The *ortho*:*para* Ratio in Aromatic Nucleophilic Substitution. Part II [1]

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The Arrhenius parameters for the reactions of the eight *o*- and *p*-halogenomononitrobenzenes with methoxide and ethoxide ions have been determined. The Arrhenius parameters for the reactions of *o*- and *p*-fluoronitrobenzenes with isopropoxide ions in isopropyl alcohol and phenoxide ions in methyl, ethyl, and isopropyl alcohols have also been measured. The results are discussed in terms of steric factors operating in the transition states of the *ortho*-isomers.

In discussing the factors affecting the *ortho* : *para* ratio in aromatic nucleophilic substitution, Bunnett and Morath [2] stated that a nitro-group *ortho* to a halogen atom (excluding fluorine) is rotated from the plane of the benzene ring leading to a reduction in conjugation. As this effect is not possible when the nitro-group is *para* to the halogen atom, this secondary steric effect should lead to a reduction in the value of the *ortho* : *para* ratio. Miller *et al.*[3] however pointed out that in the cyclohexadienide addition complexes formed during the reactions of *o*-halogenonitrobenzenes, compressions present in the ground state are substantially released, and that the

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[1] Part I, T. O. Bamkole, J. Hirst, and E. I. Udoessien, *J.C.S. Perkin II*, 1973, 110.

[2] J. F. Bunnett and R. J. Morath, *J. Amer. Chem. Soc.*, 1955, **77**, 5051.

[3] B. A. Bolto, J. Miller, and V. A. Williams, *J. Chem. Soc.*, 1955, 2926.

nitro-group could be coplanar with the benzene ring in the transition state of these reactions. They concluded that this secondary steric effect was of little or no importance in determining *ortho* : *para* ratios. This conclusion has been upheld by Pietra on the grounds that (a) the *ortho* : *para* ratios for the reactions of both fluoro- and chloro-nitrobenzenes with t-butoxide ions are >1 [4] and (b) the rate ratios for the reactions of piperidine, 2-methylpiperidine, and *trans*-2,6-dimethylpiperidine with 1-fluoro-2,4-dinitrobenzene and 1-fluoro-2- and 4-nitrobenzenes in dimethyl sulphoxide are closely similar to those for 1-chloro-2,4-dinitrobenzene in benzene and the latter substrate is only six times less reactive towards *cis*-2,6-dimethylpiperidine than towards the *trans*-isomer.[5]

In spite of extensive discussion, there are no data available for the *ortho* : *para* ratios of the eight *o*- and *p*-halogenomononitrobenzenes in more than one solvent–lyate system emanating from a single laboratory. Results of many workers have been utilised in previous discussions but in some cases there are large discrepancies between rate constants and between Arrhenius parameters for a particular compound obtained by different workers. The original intention was to measure the Arrhenius parameters of the reactions of the eight *o*- and *p*-halogenomononitrobenzenes with methoxide, ethoxide, and isopropoxide ions in their respective alcohols. As described elsewhere [1] competing reactions prevented the measurement of the rate of reaction of *p*-chloronitrobenzene (and by analogy the corresponding bromo- and iodo-compounds) with isopropoxide ions.

TABLE 1

Arrhenius parameters for the reactions of *o*- and *p*-halogenonitrobenzenes in some solvent–lyate systems and for the reactions of *o*- and *p*-fluoronitrobenzenes with phenoxide ions in methyl, ethyl, and isopropyl alcohols. Standard error of mean values: 0·1 kcal mol^{-1}

(a) *o*-Halogenonitrobenzenes

	F		Cl		Br		I	
RO^-	E/kcal mol^{-1}	log$A$	E/kcalmol^{-1}	log A	E/kcal mol^{-1}	log A	E/kcal mol^{-1}	log A
	(19·9) [a]	(10·7) [a]	26·0 [b]	11·85 [b]	27·0	12·39	27·0	12·11
MeO^-	(19·7) [c]	(10·4) [c]	25·9 [b,d]	11·81 [b,d]	26·7 [d]	12·21 [d]	(26·5) [c]	(11·9) [c]
			(23·2) [e]	(12·0) [e]	(25·5) [c]	(11·5) [c]		
			(23·5) [f]	(10·3) [f]				
	20·4 [b]	11·88 [b]	24·9 [b]	11·67 [b]	25·2	11·74	31·4	15·12
EtO^-	(20·1) [g]	(11·7) [g]						
Pr^iO^-	17·7 [b]	10·83 [b]	21·8 [b]	10·11 [b]				
	(18·4) [h]	(11·2) [h]						
PhO^-								
In MeOH	25·2	12·20						
In EtOH	22·8	11·48						
In Pr^iOH	19·3	9·94						

