Kinetics and Equilibria of Reactions between Acetic Anhydride and Substituted Phenolate Ions in Aqueous and Chlorobenzene Solutions

Salem A. Ba-Saif, Antony B. Maude and Andrew Williams*
University Chemical Laboratory, Canterbury, Kent, UK CT2 7NH

Potassium acetate, solubilised in chlorobenzene by 18-crown-6, displaces the phenolate ion from substituted phenyl acetates by a second-order (k_{-2}^{Cl}) process. Potassium phenolate ions, under similar conditions, react with acetic anhydride *via* a second-order (k_2^{Cl}) to yield the phenyl acetate. The concentration of the crown does not affect the reactivity unless it is not sufficient to solubilise the reactants.

The rate constants correlate with the ionisation of the substituted phenols in water:

$$\log k_2^{Cl} = 1.60 \pm 0.23\, pK_a^{ArOH(aq)} - 9.06 \pm 1.4$$

$$\log k_{-2}^{Cl} = -0.97 \pm 0.12\, pK_a^{ArOH(aq)} + 4.78 \pm 0.78$$

The equilibrium constant for transfer of the acetyl group between phenolate ions and acetic anhydride in chlorobenzene has a Brønsted β_{eq}^{Cl} of 2.6 measured against $pK_a^{ArOH(aq)}$.

The second-order rate constants (k_2^{aq}) have been measured for the reaction of substituted phenolate ions with acetic anhydride in water and they obey the Brønsted equation:

$$\log (k_2^{aq}) = 0.56 \pm 0.06\, pK_a^{ArOH(aq)} - 2.52 \pm 0.51$$

Comparison of the value of the Brønsted exponent for the equilibrium constant in chlorobenzene ($\beta = 2.6$) compared with that for aqueous solution ($\beta = 1.7$) indicates a greater development of effective charge consistent with the weaker solvating power of chlorobenzene.

The reaction of substituted phenoxide ion with acetic anhydride has a Leffler α value of 0.33 and 0.62 for aqueous and chlorobenzene solutions, respectively, indicating a more advanced bond formation in the transition state of the reaction in the latter solvent even though the reactions in chlorobenzene are faster than in water.

Charge development on atoms from reactant through transition state to product is one of the most important indicators of mechanism in solution because it is directly connected with the progress of bonding changes. Polar substituent effects on kinetics and equilibria are usually the most convenient tools which may be used to determine charge changes.[1] There have been few studies of polar substituent effects on equilibria in non-aqueous solution with the purpose of determining effective charge values. There are reports of effective charge measurements of the transfer of esters between bulk and micellar phases[2] and there are a considerable number of ionisation constants known for non-aqueous solvents.[3] Many catalytic reactions involve reactions of the substrate within a microphase (such as in a complex or the active site of an enzyme) by partitioning from bulk solvent. In the case of enzyme catalysis the site of the reaction is often hydrophobic and in order to interpret polar effects in these systems it is necessary to have results for standard hydrophobic media.

The solubilising power of crown ethers for the potassium ion[4] provides a useful system for studying reactions of anions in non-aqueous solvents which otherwise would not support the interaction of ionic species.[5,6] Measurements of the polar effects on equilibria in organic media are needed to provide calibration[1] of the effective charges thus obtained from rate measurements in these solvents.

In this investigation we study the forward and reverse kinetics for the reaction between phenoxide ions and acetic anhydride [eqn. (1)] in both chlorobenzene and aqueous solvents.

$$\text{Ar–O}^- + \text{Ac}_2\text{O} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Ar–O–CO–CH}_3 + \text{AcO}^- \quad (1)$$

The study provides values of β_{eq} for the transfer of the acetyl group between phenolate ions in chlorobenzene solution. This data will be useful to interpret values of β_{nuc} and β_{lg} for reactions of nucleophiles with aryl acetates in this solvent in future studies. Hajdu and Smith[5] showed that potassium carboxylate solubilised in acetonitrile with 18-crown-6 reacted with substituted phenyl esters to yield mixed anhydrides and moreover rate enhancements up to 1000-fold were observed with substrates with neighbouring cationic groups. Initial work by Hajdu and Smith[5] and Kovach[6] indicated that polar substituents have an effect on the transacetylation reaction in acetonitrile.

The choice of chlorobenzene as a solvent for study is dictated by previous work and because it is readily obtained pure and dry; it has sufficient polarity to dissolve a variety of organic reactants with reasonable concentration ranges and moreover has no obvious components which could solvate positive or negative centres.

