Polymerisation and Related Reactions involving Nucleophilic Aromatic Substitution. Part 1. The Rates of Reaction of Substituted 4-Halogenobenzophenones with the Potassium Salts of Substituted 4-Hydroxybenzophenones

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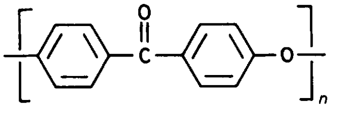
The rate of displacement of fluorine from 4′-X,4-fluorobenzophenones by the potassium salts of 4′-X,4-hydroxybenzophenones (X = CF_3, Cl, F, H, OPh, and OMe) has been studied at 175—225 °C in diphenyl sulphone as solvent. Comparison with the corresponding rate of displacement of chlorine indicates that the reaction is a bimolecular nucleophilic aromatic substitution. The reaction obeys the Hammett equation using normal σ values for substitution in both the substrate (ρ 1.19) and the phenolate (ρ −0.53). There is also a marked salt effect on the reaction rate and this has been included with the substituent constants in a general equation for the calculation of rate coefficients. The effect of an O^- substituent is more marked than would have been expected from the previous range of σ values ascribed to this substituent.

The present work was carried out to provide a detailed account of the course of some polymerisation reactions by combining a study of linear free energy relationships with a new computer program for polymerisation. The intention was to provide information on the formation and decay of the individual molecular species involved in the polymerisation and to predict the results of further substitution. The reactions studied have involved the formation of polymers (**1**) and related compounds by nucleophilic aromatic substitution. Parts 1 and 2 deal with the linear free energy relationships involved; in Part 3, the calculated rate coefficients are used in mathematical models of the polymerisations.



(1)

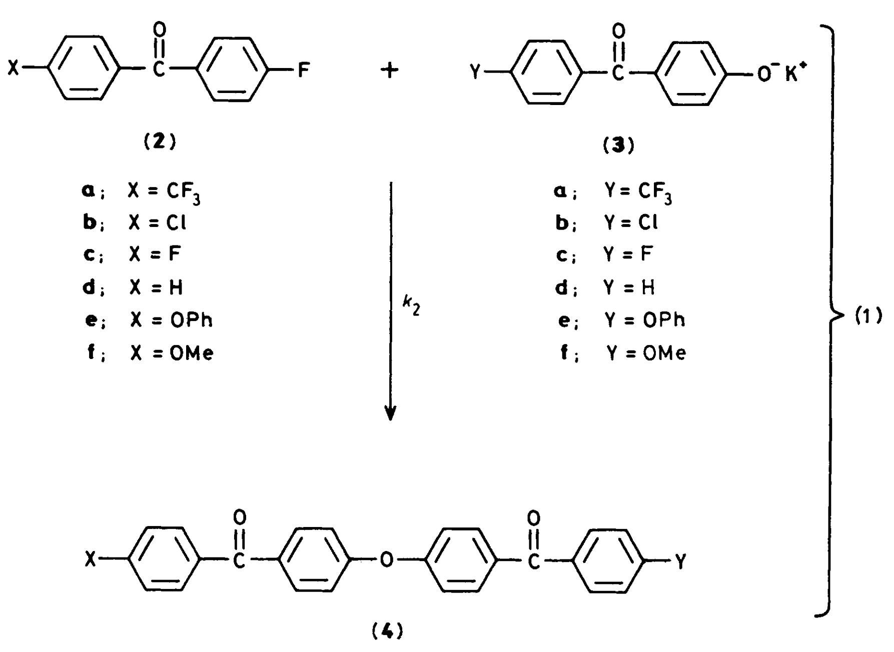
The polymers (**1**) belong to the class of engineering thermoplastics and one of the methods by which they can be prepared involves the nucleophilic displacement of a halogen atom in a substituted 4-halogenobenzophenone by an aryloxide ion derived from a substituted 4-hydroxybenzophenone.[1] This process is illustrated for a model reaction involving the formation of a dimer in equation (1). Since the carbonyl group is a weakly activating group in nucleophilic aromatic substitution,[2] the polymerisation corresponding to equation (1) has been carried out by working at high temperatures in a dipolar aprotic solvent. The use of diphenyl sulphone proved of particular value in obtaining polymers of high molecular weight[1] and the same solvent has been used in the kinetic studies now reported. Because of the unusual solvent and the rather severe conditions of reaction (at temperatures 175—225 °C), it was first necessary to look carefully at the kinetic form of the reaction and at the stability of the reactants under the reaction conditions. All the following reactions were carried out under nitrogen in a stainless steel block maintained at the stated temperatures within 0.1 °C.

