were interpreted in this way,[7] the rate coefficient for reaction of 2-hydroxyphenyl acetate with hydroxide ion which is derived is 700-fold larger than the rate coefficient for reaction of phenyl acetate with hydroxide ion. This could be explained by intramolecular acid catalysis by the hydroxy group of the attack of hydroxide ion, and originally this was the preferred explanation. However this possibility has been rejected[2,3] in favour of base catalysis of the attack of water by the ionised hydroxy group. The evidence for 2-hydroxyphenyl benzoate[6] consisted of the demonstration of the absence of catalysis for nucleophiles without a removable proton. Similar evidence was obtained for 2-hydroxyphenyl carbonate[9] and phenyl 2-hydroxybenzoate.[6,10] If the enhanced rates of hydrolysis were the result of acid catalysis of the attack of hydroxide ion by the hydroxy group, similar catalysis should be observed for reaction with other nucleophiles, including those without removable protons. Intramolecular base catalysis has been observed in reactions involving nucleophiles possessing a removable proton, for example methanol[11] and amines.[12]

Experimental and Results

Materials.—1,8-Dihydroxynaphthalene was prepared from the sultone of 1-hydroxynaphthalene-8-sulphonic acid[13] and recrystallised from toluene–light petroleum (b.p. 60—80 °C). Diacetylation was achieved by shaking with a four-fold molar excess of acetic anhydride in the presence of 1 mol dm^{-3} sodium hydroxide at 0 °C. The product was recrystallised from chloroform–light petroleum (b.p. 60—80 °C) to give a white solid, m.p. 145 °C, δ($CDCl_3$; 60 MHz) 7.2—8.0 (m, 6 H, ArH) and 2.45 (s, 6 H, Me). The monoacetylated product was obtained from reaction of 1,8-dihydroxynaphthalene at room temperature with a two-fold molar excess of acetic anhydride in the presence of sodium hydrogen carbonate. The precipitated white solid was recrystallised from chloroform–light petroleum (b.p. 60—80 °C) to give 1-acetoxy-8-hydroxynaphthalene (m.p. 95 °C), δ($CDCl_3$; 60 MHz) 8.25 (s, 1 H, OH), 6.6—7.9 (m, 6 H, ArH), and 2.45 (s, 3 H, Me).

Equilibrium Measurements.—Equilibrium and kinetic measurements were made in aqueous solution at 25 °C with an ionic strength 0.2 mol dm^{-3} maintained by addition of sodium chloride. Individual kinetic runs were reproducible to ± 2% and the uncertainty on first- and second-order rate coefficients is given in the text.

The acid dissociation of 1-acetoxy-8-hydroxynaphthalene, equation (1), was studied spectrophotometrically in the presence of carbonate buffers.



(1)

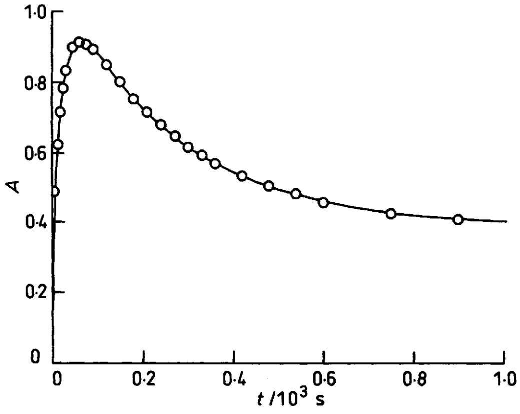


Figure 1. Change in absorbance (A) at 244 nm with time accompanying the hydrolysis of 1,8-diacetoxynaphthalene in 0.02 mol dm^{-3} sodium hydroxide. The circles are experimental values and the line is a best-fit of equation (3)

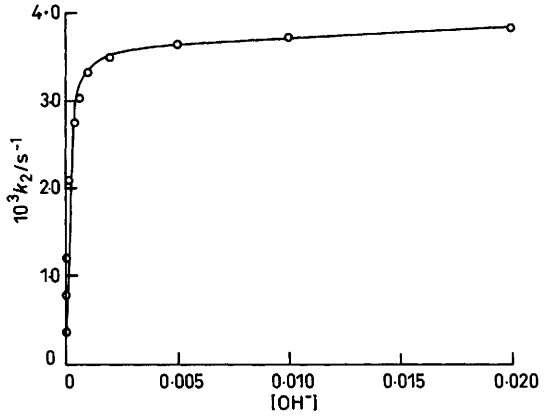
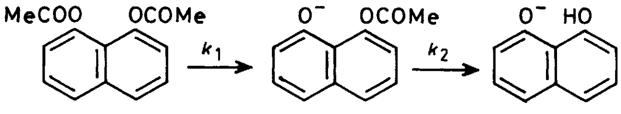


Figure 2. Variation of the first-order rate coefficient (k_2) for hydrolysis of 1-acetoxy-8-hydroxynaphthalene. The line is a best-fit of equation (4).