Experimental

Materials.—Substituted phenyl acetates were available from previous studies in this laboratory;[7] 2,3,4-trichlorophenyl acetate was obtained by stirring a solution of the phenol with acetyl chloride in dichloromethane after dropwise addition of a slight excess of pyridine. The solution was extracted with dil.

HCl, dried with $MgSO_4$ and evaporated to yield a solid which was recrystallised from aqueous ethanol to give fibrous needles, m.p. 45–46 °C (Found: C, 40.08; H, 1.99%. Calc. for $C_8H_5Cl_3O_2$: C, 40.12; H, 2.10%).

Phenols were obtained commercially and recrystallised or resublimed before use. Potassium phenolate salts were prepared by reacting the phenol with 1 equivalent of KOH in MeOH or EtOH solution followed by evaporation and then azeotropic distillation of any remaining water using toluene. The salts were purified by recrystallisation and stirred over P_2O_5. Potassium acetate was recrystallised from acetic acid and dried in a vacuum oven (100 °C/1 Torr) for 48 h. 18-Crown-6 was purchased from Lancaster Chemical Company. Acetic anhydride was obtained from a fraction distilling between 139 and 140 °C and stored in a dark bottle. Chlorobenzene (BDH) was obtained from a fraction distilling between 131 and 132 °C. Water was doubly distilled from glass and materials for buffers were of analytical reagent quality or were recrystallised or redistilled prior to use.

Methods.—Kinetics in chlorobenzene. The reactions of potassium acetate with substituted phenyl acetates in chlorobenzene were initiated by addition of an aliquot (20 μl) of a solution of the ester in chlorobenzene to a chlorobenzene solution of potassium acetate (with 18-crown-6) in a 2.5 cm^3 silica cell maintained at 25 °C in the thermostatted cell compartment of a Perkin-Elmer Lambda-5 spectrophotometer. The stock of potassium acetate was prepared with 1.5 equivalents of 18-crown-6 per equivalent of potassium acetate salt. The reactions of substituted phenolate ions with acetic anhydride in chlorobenzene were observed by addition of an aliquot of solution (*ca.* 20 μl) containing the potassium phenolate salt–crown ether in chlorobenzene to a chlorobenzene solution of acetic anhydride (at varying concentrations) in a 2.5 cm^3 silica cell in the thermostatted cell compartment of the spectrophotometer.

The stock solution of the phenolate salts were prepared by mixing 2 equivalents of 18-crown-6 per equivalent of potassium phenolate (except in the case of experiments to study the effect of crown concentration).

In both cases the change in absorbance was measured at a single wavelength determined by carrying out a trial run scanning the spectrum periodically. Separate experiments were carried out to determine the extinction coefficient change of the substituted phenol at the wavelength employed in the kinetics; this parameter was required to determine the progress of each reaction.

Pseudo-first-order kinetics were obtained by fitting the absorbance/time measurements to a first-order rate law by use of a standard fitting program and an Opus VII desk top computer.

Kinetics in aqueous solution. Reactions of substituted phenolate ions with acetic anhydride were followed kinetically in a similar fashion to that for the chlorobenzene solution except that crown ether was not employed as an additive. The acetic anhydride stock solution in acetonitrile was added to the buffer solution containing the phenol and the change in absorbance due to the consumption of the phenol was observed as a function of time. The experiments were repeated with constant phenolate ion concentration and increasing amounts of acetic anhydride. Second-order rate constants for depletion of the substituted phenol were obtained from the initial rate of absorbance change by division by anhydride and phenolate ion concentrations.

The reactant solutions were prepared from stock solutions, one containing the phenol and buffer component adjusted to the pH required for the experiment. The aqueous solutions were degassed prior to mixing the stocks and their use; the degassing procedure gave solutions which lasted for approximately one working day.