Stability of Reactants.—Analysis, by h.p.l.c., of the diphenyl sulphone supplied by I.C.I. showed the presence of trace amounts of three impurities. Recrystallisation of this material removed one of these and reduced the concentrations of the other two. The m.s. and ^1H n.m.r. spectra of the remaining impurities showed them to be the *meta*- and *para*-isomers of phenylsulphonyldiphenyl sulphone, present in a combined concentration of 0.09 mole% (3.9×10^{-3} mol kg^{-1}). At 300 °C, the phenolate (**3e**) when present in a concentration of 3.3×10^{-2} mol kg^{-1} appears to react rapidly with these impurities giving a half-life of a few minutes, but this is followed by a slower reaction with the solvent giving a half-life of *ca.* 40 min. The only identified product from these reactions was 4,4′-diphenoxybenzophenone. At 300 °C, there is also a slow decomposition of the solvent to give the isomers of phenyldiphenyl sulphone. Fortunately, the majority of the kinetic studies described below were carried out at 200 °C and, at this temperature, the above reactions do not compete significantly with the reaction in equation (1) and the reactants are stable for the time of a kinetic run.

Kinetics and Mechanism.—A product analysis, carried out by h.p.l.c., for the reaction of the aryl fluoride (**2d**) with the phenolate (**3e**) at 200 °C showed that only one product was formed, as indicated in equation (1); the reaction appears therefore to be a normal nucleophilic aromatic substitution. The extent of reaction has been determined by the spectrophotometric estimation of phenolate ions in extracted samples. Except where indicated, individual kinetic runs gave excellent second-order plots ($r > 0.99$) according to equation (2). The

$$\text{Rate} = k_2[\text{ArF}][\text{ArO}^-] \qquad (2)$$

first three results in Table 1 show that, as expected, the values of K_2 are effectively independent of the initial concentration of aryl fluoride. However, the remaining results in Table 1 show that the values of k_2 do vary significantly with the concentration of the phenolate ions and the form of variation is shown by the linear plots of log k_2 against the concentration of phenolate ions in Figure 1. The form and magnitude of this variation accords more with a salt effect than with the presence of any additional kinetic term.



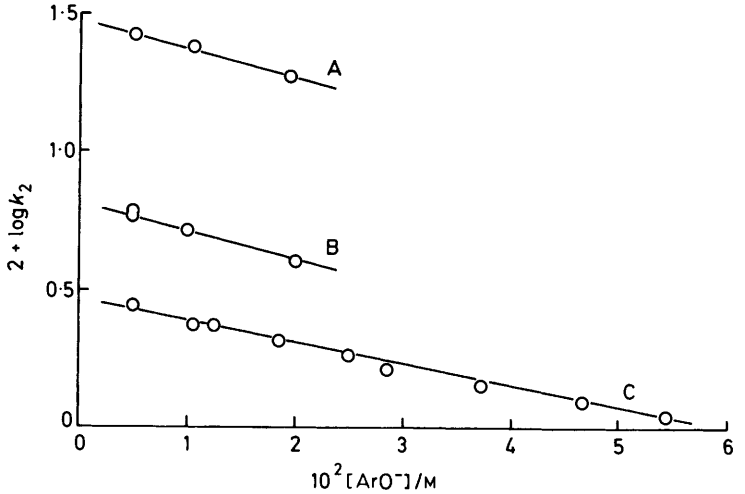


Figure 1. The variation of log k_2 for the reaction in equation (1) with the concentration of phenolate ions. A, X = CF_3; B, X = H; C, X = OMe; Y = OPh throughout. For further details see Table 1