A concentrated solution of 1-acetoxy-8-hydroxynaphthalene in dioxane was injected into the carbonate buffer to give a concentration of ester of 5 × 10^{-5} mol dm^{-3} and absorbance readings were taken immediately at 244 nm before appreciable hydrolysis had occurred. A value for the molar absorptivity of the monoanion was obtained in 0.1 mol dm^{-3} sodium hydroxide and a value for the undissociated species was measured in unbuffered aqueous solution. Absorbance readings at several buffer ratios were used to calculate $K(H_2O)$ 1.14 ± 0.1 × 10^4 dm^3 mol^{-1} for equilibrium (1). From measurements in D_2O, the result $K(D_2O)$ 2.31 ± 0.3 × 10^4 dm^3 mol^{-1} was obtained. These values correspond to pK_a (H_2O) 9.69 ± 0.06 and pK_a (D_2O) 10.24 ± 0.06 for 1-acetoxy-8-hydroxynaphthalene at ionic strength 0.2 mol dm^{-3}.

Kinetic Studies.—1,8-*Diacetoxynaphthalene*. The hydrolysis of 1,8-diacetoxynaphthalene was followed spectrophotometrically in aqueous solutions containing 0.005—0.20 mol dm^{-3} sodium hydroxide and an initial ester concentration of 5.0 × 10^{-5} mol dm^{-3}. On introduction of the ester as a concentrated solution in dioxane, the absorbance at 244 nm was observed to pass through a maximum value with time. Data obtained at a hydroxide ion concentration of 0.02 mol dm^{-3} are given in Figure 1. The final absorbance was identical to the absorbance of a solution prepared from 1,8-dihydroxynaphthalene. Assuming that hydrolysis occurs in consecutive steps as shown in equation (2), the dependence of absorbance (A) against time (t) is given by equation (3) in which C_1 refers to



(2)

(1) (2) (3)

$$A = C_1[\varepsilon_3 + k_1(\varepsilon_3 - \varepsilon_2)e^{-k_2t}/(k_2 - k_1) + \{\varepsilon_1 + (\varepsilon_2k_1 - \varepsilon_3k_2)/(k_2 - k_1)\}e^{-k_1t}] \quad (3)$$

the initial concentration of 1,8-diacetoxynaphthalene (**1**) and ε_1, ε_2, and ε_3 are the molar absorptivities of the species (**1**), (**2**), and (**3**) and k_1 and k_2 are the first-order rate coefficients for the two steps in equation (2) at a particular hydroxide ion concentration. Values of the molar absorptivities were determined in separate experiments. Under the conditions of the experiment, (**2**) and (**3**) were almost entirely in the monoanion forms, so that ε_2 and ε_3 were independent of [OH$^-$]. At each hydroxide ion concentration the value of k_2 was known from separate studies with 1-acetoxy-8-hydroxynaphthalene, see below. Theoretical fits of equation (3) to the experimental results were produced at each hydroxide ion concentration by varying the value of k_1. The solid line in Figure 1 was drawn using the values of ε_1, ε_2, and ε_3 1 400, 22 000, and 8 000 dm^3 mol^{-1} cm^{-1} respectively with C_1 4.8 × 10^{-5} mol dm^{-3}, k_1 5.4 × 10^{-2} s^{-1}, and k_2 3.78 × 10^{-3} s^{-1}. The best-fit values of k_1 at different [$^-$OH] gave a linear dependence on [OH$^-$] from which the second-order rate coefficient 3.2 ± 0.6 dm^3 mol^{-1} s^{-1} was obtained for reaction of 1,8-diacetoxynaphthalene with hydroxide ion.

1-*Acetoxy*-8-*hydroxynaphthalene*. The hydrolysis of 1-acetoxy-8-hydroxynaphthalene to 1,8-dihydroxynaphthalene was studied in sodium hydroxide solutions and in carbonate buffers. Reaction was initiated by injecting a concentrated dioxane solution of the ester into the aqueous solution to give an initial concentration of the ester of 5 × 10^{-5} mol dm^{-3}. The decrease in absorbance at 244 nm was followed and first-order rate coefficients (k_2) were measured at hydroxide ion concentrations in the range 0.001—0.2 mol dm^{-3}. Lower hydroxide ion concentrations were controlled by carbonate buffers and measurements were made at several buffer ratios ([CO_3^{2-}]/[HCO_3^-]) and different buffer concentrations ([CO_3^{2-}] 0.01—0.05 mol dm^{-3}). The first-order rate coefficient varied slightly with buffer concentration but this was due to a small change in buffer ratio as the buffer was diluted. Catalysis of the hydrolysis by buffer was negligible under these conditions. The values of k_2 up to hydroxide ion concentrations of 0.02 mol dm^{-3} are plotted in Figure 2. In the range 0.02—0.20 mol dm^{-3} a linear dependence of k_2 on [OH$^-$] was observed. Similar studies were carried out in D_2O.