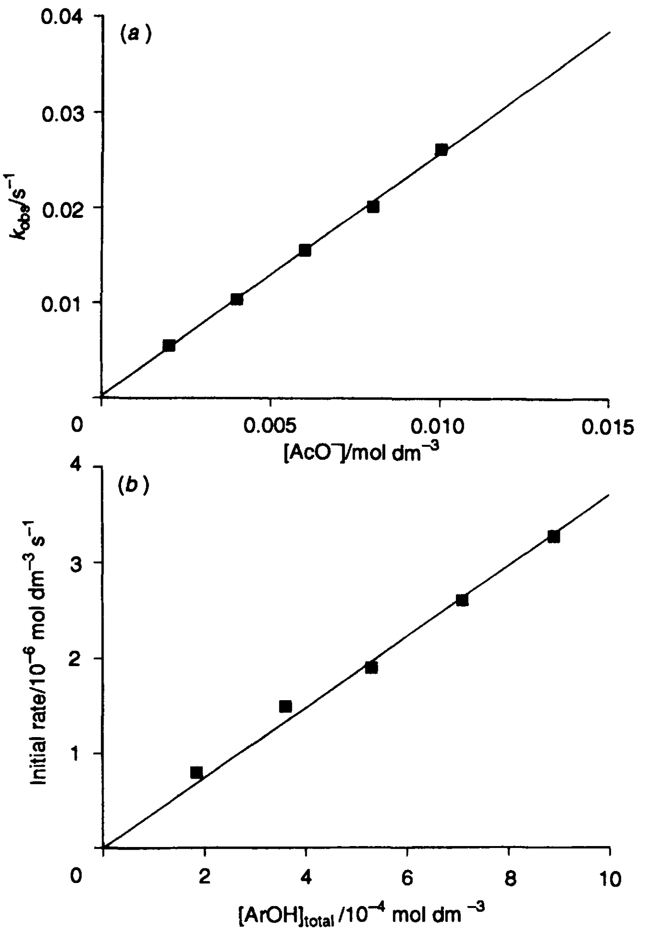


Fig. 1 (*a*) Rate constants for acetolysis of 2,5-dinitrophenyl acetate in chlorobenzene (for conditions, see Table 1); the line is calculated from the parameters in Table 1. (*b*) Initial rate in water for the depletion of the 2,3,4,5-tetrafluorophenolate ion by added acetic anhydride (conditions as in Table 3); the line is calculated from the parameters in Table 3.

The addition of the anhydride *to* the solution of phenolate ion was necessary because of the relatively rapid hydrolysis rates of the acetic anhydride. Even after taking this precaution, the rate of disappearance of phenolate ion decreased owing to the concomitant hydrolysis of the acetic anhydride and only the initial rate is of use in obtaining the second-order rate constant for acetylation of the phenolate ion. The pH decreased significantly throughout the progress of the reaction owing to the formation of acetic acid and the pH recorded in the table is that of the initial conditions under which the rate was determined. The initial rate was computed from the absorbance/time readings by use of a standard curve fitting program on a desk top computer.

Measurements of pH throughout the study were carried out with a Radiometer PHM 62 digital instrument equipped with a Russell CMAWL CL5 combination electrode. The instrument was standardised with EIL standard buffers to ± 0.01 pH units.

Results

Reactions in Chlorobenzene.—Reactions of substituted phenyl acetates with acetate ion and phenolate ions with acetic anhydride obeyed pseudo-first-order kinetics up to 90% of the total reaction. For reactions of acetate ion with phenyl acetates the values of k_{obs} were linearly dependent on acetate ion concentration [*e.g.*, Fig. 1(*a*)]. The second-order rate constants (k_{-2}^{Cl}) derived from the slope of k_{obs} *vs.* $[AcO^-]$ are collected

Table 1 Rate constants for reaction of acetate anion with substituted phenyl acetate esters in chlorobenzene solution[a]

Substituent	$pK_a^{ArOH\,b}$	k_{-2}/dm^3 mol^{-1} s^{-1}	k_2/k_{-2}	[AcO$^-$]/ mol dm$^{-3\,c}$	[Ester]/10^{-4} mol dm^{-3}	k_{obs}/10^{-3} s$^{-1\,d}$	Δε/dm^3 mol^{-1} cm^{-1}	λ/nm
2,4-Dinitro	4.09	9.74 +0.07	8.93 × 10^{-5}	2–10.10^{-4}	0.40	2.6–9.7	13 900	365
2,5-Dinitro	5.22	2.56 +0.06	0.229	2–10.10^{-3}	1.60	5.5–26	4 930	465
2-Chloro-4-nitro	5.45	0.156 ±0.002	11.0	2–10.10^{-2}	0.497	2.3–15	17 100	415
2,3,4,5-Tetrachloro	5.64	0.078 ±0.002 6		0.02–0.1	3.31	2–8	307	1 950
2,3,5-Trichloro	6.43	0.022 6 ±0.000 5	1 680	0.02–0.1	3.33	0.75–2.6	1 470	293
4-Chloro-2-nitro	6.46	0.032 2 ±0.000 5	16.5	0.02–0.1	1.2	0.5–3.3	435	5 350
2,4,5-Trichloro	6.72	0.014 5 ±0.000 6		0.02–0.1	2.58	0.07–1.7	1 720	304
2,3,5-Trichloro	6.92	0.003 72 ±0.000 4		0.05–0.25	3.22	0.27–1.0	1 510	301
4-Nitro	7.14	0.006 96 ±0.000 4	20 400	0.02–0.1	0.8	0.19–0.8	7 170	415
2-Nitro	7.20	0.002 03 ±0.000 1		0.05–0.25	1.61	0.1–0.5	3 710	430
3,4,5-Trichloro	7.68	0.003 33 ±0.000 4		0.05–0.25	2.66	0.45–1.2	1 530	300
4-Chloro-3-nitro	7.75	0.010 6 ±0.000 7		0.05–0.25	3.24	0.9–2.3	577	375