The reaction of the phenolate (**3e**) with 4-chlorobenzophenone under the conditions of the fourth reaction in Table 1 also gives good second-order kinetics with k_2 1.84 × 10^{-3} kg mol^{-1} s^{-1}. A comparison of this value with that in Table 1 shows that the replacement of fluorine by chlorine decreases the reaction rate by a factor of 31.4.

The reactions of the phenolate (**3e**) with the fluoro compounds (**2a**, **d**, and **f**) have been studied over the temperature range 175—225 °C and the results are given in Table 2. These results give good linear plots of log k against $1/T$ and yield the activation parameters given in Table 3.

The dependence of the reaction rate on the structure of the reactants is shown by the results in Table 4. The first six results indicate how the reaction rate varies with the substituents present in the fluoro compound. Because of the salt effect mentioned above, the initial concentration of the phenolate was maintained effectively constant for this set of kinetic runs. The initial concentration of the fluoro compound exceeded that of the phenolate by a factor of 2—4 and, as a result, even those substrates in which a second slower reaction is possible (when X = Cl, F) gave good second-order kinetics. When X = F, it is of course necessary to divide the observed rate coefficient by two because of the statistical factor involved.

The next six runs in Table 4 show how the reaction rate depends on the substituent present in the phenolate, again using very similar initial concentrations of phenolate.

For several reasons, the last two results in Table 4 are in a special category. With these substituents, the two reactants become identical and the reaction becomes the polymerisation of the fluorophenolate. To avoid the complications that this involves, the rate coefficient has been calculated from the initial rate of reaction and this has been assumed to refer to the initial dimerisation. Fortunately, these reactions are much slower, and this facilitates the determination of the initial rate. The rate coefficient has been divided by two because of the statistical factor involved.

Table 1. The variation of the second-order rate coefficient (k_2) with the concentration of the reactants in equation (1; Y = PhO); temperature 200 °C

X	10^3 [ArO$^-$] / mol kg^{-1}	10^3 [ArF] / mol kg^{-1}	$10^2 k_2$ / kg mol^{-1} s^{-1}
H	5.01	5.8	6.07
H	5.03	11.6	5.83
H	5.04	23.0	5.95
H	10.0	23.1	5.18
H	20.0	23.0	4.01
CF_3	5.09	9.9	26.6
CF_3	10.4	12.5	24.1
CF_3	19.4	23.7	18.8
OMe	5.02	21.4	2.97
OMe	10.5	40.1	2.36
OMe	12.5	24.9	2.35
OMe	18.5	84.3	2.08
OMe	24.9	28.5	1.83
OMe	28.6	115.3	1.63
OMe	37.3	149.7	1.42
OMe	46.8	148.1	1.24
OMe	54.5	174.2	1.10

Table 2. The variation of the second-order rate coefficient (k_2) with temperature for the reaction in equation (1; Y = PhO)

X	T/°C	$10^2 k_2$/kg mol^{-1} s^{-1}
CF_3	175	7.35
CF_3	200	24.1
CF_3	225	75.3
H	175	1.72
H	200	5.19
H	225	15.5
OMe	175	0.7
OMe	200	2.36
OMe	225	7.19

Table 3. Activation parameters for the reaction in equation (1; Y = OPh)

X	E / kJ mol^{-1}	log A	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J mol^{-1} K^{-1}
CF_3	86.3	8.92	82.4	−86.2
H	81.5	7.73	77.6	−109.0
OMe	86.5	7.92	82.5	−105.4

Table 4. The variation of the second-order rate coefficient (k_2) with the structure of the reactants in equation (1). Temperature 200 °C