(b) *p*-Halogenonitrobenzenes

	F		Cl		Br		I	
RO^-	E/kcal mol^{-1}	log$A$	E/kcalmol^{-1}	log A	E/kcal mol^{-1}	log A	E/kcal mol^{-1}	log A
	20·4 [b]	11·19 [b]	23·9 [b]	11·15 [b]	24·5	11·47	25·1	11·51
MeO^-	(20·1) [a]	(11·0) [a]	(23·0) [e]	(12·5) [e]	(24·7) [k]	(11·5) [k]	25·1 [d]	11·5 [d]
	(21·2) [g]	(11·75) [g]	(25·7) [f]	(10·98) [f]			(25·0) [k]	(11·4) [k]
			(24·1) [k]	(11·2) [k]				
EtO^-	18·9 [b]	10·63 [b]	20·2 [b]	9·03 [b]	20·5	9·28	22·1	9·76
	(19·0) [g]	(10·7) [g]	(20·1) [g]	(9·0) [g]	(20·3) [g]	(9·2) [g]		
Pr^iO^-	15·7 [b]	8·05 [b]						
	(16·1) [h]	(8·34) [h]						
PhO^-								
In MeOH	21·9	10·15						
	(21·6) [i]	(10·2) [i]						
In EtOH	20·9	9·70						
	(19·6) [i]	(9·0) [i]						
In Pr^iOH	16·1	6·55						
	16·4 [j]	6·71 [j]						
	(18·2) [i]	(8·2) [i]						

[a] C. W. L. Bevan and G. C. Bye, *J. Chem. Soc.*, 1954, 3091. [b] Ref. 1. [c] Ref. 2. [d] Rate constants determined by potentiometric titration of halide ion. [e] A. F. Holleman, W. J. de Mooy, and J. ter Weel, *Rec. Trav. chim.*, 1925, **35**, 1. [f] J. Miller and V. A. Williams, *J. Chem. Soc.*, 1953, 1475. [g] C. W. L. Bevan, *J. Chem. Soc.*, 1951, 2340; 1953, 655. [h] Ref. 6. [i] J. Miller and A. J. Parker, *J. Amer. Chem. Soc.*, 1961, **83**, 117. [j] Rate constants determined spectrophotometrically. [k] G. P. Briner, J. Miller, M. Liveris, and P. G. Lutz, *J. Chem. Soc.*, 1954, 1265.

RESULTS AND DISCUSSION

The results and those for the reactions of *o*- and *p*-fluoronitrobenzenes with phenoxide ions in methyl, ethyl, and isopropyl alcohols, together with the results of previous workers are given in Table 1. Generally, agreement of the present results with those in the literature is good, but there are three major discrepancies. There are two sets of Arrhenius parameters reported in the literature for the reaction of *o*-chloronitrobenzene with methoxide ions. The activation energies reported

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[4] F. Pietra, D. Vitali, F. Del Cima, and F. Cardinale, *J. Chem. Soc. (B)*, 1970, 1659.

[5] F. Pietra and F. Del Cima, *J. Org. Chem.*, 1968, **33**, 1411.

agreed with each other, but there is a difference of 1·7 in the log A factors. The log A factor obtained in the present work is in agreement with one of the literature values, but the activation energy is *ca.* 2·5 kcal mol^{-1} higher than those reported. Similarly the activation energy obtained for the reaction of methoxide ions with *o*-bromonitrobenzene is 1·5 kcal mol^{-1} higher than the literature value. For these two compounds, duplicate runs were done at each of four temperatures, the rate being followed by titration of unchanged methoxide ions. Good second-order constants were obtained and the infinity titres agreed with the calculated values. The runs were repeated, following the liberation of halide ion by potentiometric titration with silver nitrate. Again good constants were obtained, the infinity titres agreeing with the calculated ones. The activation parameters obtained by the two methods were in excellent agreement.