[a] T = 25 °C. [b] Values of pK_a^{ArOH} are from W. P. Jencks and J. Regenstein in *Handbook of Biochemistry*, 2nd edn., ed. H. A. Sober, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970, section j–187. [c] Range of KOAc concentrations employed. [d] Range of observed pseudo-first-order rate constants. Five data points were employed for each value of k_2 (not including duplicate runs).

Table 2 Rate constants for reaction of substituted phenolate ions with acetic anhydride in chlorobenzene solution[a]

Substituent	pK_a^{ArOH}	k_2/dm^3 mol^{-1} s^{-1}	[ArO$^-$]/ 10^{-5} mol dm^{-3}	[Ac$_2$O]/mol dm^{-3}	N^b	λ/nm	Δε/dm^3 mol^{-1} cm^{-1}	k_{obs}/ 10^{-3} s^{-1}
2,4-Dinitro	4.09	8.7 ± 0.5 × 10^{-4}	8.0	0.2–1.0	10	365	13 900	0.9–1.7
2,5-Dinitro	5.22	0.586 ± 0.028	0.8; 16.0	1–2 × 10^{-3}	10	480	6 530	1.5–3.9
2-Chloro-4-nitro	5.45	1.72 ± 0.15	4.0	1–2 × 10^{-3}	10	415	17 100	2.9–10
2,3,5-Trichloro	6.43	38 ± 4	4.35	1–5 × 10^{-4}	5	320	1 690	11.4–2 6.7
4-Chloro-2-nitro	6.46	0.530 ± 0.06	4.0	2–6 × 10^{-3}	15	455	3 160	2–4 × 10^{-3}
4-Nitro	7.14	142 ± 13	4.0	2–5 × 10^{-4}	4	415	7 170	45–90

[a] T = 25 °C. [b] Number of data points not including duplicate runs.

in Table 1. Pseudo-first-order rate constants for reaction of substituted phenolate ions with acetic anhydride are linearly related to the anhydride concentration; the second-order rate constants (k_2^{Cl}) obtained from the slope of the linear plots are collected in Table 2.

The effect of the crown concentration on the rates was measured for the reaction of 2,5-dinitrophenolate ion with acetic anhydride. The rate constants are identical within experimental error over a range of [18-crown-6] from 2 × 10^{-4} to 0.1 mol dm^{-3} with the [2,5-dinitrophenolate ion] at 80 μmol dm^{-3} and [Ac$_2$O] at 5 mmol dm^{-3}.

The second-order rate constants are correlated with the aqueous pK_a of the leaving and attacking phenol (Fig. 2) according to eqns. (2) and (3). Eqns. (2) and (3) may be combined

$$\log k_{-2}^{Cl} = -0.97 \pm 0.12\, pK_a^{ArOH(aq)} + 4.78 \pm 0.78 \quad (n = 12;\, r = 0.9312) \qquad (2)$$

$$\log k_2^{Cl} = 1.60 \pm 0.23\, pK_a^{ArOH(aq)} - 9.06 \pm 1.4 \quad (n = 6;\, r = 0.9598) \qquad (3)$$

to give a Brønsted correlation for the equilibrium constant [eqn (4*a*)]. Eqn. (4*a*) is similar to that of eqn. (4*b*) obtained from a Brønsted correlation of the equilibrium constant explicitly determined by division of rate constants ($K_{eq} = k_2^{Cl}/k_{-2}^{Cl}$).

$$\log K_{eq}^{Cl} = 2.57 \pm 0.35\, pK_a^{ArOH} - 13.84 \pm 2.18 \qquad (4a)$$

$$\log K_{eq}^{Cl} = 2.58 \pm 0.40\, pK_a^{ArOH} - 14.14 \pm 2.33 \quad (n = 6;\, r = 0.9561) \qquad (4b)$$

The Brønsted correlations for equilibrium in chlorobenzene and aqueous solutions are illustrated in Fig. 3; we take 2.6 as being a working value for β_{eq} for acetyl transfer from phenolate ions in chlorobenzene.