X	σ_p^x	Y	10^3 [ArO$^-$] / mol kg^{-1}	$10^2 k_2$ / kg mol^{-1} s^{-1}
CF_3	0.54 (0.74)[a]	OPh	5.09	26.6
Cl	0.22	OPh	5.01	13.4
F	0.06	OPh	5.01	9.46[b]
H	0.00	OPh	5.04	5.95
OPh	−0.09[c]	OPh	5.01	5.12
OMe	−0.28	OPh	5.02	2.97
OPh		CF_3	11.0	1.95
OPh		Cl	11.0	3.18
OPh		F	9.7	4.89
OPh		H	10.9	4.55
OPh		OPh	10.9	4.46
OPh		OMe	10.9	5.16
O^-	−1.1[d]	F	3.2	0.27[b,e]
O^-	−1.2[d]	F	12.6	0.16[b,e]

[a] σ_p^- Value. [b] Corrected for the statistical factor. [c] The mean of the σ_p values for the dissociation of the benzoic acids in water and 50% aqueous ethanol. [d] Calculated from observed rate coefficient. [e] Calculated from the initial reaction rate.

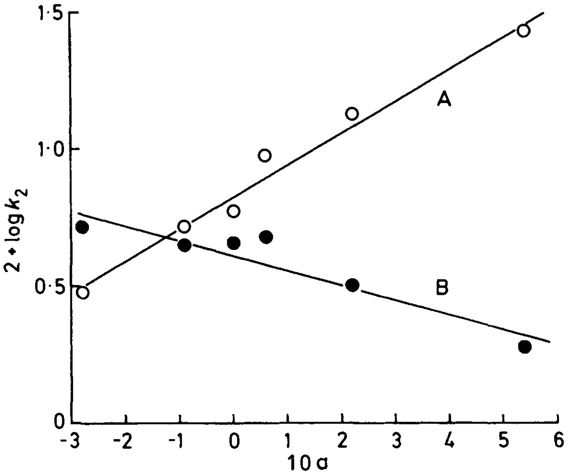


Figure 2. The variation of log k_2 for the reaction in equation (1) with σ values of the substituents: A, variation of σ_x; B, variation of σ_y. For further details see Table 4

Discussion

The presence of a very weak activating group (CO) in the substrate undergoing substitution is one of the factors favouring the benzyne mechanism[3] but, in the systems studied here [equation (1)], the isolation of a single product and the fact that the fluoro compound is more reactive than the chloro compound points strongly to a conventional bimolecular substitution reaction with the attack of the nucleophile as the rate-determining stage.[4] This mechanism will therefore be assumed in the following discussion.

The excellent bimolecular kinetics [equation (2)] accord with this mechanism and the salt effect (Figure 1) is then also consistent with reactions in which the charge is spread in the transition state.[5] It is more likely, however, that the salt effect arises from greater ion association in the more concentrated solutions since the work in Part 2 shows that the reaction rate depends on the cation present. There is some support for this interpretation since conductivity studies suggest that potassium phenoxide (0.025 mol dm^{-3}) is 50—60% associated as ion pairs in acetonitrile and dimethylformamide;[6] in diphenyl sulphone, the association is probably much greater. There is also evidence for the effect of association on the nucleophilic reactivity of phenoxides for, in dioxane as solvent, the rate of reaction of phenoxide ions with n-butyl bromide is increased by a factor of 3×10^4 when the majority of the counter-ions are changed from potassium ions to tetra-n-butylammonium ions.[7]

Since the potassium fluoride formed in the reaction is almost insoluble in diphenyl sulphone, the ionic strength of the solution should decrease in the course of a kinetic run and this should lead to upward curvature of a conventional second-order plot. In practice, this effect was seen in only a few kinetic runs carried out with the highest concentrations of phenolate ions; in most of the kinetic runs, the change in ionic strength during reaction is too small to have a significant effect on the second-order rate coefficient.