There is a difference of *ca.* 2 kcal mol^{-1} in the activation energy and 1·7 in the log A factor between the present results and those reported in the literature for the reaction of *p*-fluoronitrobenzene with sodium phenoxide in isopropyl alcohol. To avoid solvolysis all reactions involving phenoxide ions were carried out in the presence of a ten-fold excess of phenol to shift the equilibrium $PhO^- + ROH \rightleftharpoons PhOH + RO^-$ to the left. No experimental details are given of the methods used to determine the values quoted in the literature, and it is not known whether precautions were taken to exclude solvolysis. Solvolysis leads to the formation of alkyl ethers, and in both the *ortho*- and *para*-series these were shown to be absent in the reaction mixtures by t.l.c. For *p*-fluoronitrobenzene in all three solvents the amounts of *p*-nitrophenyl phenyl ether found at infinity were measured spectrophotometrically and agreed with the calculated values. Finally, for the reaction of *p*-fluoronitrobenzene in isopropyl alcohol, good agreement was obtained between the activation parameters derived from runs followed by acid–base titration and by spectrophotometric measurement of the *p*-nitrophenyl phenyl ether formed. The spectrophotometric measurements were not possible with the *ortho*-isomer, as *o*-nitrophenyl phenyl ether has a broad absorption band with a weak maximum at 310 nm, which covers the wavelengths at which the reactants and phenol absorb.

Before discussing the results, it is convenient to specify the following terms: (a) primary steric effects, due directly to the difference in non-bonded compressional energy between the initial and transition states of the reaction; (b) secondary steric effects as postulated for the nitro-group, due to a reduction in the activating power of the group resulting from interference by an *ortho*-substituent with the attainment of coplanarity of the nitro-group with the aromatic ring; and (c) steric inhibition of solvation, due to the crowding of atoms around the reaction centre in the transition states of *ortho*-substituted compounds excluding the presence of solvent molecules.

The results for the fluoro-substrates are considered first as the fluorine atom is small, and construction of models of the transition states shows that neither primary nor secondary steric effects are important in the reactions of *o*-fluoronitrobenzene. Rate constants, calculated at various temperatures and *ortho* : *para* ratios are presented in Table 2. The pattern of results is the same as that obtained by Bevan *et al.*[6] These authors have discussed the results in detail in terms of steric inhibition of solvation of the transition states of the *ortho*-isomer. Additional support for this concept has been presented by the present authors.[1]

TABLE 2

Rate constants and *ortho* : *para* ratios calculated at various temperatures for the reactions of *o*- and *p*-fluoronitrobenzenes in some solvent–lyate systems

Solvent		MeOH	EtOH	Pr^iOH
$10^4k_2^{25}$/l mol^{-1} s^{-1}	*ortho*	1·29 [a]	8·13	70·8
	para	1·70	5·89	3·47
	o : *p*	0·7	1·4	20·4
$10^3k_2^{50}$/l mol^{-1} s^{-1}	*ortho*	1·74 [a]	12·0	70·8
	para	2·46	7·08	2·69
	o : *p*	0·7	1·7	25·8
$10^2k_2^{100}$/l mol^{-1} s^{-1}	*ortho*	11·0 [a]	83·2	288
	para	17·4	35·5	7·11
	o : *p*	0·6	2·3	40·5

[a] Calculated from data by C. W. L. Bevan and G. C. Bye, *J. Chem. Soc.*, 1954, 3091.

In the three solvent–lyate systems investigated, both the size of the nucleophile and the size of solvent molecules increase from methyl to isopropyl alcohol and the possibility exists that the progressive increase in the *ortho* : *para* ratio is due solely to the increase in size of the nucleophile. The reactions of *o*- and *p*-fluoronitrobenzenes with sodium phenoxide in methyl, ethyl, and isopropyl alcohols have been investigated and the rates and *ortho* : *para* ratios calculated at various temperatures are given in Table 3. The pattern is similar to that observed in the solvent–lyate systems, values of the ratio increasing for methyl, through ethyl, to isopropyl alcohol. Hence at least part of the progressive increase in the ratio observed in the solvent–lyate systems is due to increased steric inhibition of solvation caused by the increased size of the solvent molecules in going from methyl to isopropyl alcohol.