Reactions in Aqueous Solution.—The concentration of the acetic anhydride falls off and the pH drops as the reaction with the phenolate ion proceeds in aqueous solution. However, the rate can be determined under precisely known conditions of concentration of phenolate ion and acetic anhydride at the time of addition of the anhydride. The initial rates are proportional to the overall phenol concentration. Second-order rate constants are obtained from the slopes of the initial rate *vs.* total phenol concentration [*e.g.* Fig. 1(*b*)] by division by initial concentration of acetic anhydride and by the fraction of total phenol present as phenolate ion; the latter is obtained from the pH and the pK_a of the phenol. The initial rate, originally the change in absorbance with time, is converted into rate of change in molar concentration by use of the extinction coefficients determined separately.

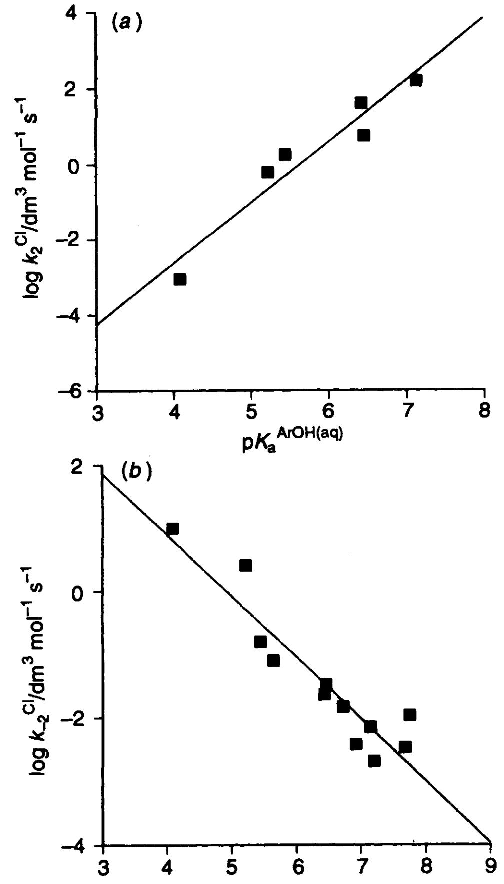


Fig. 2 (*a*) Brønsted dependence of the values of k_2^{Cl} for attack of aryloxide ions on acetic anhydride in chlorobenzene. Conditions as in Table 2; the line is drawn from eqn. (3). (*b*) Brønsted dependence of k_{-2}^{Cl} for nucleophilic attack of acetate ion on substituted phenyl acetates in chlorobenzene. Conditions as in Table 1; line is drawn from eqn. (2).

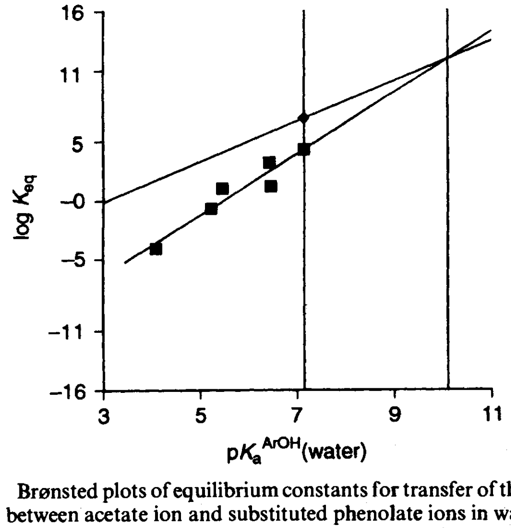


Fig. 3 Brønsted plots of equilibrium constants for transfer of the acetyl group between acetate ion and substituted phenolate ions in water and chlorobenzene. The lines are drawn from eqns. (4*b*) and (6): ■, chlorobenzene solution (data from Table 1); ◆, 4-nitrophenolate ion in water (data from Table 3). The vertical lines represent the pK_a value for 4-nitrophenol and that of the hypothetical phenol where the equilibrium constants in water and chlorobenzene are identical.