Linear free energy correlations for bimolecular nucleophilic aromatic substitution are normally based on the σ_p^- substituent constants[8] but a plot of the logarithms of the first six rate coefficients in Table 4 against the σ_p^- values for the substituents (X) gave a marked deviation for the trifluoromethyl substituent. A corresponding plot using the σ_p values from the dissociation of benzoic acids[9] (Table 4) was much more satisfactory (Figure 2) (r 0.99). The only significant deviation occurs with the fluoro substituent and here there is a possibility of some subsequent reaction of the initial dimer with phenolate ions. A detailed kinetic analysis of this system is given elsewhere[10] but it is simplest to omit this point in calculating the ρ value of the reaction which is then 1.19. The reason why the σ_p^- values are not applicable to this reaction is presumably that the substituent and the site of reaction are in different rings and that the direct conjugation of the substituent and the reaction site is blocked by the carbonyl group. For the substituents used here, the only significant difference between the σ_p and σ_p^- values occurs with the trifluoromethyl group.

The rate coefficients in Table 2 have been used to calculate the corresponding values of ρ at different temperatures with the following results: 175 °C, ρ 1.24 (r 1.00); 225 °C, ρ 1.25 (r 1.00). Any variation of ρ with temperature is probably less than the error of the measurements.

The σ_p values should also be appropriate for the corresponding plot for the substituents (Y) present in the phenolate (Table 4) and this is included in Figure 2. The point for the fluoro substituent is off the line and again, for the reason outlined above, this point has been ignored in the calculation of the slope. The resulting value of ρ is -0.53 (r 0.98). For convenience, the ρ value for substitution in the substrate (ArF) will be written ρ_S and that for substitution in the nucleophile (ArO^-) ρ_N.

The signs of these ρ values clearly accord with the expected substituent effects on the reaction, for rate-determining attack of the nucleophile should be facilitated by electron withdrawal in the fluoro compound and electron donation in the phenolate. The results are similar to those obtained[11] in a study of substituent effects on the reaction of chlorodiphenyl sulphones with hydroxide ions in aqueous dimethyl sulphoxide at 80 °C; the analogous ρ value for substitution in the second ring is 0.79 (based on the substituents *p*-Cl, *m*-Cl, and *p*-Me).

On the usual assumption* that, to a first approximation, ρ_S can be taken to be independent of Y and ρ_N can similarly be taken to be independent of X, the linear relationships in Figure 2 can, in principle, be expressed by equation (3) when the concentration of phenolate ions is constant.

$$\log (k_{X,Y}/k_{H,H}) = \rho_S\sigma_X + \rho_N\sigma_Y \tag{3}$$

However, as shown in Figure 1, the rate coefficients also depend on the concentration of phenolate ions present and, over the concentration range studied, obey equation (4). This equation has therefore been combined with equation (3) to yield (5). The values of the constants in equation (5) have been calculated from the complete set of results in Tables 1 and 4 (excluding those where X or Y = F) and the resulting linear plot of $\log k_{X,Y}$ against the right-hand side of the equation has a correlation coefficient of 0.996 and a standard error of 0.032. This equation has been used for the calculation of rate coefficients for the polymerisation reactions in Part 3.

$$\log k_{X,Y} = \text{Const} - 8.34\,[ArO^-] \tag{4}$$

$$\log k_{X,Y} = 1.19\,\sigma_X - 0.53\,\sigma_Y - 8.34\,[ArO^-] - 1.24 \tag{5}$$

The last results in Table 4 have been excluded from the above discussion since the σ_p value for the O^- substituent is known to depend on the medium.[13] Instead, the appropriate values of $\sigma_{p\text{-}O^-}$ have been calculated from the rate coefficients using equation (5) and the results are included in Table 4. It is clear that the O^- substituent in this reaction is much more deactivating than would be expected from earlier estimates of this substituent constant (-0.52 to -0.82).[9] Any contribution from stages following the dimerisation of the fluorophenolate cannot explain this result since such reactions would increase the rate of consumption of phenolate ions.