TABLE 3

Rate constants and *ortho* : *para* ratios calculated at various temperatures for the reactions of *o*- and *p*-fluoronitrobenzenes with sodium phenoxide in methyl, ethyl, and isopropyl alcohols in the presence of a ten-fold excess of phenol

Solvent		MeOH	EtOH	Pr^iOH
$10^7k_2^{25}$/l mol^{-1} s^{-1}	*ortho*	5·25	58·9	603
	para	12·6	24·0	66·1
	o : *p*	0·4	2·5	9·1
$10^5k_2^{50}$/l mol^{-1} s^{-1}	*ortho*	1·45	11·5	77·6
	para	2·19	3·63	5·37
	o : *p*	0·7	3·2	14·5
$10^4k_2^{100}$/l mol^{-1} s^{-1}	*ortho*	26·9	132	427
	para	20·9	28·2	15·1
	o : *p*	1·3	4·7	28·2

In all these reactions an additional factor affecting

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[6] C. W. L. Bevan, A. J. Foley, J. Hirst, and W. O. Uwamu, *J. Chem. Soc.* (*B*), 1970, 794.

the *ortho* : *para* ratio particularly in isopropyl alcohol, may be attack by ion pairs, leading to a bridging by the sodium ion between the nucleophile and the oxygen atoms of the *ortho*-nitro-group as postulated by Pietra and del Cima.[7] Experiments are in hand to check this point.

Rate constants and *ortho* : *para* ratios at various temperatures for the reactions of *o*- and *p*-chloro-, bromo-, and iodo-nitrobenzenes with sodium methoxide and ethoxide are given in Table 4. The magnitude of the ratios increases with increasing temperature due to the fact that in all cases the values of the activation energies and log A factors are greater for the *ortho*- than for the *para*-isomer. For a given solvent and temperature the magnitude of the ratios are always less than that for the fluoro-substrate under the same conditions. With the exception of the iodonitrobenzenes in ethanol at 25°, the *ortho* : *para* ratios for the three halogens in a given solvent are approximately the same and do not show any obvious trend. With the same exception, at low temperatures, there is little difference in the values obtained in methyl and ethyl alcohols; the sequence ethyl > methyl alcohol observed for the fluoro-substrates is only observed at 100 °C and above. At 25 °C the value of the ratio for the iodobenzenes is five times greater in methyl than in ethyl alcohol.

TABLE 4

Rate constants and *ortho* : *para* ratios calculated at various temperatures for the reactions of *o*- and *p*-chloro-, bromo-, and -iodo-nitrobenzenes in some solvent–lyate systems

Halogen		Cl			Br		I	
Solvent		MeOH	EtOH	Pr^{i}OH	MeOH	EtOH	MeOH	EtOH
$10^8k_2^{25}$/l mol^{-1} s^{-1}	*ortho*	6·17	26·3	132	3·89	18·2	2·04	1·26
	para	42·7	166		31·6	178	12·6	36·3
	o : *p*	0·15	0·16		0·12	0·10	0·16	0·035
$10^6k_2^{50}$/l mol^{-1} s^{-1}	*ortho*	1·82	6·61	23·4	1·32	5·01	0·692	0·776
	para	9·77	22·9		7·76	25·7	3·39	6·46
	o : *p*	0·19	0·29		0·18	0·20	0·20	0·12
$10^4k_2^{100}$/l mol^{-1} s^{-1}	*ortho*	4·07	12·3	29·1	3·72	9·33	1·95	5·25
	para	13·8	15·5		13·2	18·6	6·31	6·46
	o : *p*	0·30	0·78		0·28	0·50	0·31	0·81

More informative is a consideration of the difference in Arrhenius parameters of the *ortho* and *para*-isomers ($\Delta E = E_{ortho} - E_{para}$; $\Delta \log A = \log A_{ortho} - \log A_{para}$), values of which are given in Table 5. In methyl alcohol there is a big increase in both ΔE and $\Delta \log A$ in going from fluorine to chlorine, after which the values remain approximately the same. In ethyl alcohol, again there is a large increase in the two values between fluorine and chlorine, the values for chlorine and bromine are the same, but there is a second jump between bromine and iodine. The magnitudes of both ΔE and $\Delta \log A$ are greater in ethyl alcohol than in methyl alcohol.