1-*Acetoxynaphthalene*. The hydrolysis of 1-acetoxynaphthalene was studied in aqueous sodium hydroxide by measuring the decrease in absorbance at 330 nm which occurred on introduction of the ester (8 × 10^{-5} mol dm^{-3}) into the aqueous solution. The first-order rate coefficient was directly proportional to [OH$^-$] for concentrations in the range 0.005—0.20 mol dm^{-3} and a value of 1.40 ± 0.05 dm^3 mol^{-1} s^{-1} was obtained for the second-order rate coefficient. In D_2O, the result was 1.78 ± 0.06 dm^3 mol^{-1} s^{-1}.

Discussion

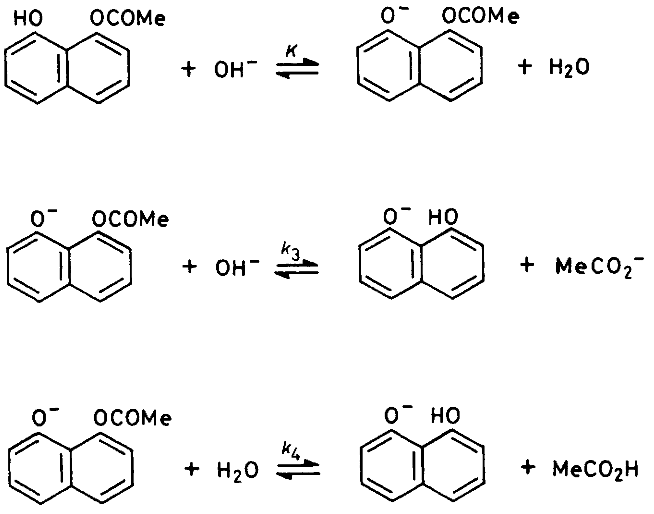
Typical data for the hydrolysis of 1,8-diacetoxynaphthalene, analysed according to equations (2) and (3), are shown in Figure

1. The linear variation of the best-fit values of k_1 with hydroxide ion concentration was used to obtain a value for the second-order rate coefficient for reaction of 1,8-diacetoxynaphthalene with hydroxide ion and the result is given in the Table.

The experimental values of the first-order rate coefficient (k_2) for the hydrolysis of 1-acetoxy-8-hydroxynaphthalene are plotted in Figure 2. The result k_3 5.5 ± 0.5 × 10^{-3} dm^3 mol^{-1} s^{-1} was obtained for the second-order rate coefficient for reaction of the monoanion of 1-acetoxy-8-hydroxynaphthalene with hydroxide ion from the linear dependence of k_2 on $[OH^-]$ in the range 0.02—0.20 mol dm^{-3}. The overall variation of k_2 is explained by the mechanism in the Scheme, from which equation (4) is derived on the assumption that the ionisation of

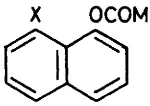
$$k_2 = k_4K[OH^-]/(1 + K[OH^-]) + k_3K[OH^-]^2/(1 + K[OH^-]) \quad (4)$$

1-acetoxy-8-hydroxynaphthalene is established rapidly. The solid line in Figure 2 is a best-fit of equation (4) using the value K 1.14 × 10^4 dm^3 mol^{-1} from equilibrium studies and k_3 5.5 × 10^{-3} dm^3 mol^{-1} s^{-1} obtained at high hydroxide ion concentrations and k_4 3.7 ± 0.4 × 10^{-3} s^{-1}. In D_2O the results were fitted using K 2.31 × 10^4 dm^3 mol^{-1}, k_3 5.5 ± 0.5 × 10^{-3} dm^3 mol^{-1} s^{-1}, k_4 1.70 ± 0.2 × 10^{-3} s^{-1}.



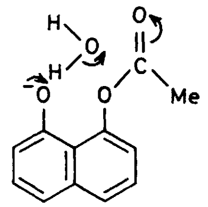
Scheme.

Table. Rate coefficients for reaction of 1-naphthylacetates with hydroxide ion[a]



[X]	Rate coefficient/dm^3 mol^{-1} s^{-1}	Ref.
H	1.40 ± 0.05	*b*
OCOMe	3.2 ± 0.6	*b*
O^-	5.5 ± 0.5 × 10^{-3}	*b*
NHCOMe	1.33 ± 0.01	1

[a] Aqueous solution at 25 °C and ionic strength 0.2 mol dm^{-3}. [b] Present work.