In the later stages of this work, the value of -1.2 has been used for $\sigma_{p\text{-}O^-}$ when the initial concentration of phenolate ions is 0.01 mol kg^{-1}. For a reaction in dimethyl sulphoxide (dielectric constant 46.7), the application of Wepster's theory[13] to a reaction with an effective charge separation of 6 Å and a ρ value of 1 would give $\sigma_{p\text{-}O^-}$ -1.39 at 25 °C reducing to -1.0 at 200 °C. Since the dielectric constant of diphenyl sulphone is probably below that of dimethyl sulphoxide, the values listed in Table 4 for $\sigma_{p\text{-}O^-}$ are in the expected region.

Experimental

Materials.—Analytical data for the reactants are given in Table 5.

4-Fluoro- (Fluorochem), 4,4′-difluoro- (Bayer), and 4-chloro-benzophenone (Aldrich) were commercial samples and were purified by recrystallisation from aqueous ethanol. 4-Fluoro-4′-hydroxybenzophenone was prepared by the reaction of 4,4′-difluorobenzophenone (1 mol) with potassium hydroxide (2 mol) in aqueous dimethyl sulphoxide at 60 °C for 18 h. The mixture was then poured into water, extracted with toluene (to remove unchanged starting material), and acidified. The product was filtered off and recrystallised from aqueous ethanol (yield 81%). 4-Fluoro-4′-phenoxybenzophenone was prepared in a similar way by the slow addition of phenol (1 mol) to a mixture of 4,4′-difluorobenzophenone (1 mol) and potassium carbonate (1 mol) in dimethyl sulphoxide at 60 °C. After a week at this temperature and a further 4 h at 80 °C, the hot solution was filtered and much of the solvent was removed on a rotary evaporator. The residue was poured into water and the precipitated product was recrystallised from aqueous ethanol, distilled *in vacuo* (180—182 °C and 0.38 mmHg), and recrystallised from ethanol (yield 85%).

4-Fluoro-4′-methoxybenzophenone was prepared by passing a controlled supply of methyl chloride into a solution of the potassium salt of 4-fluoro-4′-hydroxybenzophenone in dimethyl sulphoxide at 70—80 °C until the solution became colourless. Nitrogen was then passed through the mixture (to remove excess of methyl chloride) and the solution was poured into water and filtered. The precipitated material was recrystallised from ethanol, distilled (148—152 °C and 1.1—1.5 mmHg) and further recrystallised to give 4-fluoro-4′-methoxybenzophenone in a yield of 52%.

4-Fluoro-4′-trifluoromethylbenzophenone was prepared by refluxing under nitrogen a mixture of *p*-trifluoromethylbenzoyl chloride (0.5 mol) with fluorobenzene (2 mol) and trifluoromethylsulphonic acid (10 g). The extent of reaction was monitored by neutralisation of the hydrochloric acid evolved. After six days, the excess of fluorobenzene was removed by steam distillation and the product was recrystallised from aqueous ethanol and from light petroleum (b.p. 80—100 °C). It was then distilled (164—165.5 °C and 10 mmHg) and recrystallised from light petroleum (b.p. 60—80 °C) (yield 91%). A similar process was used to prepare 4-chloro-4′-fluorobenzophenone from *p*-chlorobenzoyl chloride in a 45% yield.

4-Hydroxybenzophenone (Aldrich) was purified by distillation (168—170 °C and 0.45 mmHg) and recrystallisation from aqueous ethanol. The substituted hydroxybenzophenones were obtained from the corresponding fluoro compounds by reaction under nitrogen with potassium hydroxide in aqueous dimethyl sulphoxide as outlined above for 4-fluoro-4′-hydroxybenzophenone. Full details are available elsewhere.[10]

The potassium salts of the hydroxybenzophenones were prepared by treatment of the phenols with 99.8% of the

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* Cross-interaction terms are now beginning to be investigated but should not be important here because of the distance between the substituents in the transition state.[12]

Table 5. Analytical data for the reactants (with the calculated compositions in parentheses)