TABLE 5

The differences between the Arrhenius parameters of the *ortho*- and *para*-isomers ($\Delta E = E_{ortho} - E_{para}$; $\Delta \log A = \log A_{ortho} - \log A_{para}$) for the reactions of *o*- and *p*-fluoro-, -chloro-, -bromo-, and -iodo-nitrobenzenes in some solvent–lyate systems

Solvent	MeOH				EtOH			
Halogen	F	Cl	Br	I	F	Cl	Br	I
ΔE/kcal mol^{-1}	−0·5	2·1	2·5	1·9	1·5	4·7	4·7	9·3
$\Delta \log A$	−0·49	0·70	0·92	0·6	1·25	2·64	2·46	5·36

The jump in the ΔE values between fluoro- and chloro-nitrobenzenes is mainly due to the difference in the activation energies of the *ortho*-isomers. These jumps could be due to either differences in steric occlusion of solvation in the transition states of the reaction or to the nitro-group in *o*-chloronitrobenzene not being fully coplanar with the benzene ring in the transition state or a combination of these two effects. There are two reasons why the jumps cannot be due solely to steric occlusion of solvation. If this were the case, it would imply that steric occlusion of solvation was more important for the chloro- than for the fluoro-substrate, presumably due to the greater size of the chlorine atom. On this basis the values of ΔE in methyl alcohol would be expected to increase from the chloro- to the iodo-substrates and particularly between the bromo- and iodo-compounds, which is not the case. Secondly, the difference between the Arrhenius parameters of the *ortho*-chloro- and *ortho*-fluoro-compounds ($E_{ortho}^{\mathrm{Cl}} - E_{ortho}^{\mathrm{F}}$; $\log A_{ortho}^{\mathrm{Cl}} - \log A_{ortho}^{\mathrm{F}}$) in going from methyl to ethyl alcohol should increase, possibly in absolute magnitude, but certainly relative to the corresponding change in magnitude of the *para*-isomers ($E_{para}^{\mathrm{Cl}} - E_{para}^{\mathrm{F}}$; $\log A_{para}^{\mathrm{Cl}} - \log A_{para}^{\mathrm{F}}$). As is shown in Table 6, in both the *ortho*- and the *para*-series, the values of these quantities decrease in moving from methyl to ethyl alcohol, and the magnitude of the decrease is approximately the same in both series. Hence it is concluded that the difference between the ΔE

TABLE 6

Values of the differences between the activation parameters of *o*-chloro- and -fluoro-nitrobenzenes and of *p*-fluoro- and -chloro-nitrobenzenes for the reactions of *o*- and *p*-fluoro- and -chloro-nitrobenzenes in some solvent–lyate systems

Solvent	MeOH	EtOH	Pr^{i}OH
$E_{ortho}^{\mathrm{Cl}} - E_{ortho}^{\mathrm{F}}$/kcal mol^{-1}	6·3	4·5	4·1
$E_{para}^{\mathrm{Cl}} - E_{para}^{\mathrm{F}}$/kcal mol^{-1}	3·5	1·3	
$\log A_{ortho}^{\mathrm{Cl}} - \log A_{ortho}^{\mathrm{F}}$	1·5	−0·2	−0·7
$\log A_{para}^{\mathrm{Cl}} - \log A_{para}^{\mathrm{F}}$	0	−1·6	

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[7] F. Pietra and F. Del Cima, *Chem. Comm.*, 1968, 216.

values of the fluoro-substrates and the other halogenonitrobenzenes cannot be accounted for in terms of steric occlusion of solvation alone, and is due to the existence of a secondary steric effect in the reactions of *o*-chloro-, -bromo- and -iodo-nitrobenzenes. Since for all four halogens the values of ΔE and $\Delta \log A$ are greater in ethyl than methyl alcohol, there is some indication that steric occlusion of solvation occurs in the transition states of the reactions of all four *o*-halogenonitrobenzenes in ethyl alcohol.

When the nucleophile is ethoxide ion, there is sudden increase in the activation parameters between *o*-bromonitrobenzene and *o*-iodonitrobenzene, the activation energy by 6·2 kcal mol^{-1} and log A by 3·38. This increase is not observed in the corresponding reaction of the *para*-isomers nor with *o*-iodonitrobenzene when the nucleophile is methoxide ion. Construction of models of the intermediates formed by the reaction of methoxide ions with the *o*-halogenonitrobenzenes showed that conformations are available to all four halogeno-compounds in which steric interactions are negligible and the nitro-group is coplanar with the benzene ring. When models using ethoxide ions were constructed this was also found to be the case for *o*-fluoro-, -chloro-, and -bromo-nitrobenzenes, but not for *o*-iodonitrobenzene. For the latter compound there was found to be steric compression between the nucleophile and the iodine atom. We therefore attribute the dramatic increase in activation energy to a primary steric effect in the ethoxydeiodination reaction. In aliphatic nucleophilic substitution, primary steric effects result in an increase in the activation energy and a decrease in the log A factor.[8] The observed increase in the frequency factor may be due to the superposition of steric occlusion of solvation on the primary steric effect.