(4)

The rate coefficient k_4 refers to reaction of the anion of 1-acetoxy-8-hydroxynaphthalene with water. For 1-acetoxynaphthalene, reaction with solvent makes a negligible contribution compared to reaction with hydroxide ion and a value of the rate coefficient (k_0) for spontaneous hydrolysis cannot be deduced from the studies in sodium hydroxide solutions. An approximate value of k_0 *ca.* 7 × 10^{-8} s^{-1} can be estimated from the value k_0 6.6 × 10^{-8} s^{-1} for phenyl acetate[5,14] by assuming that the ratio of k_0 values for the two esters is similar to the ratio of the rate coefficients for their reaction with hydroxide ion.[15] It follows that the hydroxy substituent in 1-acetoxy-8-hydroxynaphthalene brings about a *ca.* 5 × 10^4-fold increase in the rate of spontaneous hydrolysis over that for 1-acetoxynaphthalene. This effect can be explained by intramolecular base catalysis of the attack of solvent, as in (**4**). The efficiency of the base catalysis is illustrated by converting k_4 into second-order units (6.7 × 10^{-5} dm^3 mol^{-1} s^{-1}) and comparing this value which refers to the attack of water on the ester carbonyl of 1-acetoxy-8-hydroxynaphthalene anion with the value k_3 5.5 × 10^{-3} dm^3 mol^{-1} s^{-1} for the attack of hydroxide ion. For the anion of 2-hydroxyphenyl acetate, the value k_0 4.3 × 10^{-3} s^{-1} has been found[7] and this represents a 6.5 × 10^4-fold increase over the value for phenyl acetate. An effective molarity of *ca.* 80 mol dm^{-3} has been calculated[3] for the ionised hydroxy group in 2-hydroxyphenyl acetate and it is probable that a similar value applies to 1-acetoxy-8-hydroxynaphthalene. Lower values have been calculated[3] for the effective molarities of the ionised hydroxy groups in phenyl 2-hydroxybenzoate[6] and 2-hydroxyphenyl benzoate[6] and for the carboxylate group in 2-carboxyphenyl acetate.[16] The size of the solvent isotope effect on the spontaneous hydrolysis of ionised 1-acetoxy-8-hydroxynaphthalene, $k_4(H_2O)/k_4(D_2O)$ 2.2 ± 0.5, is similar to the results obtained for 2-hydroxyphenyl benzoate,[6] $k_0(H_2O)/k_0(D_2O)$ 1.8, and 2-hydroxy-5-nitrophenyl carbonate,[9b] $k_0(H_2O)/k_0(D_2O)$ 2.3.

The mechanism in the Scheme provides a satisfactory explanation for the variation of k_2 with $[OH^-]$ in Figure 2, but a similar dependence is predicted by a mechanism in which the step involving reaction of ionised 1-acetoxy-8-hydroxynaphthalene with solvent is replaced by the kinetically equivalent reaction of undissociated 1-acetoxy-8-hydroxynaphthalene with hydroxide ion. The first term in equation (4) is then replaced by the term $k_5[OH^-]/(1 + K[OH^-])$ in which k_5 is the second-order rate coefficient for reaction between the undissociated ester and hydroxide ion. A fit to the experimental results is obtained with k_5 42.0 ± 2 dm^3 mol^{-1} s^{-1}. The result k_5 39.2 ± 2 dm^3 mol^{-1} s^{-1} is found in D_2O, giving a solvent isotope effect of 1.07 ± 0.1 which is similar to the results obtained for the reaction of hydroxide ion with 1-acetoxynaphthalene (0.79 ± 0.06) and with ionised 1-acetoxy-8-hydroxynaphthalene (1.0 ± 0.2) and within the range expected for nucleophilic attack by hydroxide ion.[17] Values of the second-order rate coefficients obtained in this work for reaction of various naphthyl esters with hydroxide ion are given in the Table. These results fit a scattered $\sigma\rho$ plot using σ_m values[18] and the very approximate value $\rho = 2.5 \pm 1.0$ is obtained. The value k_5 42.0 ± 2 dm^3 mol^{-1} s^{-1} for 1-acetoxy-8-hydroxynaphthalene gives a 40-fold positive deviation from these data and to explain this it would be necessary to propose intramolecular catalysis by the hydroxy group in the attack of hydroxide ion. It follows that the variation of k_2 with $[OH^-]$ for 1-acetoxy-8-hydroxynaphthalene can be explained either in terms of a reaction of the undissociated ester with hydroxide ion in which the hydroxy group behaves as an intramolecular acid catalyst or in terms of a reaction between the ionised ester and solvent, with the ionised hydroxy group acting as an intramolecular base catalyst. In other examples,[2] participation of an ionised phenolic group as an intramolecular base catalyst is preferred and acid catalysis of the attack of hydroxide ion is considered unlikely.[2]

Acknowledgements

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