Substituent	M.p. (°C) (lit. value in parentheses)	C (%)	H (%)
Fluoro compounds (**2**)			
CF_3	99.7 (101)[a]	62.4 (62.7)	3.1 (3.0)
Cl	114.5 (114)[a]	66.2 (66.5)	3.5 (3.4)
F	107 (107)[a]	71.4 (71.6)	3.8 (3.7)
H	49 (45—50)[a]	78.3 (78.0)	4.6 (4.5)
OPh	99 (101.5)[a]	78.1 (78.1)	4.5 (4.5)
OMe	94 (97)[a]	72.9 (73.0)	4.9 (4.8)
OH	168 (169—171)[b]	72.1 (72.2)	4.2 (4.2)
Free phenols corresponding to (**3**)			
CF_3	147 (144—145)[c]	63.1 (63.2)	3.7 (3.4)
Cl	179.5 (176—177)[d]	67.1 (67.1)	4.3 (3.9)
F	168 (169—171)[b]	72.1 (72.2)	4.2 (4.2)
H	133 (135)[e]	78.9 (78.8)	5.1 (5.1)
OPh	143 (214)[f]	78.3 (78.6)	4.9 (4.9)
OMe	155 (153—154)[g]	73.5 (73.7)	5.6 (5.3)
Potassium salts of phenols (**3**)			
CF_3		54.9 (55.2)	2.7 (2.7)
Cl		57.4 (57.7)	3.4 (3.0)
F		60.9 (61.4)	3.6 (3.2)
H		66.4 (66.1)	4.1 (3.8)
OPh		69.5 (69.5)	4.4 (4.0)
OMe		62.8 (63.1)	4.3 (4.2)

[a] R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Am. Chem. Soc.*, 1967, **89**, 2391. [b] T. E. Attwood, P. C. Dawson, J. L. Freeman, L. R. J. Hoy, J. B. Rose, and P. A. Staniland, *Polymer*, 1981, **22**, 1096. [c] J. R. Do Amaral, E. J. Blanz, and F. A. French, *J. Med. Chem.*, 1969, **12**, 21. [d] Personal communication, M. Cinderey, I.C.I. Petrochemicals and Plastics Division. [e] C.R.C. Handbook of Chemistry and Physics, ed. R. C. Weast, CRC Press, Boca Raton, 64th edn, 1983, p. c-162. [f] W. Dilthey and F. Harenberg, *J. Prakt. Chem.*, 1933, **136**, 49. [g] W. L. Bencze, U.S.P., 1959, 3 007 935.

Table 6. Kinetic data for the reaction of 4-fluorobenzophenone (2.306×10^{-2} mol kg^{-1}) with the potassium salt of 4-hydroxy-4′-phenoxybenzophenone (1.0×10^{-2} mol kg^{-1}) in diphenyl sulphone at 200 °C. The absorbance (A) was measured at 358 nm and the infinity reading was taken after 45 min at 300 °C

Time (min)	Mass of sample (g)	A	$\frac{10^3\,[\mathrm{ArO}^-]}{\mathrm{mol\ kg}^{-1}}$
0	1.656	1.334	10.0
3	1.890	1.250	8.17
6	1.774	0.986	6.82
9	2.070	0.984	5.80
12	1.773	0.680	4.64
18	1.910	0.540	3.35
27	1.623	0.306	2.16
36	1.974	0.271	1.50
	1.592	0.030	0.0

k_2 5.18×10^{-2} kg mol^{-1} s^{-1}, r 0.999

equivalent amount of potassium hydroxide in aqueous methanol. The solvent was removed under reduced pressure while the temperature of the salt was raised to 98 °C. The salt was then powdered under nitrogen and dried at 85—90 °C for 18 h using a vacuum line (pressure 0.001 mmHg). The salts were kept over calcium hydride in a dessicator which was itself kept under nitrogen in a dry-box. The analytical results on these salts are included in Table 5.