The initial rate is that for removal of phenolate ion and hence the technique measures only the nucleophilic attack of phenolate ion on the anhydride; it does *not* measure the hydrolysis of the anhydride or that of the phenyl acetate.

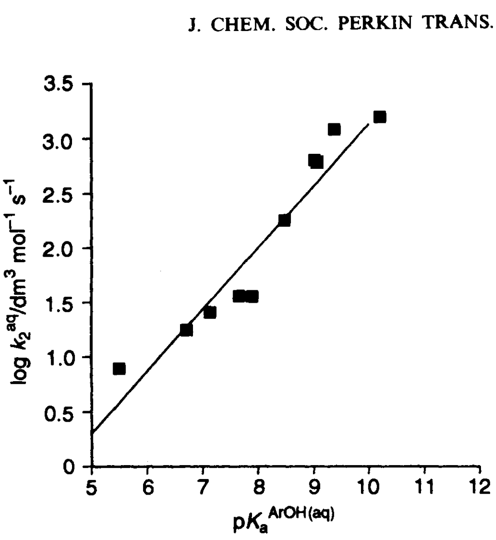


Fig. 4 Brønsted dependence of k_2^{aq} for attack of aryloxide ions on acetic anhydride in aqueous solution. Conditions in Table 3; the line is drawn from eqn. (5).

The second-order rate constants k_2^{aq} are collected in Table 3 and they obey a Brønsted correlation [eqn. (5) and Fig. 4].

$$\log k_2^{aq} = 0.56 \pm 0.06\,pK_a^{ArOH} - 2.52 \pm 0.51 \qquad (n = 9; r = 0.9594) \qquad (5)$$

Discussion

Equilibrium Constants.—Division of forward by reverse constants for chlorobenzene solution yields the equilibrium constants and these obey the Brønsted eqn. (4*b*) which is close to that obtained indirectly by subtraction of the Brønsted equation for k_{-2}^{Cl} from that of k_2^{Cl}. The equilibrium constants for the reaction in water cannot be determined simply from the ratio of the rate constants. The value k_{-2}^{aq} cannot be measured accurately[8] because the reaction of acetate ion with phenyl acetates is a mixture of nucleophilic and general base catalysed terms which cannot readily be separated.[9,10] The equilibrium constant between acetic anhydride and the 4-nitrophenolate ion may be measured by an indirect route;[11,12] the value of β_{lg} for k_{-2}^{aq} may be deduced from β_{nuc} (for k_2^{aq}) and the known β_{eq} for the reaction ($\beta_{lg} = -1.7 + 0.56 = -1.14$). The value of K_{eq}^{aq} for the 4-nitrophenol equilibrium (pK_a = 7.14) is 8.85 × 10^6 and thus the constant (*C*) in eqn. (6) is −5.19. The Brønsted dependence of K_{eq}^{aq} [eqn. (6)] is illustrated in comparison with that for chlorobenzene in Fig. 3.

$$\log K_{eq}^{aq} = \log k_2^{aq}/\log k_{-2}^{aq} = 1.7\,pK_a + C \qquad (6)$$

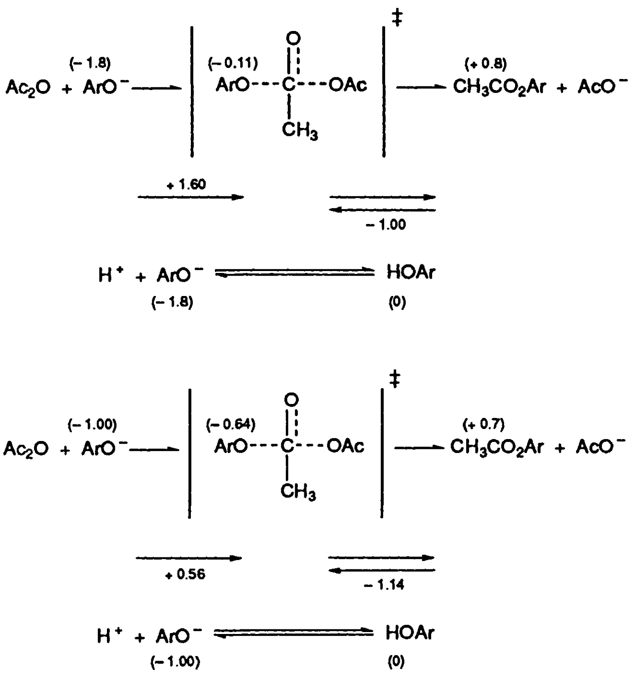
Eqns. (4*a*) and (6) indicate that the equilibrium constants for chlorobenzene and water become unity at pK_a values of phenol of 5.5 and 3.1, respectively (Fig. 3). Phenols with smaller pK_a values than these require a more energetic acetylating agent to yield the esters.