EXPERIMENTAL

Materials.—The purification of *o*- and *p*-fluoro- and -chloro-nitrobenzenes has already been described.[1] *o*-Bromonitrobenzene, m.p. 43 °C, *p*-bromonitrobenzene, m.p. 126·5—127 °C, *o*-iodonitrobenzene, m.p. 49—49·5 °C, and *p*-iodonitrobenzene, m.p. 174—174·5 °C, were recrystallized commercial samples. An AnalaR sample of phenol was dried ($CaCl_2$) and distilled under reduced pressure.

p-*Nitroanisole*.—A solution of *p*-fluoronitrobenzene (4·23 g) in 2·0M-sodium methoxide (25 cm^3) was maintained at 35 °C for 24 h. The solvent was distilled off, the residue was poured into water, and extracted with ether. The residue from the ether extract was recrystallized from methyl alcohol, giving *p*-nitroanisole (73%), m.p. 53—53·5 °C (lit.,[9] 53—54 °C).

o-*Nitroanisole*.—This was prepared in an analogous way from *o*-fluoronitrobenzene and had b.p. 130—131 °C at 9 mmHg (lit.,[10] 132—133 °C at 11 mmHg) (Found: C, 54·8; H, 4·7; N, 9·3. Calc. for $C_7H_7NO_3$: C, 54·9; H, 4·6: N, 9·1%).

p-*Nitrophenetole*.—*p*-Nitrophenol (1·4 g) and ethyl iodide (2·0 g) were added to 0·2M-sodium ethoxide (50 cm^3) and the solution refluxed until it was no longer alkaline. The solvent was distilled off, the residue was diluted with ether, and the ether solution washed with 2N-NaOH and water and dried (Na_2SO_4). Evaporation of the ether and recrystallization of the residue from light petroleum gave *p*-nitrophenetole (98%), m.p. 59·5—60 °C (lit.,[9] 60 °C).

o-*Nitrophenetole*.—*o*-Nitrophenol (1·4 g) was dissolved in 2·68M-sodium methoxide solution (5 cm^3). The phenolate was added to dimethylformamide (8 cm^3) and ethyl iodide (2·3 g). The mixture was heated in a sealed tube at 90 °C for 3 days and then poured into water and extracted with toluene. The toluene was washed with 2N-NaOH and water and dried (Na_2SO_4). Distillation of the residue from the toluene extract gave *o*-nitrophenetole (98%) b.p. 134—135 °C at 8 mmHg (lit.,[11] b.p. 134·2 °C at 8 mmHg) (Found: C, 57·8; H, 5·7; N, 8·4. Calc. for $C_8H_9NO_3$: C, 57·5; H, 5·4; N, 8·4%).

o- *and* p-*Nitrophenyl Isopropyl Ether*.—The *ortho*-isomer (90%), b.p. 139—140 °C at 8 mmHg (lit.,[9] b.p. 152 °C at 17 mmHg) (Found: C, 60·0; H, 6·2; N, 7·6. Calc. for $C_9H_{11}NO_3$: C, 59·7; H, 6·1; N, 7·7%) and the *para*-isomer (92%), b.p. 140—141 °C at 8 mmHg (lit.,[9] b.p. 154 °C at 13 mmHg) (Found: C, 60·0; H, 6·2; N, 7·8%); were prepared from isopropyl bromide and *o*- and *p*-nitrophenols respectively by the same procedure as for *o*-nitrophenetole.

o-*Nitrophenyl Phenyl Ether*.—This (93%), prepared by the method of Jones and Cook,[12] had b.p. 143—145 °C at 0·2 mmHg (lit.,[12] b.p. 195—197 °C at 45 mmHg) (Found: C, 67·5; H, 4·2; N, 6·7. Calc. for $C_{12}H_9NO_3$: C, 67·0; H, 4·2; N, 6·5%).

p-*Nitrophenyl Phenyl Ether*.—*p*-Fluoronitrobenzene (3·5 g) was added to a solution of potassium hydroxide (1·5 g) in molten phenol (7·5 g), and heated at 150—160 °C for 30 min. The ether (95%) was precipitated by pouring into dilute sodium hydroxide solution and was recrystallized from methyl alcohol, m.p. 61—61·5 °C (lit.,[13] 61 °C).