Products.—A sample of 4,4′-diphenoxybenzophenone was required for comparison with the product of reaction of the salt (**3e**) with the solvent. It was obtained as one of the fractions (240—260 °C and 0.35—0.4 mmHg; yield 7%) in the distillation stage of the preparation of 4-fluoro-4′-hydroxybenzophenone above. After recrystallisation from aqueous ethanol, the product had m.p. 146 °C (lit.,[14] 146—147 °C) (Found: C, 78.1; H, 4.5. Calc. for $C_{25}H_{18}O_3$: C, 78.1; H, 4.5%).

A mixture of 4-fluorobenzophenone (0.02 mol), 4-hydroxy-4′-phenoxybenzophenone (0.02 mol), and potassium carbonate (0.02 mol) in dimethyl sulphoxide (15 cm^3) was maintained at 110—120 °C for 18 h under nitrogen. Some of the solvent was then removed under reduced pressure and the remaining material was poured into water, stirred vigorously (to dissolve potassium fluoride formed), and filtered. The solid product was recrystallised from a mixture of toluene and light petroleum (b.p. 100—120 °C) to give *4-benzoyl-4′-(4-phenoxybenzoyl)-diphenyl ether* (**4**; X = H, Y = OPh), m.p. 190.0—190.4 °C; yield 77% (Found: C, 81.3; H, 4.4. $C_{32}H_{22}O_4$ requires C, 81.7; H, 4.7%); $\delta_H(CDCl_3)$ 7.3 (9 H, m), 7.7 (5 H, m), and 7.9 (8 H, m). Analysis by h.p.l.c. indicated that the same product is formed by the reaction between these components under the conditions of a kinetic run.

Kinetics.—The reactions were carried out under nitrogen in a stainless steel cylindrical block of capacity 130 cm^3 surrounded by an electrically heated jacket and an insulating layer of fibre glass padding. The whole was encapsulated in a stainless steel casing and insulated above and below by asbestos slabs. The glass apparatus above the stainless steel reactor was connected to it by a PTFE O ring and comprised an angled delivery tube (ending in a weighing bottle), a nitrogen inlet, an inlet for the stirrer, and a spare side-arm. At the bottom of the reactor, a B14 stopper with a PTFE sleeve permitted easy removal of the molten solvent after reaction. The temperature was maintained constant by the use of two thermocouples: one regulated the current to the heating jacket and the other provided an independent check on the temperature of the reactor with an accuracy of 0.1 °C. A diagram of the apparatus is given in ref. 10.

Before the start of reaction, the reactor core was thoroughly cleaned with acetone, allowed to dry, and brought to *ca.* 200 °C. The reactor was then flushed with nitrogen for 10 min (with the exit at the bottom of the reactor open). A weighed amount of diphenyl sulphone and of the potassium phenolate (the latter weighed under nitrogen) were then placed in the reactor by rotation of the delivery tube to invert the weighing bottle. After the reactor and its contents had been maintained at the required temperature for *ca.* 15 min, the required amount of the aromatic fluoro compound was added and a stopwatch started. Samples were then withdrawn through the delivery tube at appropriate times (using a PTFE tube with a teat at one end) and were run into a preweighed beaker. At these times, and whenever the delivery tube was opened, the nitrogen pressure was increased to prevent the accidental ingress of air. The final sample (corresponding to complete reaction) was taken after the temperature had been raised to 300 °C for 10—50 min.

After the weight of each sample had been determined, the sample was dissolved in acetone (Pronalys), basified by the addition of potassium hydroxide (*ca.* 0.04 cm^3, 1 mol dm^{-3}) in aqueous methanol, and brought to 100 cm^3; the u.v. spectrum was then determined on a Perkin-Elmer 554 spectrophotometer. The amount of alkali added in making the solutions basic needs to be carefully adjusted since it must be sufficient to compensate for any partial neutralisation of the phenolate by carbon dioxide during the extraction but insufficient to cause any cloudiness in the solution. The extent of reaction was calculated from the change in absorbance at the absorption maximum (usually 360 nm) after taking account of the different masses of the samples. The calculations for a typical kinetic run are shown in Table 6.

Acknowledgements

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