The large value of β_{eq} of 2.6 for chlorobenzene is consistent with more charge destruction in the equilibrium consistent with the poor solvating power of chlorobenzene compared with that of water (β_{eq} = 1.7). The value of β_{eq} for the ionisation of phenols in chlorobenzene has recently been measured (1.8)[13] against water as the standard. Relative to chlorobenzene as standard β_{eq} for the transfer of the acetyl group between phenolate ions is therefore 2.6/1.8 = 1.4. The small decrease in effective charge change (defined on the chlorobenzene scale) for the equilibrium relative to that for aqueous solution (β_{eq} = 1.7) is probably not significant considering the accumulation of uncertainty in determining these values. The charge change in the acetyl group transfer relative to that of the ionisation in

Table 3 Rate constants for reaction of substituted phenolate ions with acetic anhydride in aqueous solution[a]

Substituents	pK_a	pH[b]	Initial rates/ 10^{-6} dm^3 mol^{-1} s^{-1}	[ArOH]/10^{-4} mol dm^{-3}	k_2[c]/dm^3 mol^{-1} s^{-1}	λ/nm	$\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}	[Ac_2O]/10^{-4} mol dm^{-3}
2-Chloro	8.48	8.00	2.8–11	1.85–9.23	177 ± 11	300	1 143	6.32
2,4,5-Trichloro	6.72	7.50	2–10	1.4–7.22	17.5 ± 0.9	315	1 600	8.46
4-Methoxy	10.2	8.00	1.8–5.5	0.85–4.24	1 530 ± 85	288	2 930	31.1
4-Formyl	7.66	7.94	0.4–1.7	0.19–0.98	36 ± 1.2	330	19 300	15.0
2,3,4,5-Tetrafluoro	5.50	6.00	0.8–3.3	2–8.9	7.8 ± 0.05	275	800	6.3
4-Cyano	7.90	9.00	3.6–13	0.19–0.95	35.6 ± 1.5	275	20 700	12.2
4-Nitro	7.14				25.4[d]			
4-Chloro	9.38	8.00	4.5–8.0	1.8–4.6	1 190 ± 92	280	1 740	11.8
3-Chloro	9.02	8.00	2.3–10.7	1.7–8.6	626 ± 25	275	1 480	7.23

[a] T = 25 °C; ionic strength = 0.5 mol dm^{-3} made up with KCl. [b] pH of the rate determinations; buffers employed were phosphate for pH up to 7.50 and tris(hydroxymethylamino)methane up to pH 9.00. [c] Five data points, not including duplicates, were employed for each k_2 value. [d] Taken from ref. 9.



Scheme 1 Values of β^{Cl}_{nuc}, β^{Cl}_{lg} and β^{Cl}_{eq} are rounded to 1.6, −1.0 and 2.6, respectively

each solvent is thus about the same for these two very disparate solvents.

Eqns. (4*a*) and (6) predict that the equilibrium constants become identical for a phenol with pK_a = 10.17 (see Fig. 3); this indicates that for acidic phenols the reaction is more favoured thermodynamically in water than in chlorobenzene.

Reactivity.—The effect of crown ether on the acetylation reactions studied here is to solubilise the cationic counterions and may therefore be neglected in the equilibria because it is not consumed during reaction. In the case of the reactivity studies the crown ether has no effect when its concentration is above the equivalence point for the counterion. All the kinetic data were collected in the concentration region of 18-crown-6 above the equivalence point. The various rate laws do not therefore include crown ether concentration terms. Under the conditions of these experiments the crown ether is not involved differentially between reactant and transition states except in-so-far as it solvates the potassium ion component of these states.