Solvents.—Methyl, ethyl, and isopropyl alcohols were dried as previously described [1] and the water content was checked by Karl Fischer titration.

Kinetic Measurements.—The progress of the reactions was followed by acid–alkali titration. Each run was duplicated and the average value of the constants for a given run agreed with that of its duplicate to within ±2%. Rate constants for *o*-chloro-, *o*-bromo-, and *p*-iodo-nitrobenzene with methoxide ions at four temperatures were also determined by potentiometric titration of the halide ion liberated. For the rest of the substrates, excluding the fluoronitrobenzenes, the rates for at least one temperature were checked by titration of halide ion. In all cases infinity titres agreed with the theoretical ones. Details of the experimental procedure have already been given.[1] The results at different temperatures are given in Table 7.

Spectrophotometric determination of rate constants. Samples were removed from the thermostat at known times, and after appropriate dilution with methyl alcohol, their optical densities were measured at 302·5 nm, using a Unicam SP 500 spectrophotometer.

Product Analysis of the Reactions of Sodium Phenolate with o- *and* p-*Fluoronitrobenzenes*.—Preliminary experiments showed that, with the exception of *o*-nitrophenyl isopropyl

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[12] H. I. Jones and A. N. Cook, *J. Amer. Chem. Soc.*, 1916, **38**, 1534.

[13] L. E. Raiford and J. C. Colbert, *J. Amer. Chem. Soc.*, 1926, **48**, 2659.

Table 7

Rate constants for the reactions of *o*- and *p*-bromo- and -iodo-nitrobenzenes with methoxide and ethoxide ions and for *o*- and *p*-fluoronitrobenzenes with phenoxide ions at various temperatures

	MeO^-		EtO^-			MeO^-		EtO^-	
Substrate	t/°C	10^4k_2/ l mol^{-1} s^{-1}	t/°C	10^4k_2/ l mol^{-1} s^{-1}	Substrate	t/°C	10^4k_2/ l mol^{-1} s^{-1}	t/°C	10^4k_2/ l mol^{-1} s^{-1}
o-Bromonitrobenzene	129·7	53·1	120·5	55·9	*o*-Iodonitrobenzene	130·0	29·6	109·3	14·8
	120·0	23·2	110·9	24·9		120·0	12·5	99·45	4·97
	110·0	9·56	100·6	10·1		110·1	5·14	89·55	1·57
	100·5	3·85	90·8	4·07		101·05	2·18	82·1	0·627
p-Bromonitrobenzene	129·0	144	115·0	54·7	*p*-Iodonitrobenzene	131·0	84·2	128·9	56·2
	121·15	78·1	105·3	27·6		120·0	35·1	119·5	28·9
	111·0	34·1	96·1	14·1		110·3	15·5	109·5	13·9
	101·0	14·6	85·7	6·26		101·1	6·88	98·95	6·08

	PhO^-					
	MeOH		EtOH		Pr^{i}OH	
	t/°C	10^4k_2/l mol^{-1} s^{-1}	t/°C	10^4k_2/l mol^{-1} s^{-1}	t/°C	10^4k_2/l mol^{-1} s^{-1}
o-Fluoronitrobenzene	122·05	180	99·8	132	80·9	104
	111·5	74·2	90·2	57·5	69·05	40·4
	100·6	28·6	80·7	24·5	60·4	19·5
	91·4	12·1	70·3	9·25	50·8	8·17
p-Fluoronitrobenzene	122·5	112	111·2	63·9	120·7	46·5
	111·5	50·6	99·8	27·8	111·3	28·3
	99·5	20·4	90·55	13·6	99·9	15·0
	91·2	10·3	79·70	5·52	89·45	8·00

ether, mixtures of phenol, *o*-nitrophenyl phenyl ether, and alkyl *o*-nitrophenyl ethers and also mixtures of phenol with the corresponding *para*-compounds could be separated by t.l.c. using 1 : 1 benzene–light petroleum (b.p. 60—80 °C) as solvent. In all cases, no alkyl nitrophenyl ether could be detected by t.l.c. analysis of infinity samples of the reaction solutions.

[3/1209 *Received*, 11*th June*, 1973]