The reactions of phenolate ions with phenyl esters are believed to be concerted and to possess single transition states which vary in structure from almost tetrahedral to almost square planar depending on the basicity of the nucleophile and nucleofuge[14] (but see Buncel[15] and Kwon[16]). It seems unlikely that the reaction in a solvent less polar than water will proceed *via* an anionic tetrahedral intermediate because this should be even less stable than the corresponding intermediate in water; as the tetrahedral intermediate becomes less thermodynamically stable we expect the barrier for the reaction to become progressively smaller. It is recognised that the stability of the putative tetrahedral intermediate is most important in directing the course of the reaction and a solvent such as dimethyl sulfoxide could enable a stepwise process to occur[15] by stabilising charged intermediates. The various β values for the proposed concerted process combine to give effective charge maps as shown in Scheme 1. The data indicate a substantial difference between the electronic distribution in the two solvents. There are larger changes in effective charge for chlorobenzene than for water. The ratio of effective charge on the phenyl oxygen from reactant to transition state relative to that from reactant to product (Leffler's α parameter; $\alpha = \beta_{nuc}/\beta_{eq}$ for k_2)[17] differs significantly for the two solvents ($\alpha^{aq} = 0.33$ and $\alpha^{Cl} = 0.62$). The α-values indicate that bond formation between aryl oxygen and the carbonyl carbon is more advanced in the chlorobenzene case.

Although the water solvent is favoured thermodynamically over chlorobenzene for the synthesis of phenyl esters of acidic phenols the reactivity of the synthesis step (k_2) is much greater in chlorobenzene than in water. The explanation of the rate enhancement for chlorobenzene is probably that the charge is less diffuse in the reactant and product states than in the transition state. For water the charge is likely to be diffused in all states (due to solvation) and the enhancement rests on reactant instability ascribed to some form of 'naked' anion effect. The Brønsted dependences indicate that the reaction in chlorobenzene ($\beta^{Cl}_{nuc} = 1.60$) will become more favourable than that in water ($\beta^{aq}_{nuc} = 0.56$) for more basic phenolate ions. Although the equilibrium may be less favourable in chlorobenzene for most phenols the case may often be that this solvent will be favoured on the grounds of reactivity. It is likely that this conclusion will hold for other slightly polar solvents (such as dichloromethane) relative to other highly polar solvents such as dimethylformamide.

Acknowledgements

We thank the SERC for a research grant.

References

1 A. Williams, *Adv. Phys. Org. Chem.*, 1992, **27**, 1.
2 N. Al-Awadi and A. Williams, *J. Org. Chem.*, 1990, **55**, 2001; 4359.
3 F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.
4 J. M. Lehn, *Acc. Chem. Res.*, 1978, **11**, 49.
5 J. Hajdu and G. M. Smith, *J. Am. Chem. Soc.*, 1980, **102**, 3960; 1981, **103**, 6192.

6 I. M. Kovach, *J. Org. Chem.*, 1982, **47**, 2235.

7 S. A. Ba-Saif, M. Colthurst, M. A. Waring and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1901.

8 E. Chrystiuk, A. Jusoh, D. Santafianos and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1986, 163.

9 S. A. Ba-Saif, A. K. Luthra and A. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6362.

10 S. A. Khan and A. J. Kirby, *J. Chem. Soc. B*, 1970, 1172.

11 W. P. Jencks, F. Barley, R. Barnett and M. Gilchrist, *J. Am. Chem. Soc.*, 1966, **88**, 4464.

12 J. Gerstein and W. P. Jencks, *J. Am. Chem. Soc.*, 1964, **86**, 4655.

13 A. B. Maude and A. Williams, manuscript in preparation.

14 (*a*) A. Williams, *Chem. Soc. Rev.*, 1994, **23**, 93; (*b*) D. Stephanidis, S. Cho, S. Dhe-Paganon and W. P. Jencks, *J. Am. Chem. Soc.*, 1993, **115**, 1650; (*c*) P. H. Guthrie, *J. Am. Chem. Soc.*, 1991, **113**, 3941; (*d*) A. Hengge, *J. Am. Chem. Soc.*, 1992, **114**, 6575.

15 E. Buncel, I. H. Um and S. Hoz, *J. Am. Chem. Soc.*, 1989, **111**, 971.

16 D. S. Kwon, G. J. Lee and I. H. Um, *Bull. Korean Chem. Soc.*, 1990, **11**, 262.

17 A. Williams, *Acc. Chem. Res.*, 1984, **17**, 425.

Paper 4/04343J
Received 15*th July* 1994
Accepted 15*th August* 1994