

The *ortho* : *para* Ratio in Aromatic Nucleophilic Substitution. Part I

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ortho : *para* Ratios have been measured for the reactions of *o*- and *p*-fluoro- and -chloro-nitrobenzenes with methoxide, ethoxide, and isopropoxide ions. The rates of substitution at the 2- and 4-positions of 2,4-difluoro- and 2,4-dichloro-1-nitrobenzenes by these three anions have also been determined. The results are discussed in terms of steric exclusion of solvation in the transition states of the reactions, and for 2,4-dichloro-1-nitrobenzene, the effect of rotation of the nitro-group out of the plane of the benzene ring is examined.

BUNNETT and MORATH¹ have pointed out that in the nucleophilic displacement reactions of 2,4-difluoro- and 2,4-dichloro-1-nitrobenzenes, the 2-halogen is preferentially displaced indicating that *ortho*-activation of the nitro-group predominates. In the reaction of *o*- and *p*-fluoronitrobenzenes with methoxide ions² the *ortho* : *para* ratio is less than unity indicating that a *para*-nitro-group is more activating than an *o*-nitro-group, but when the nucleophile is changed to ethoxide ions³ the ratio becomes greater than unity. We have reinvestigated these apparently contradictory reactions and a preliminary communication of the reactions of 2,4-difluoro-1-nitrobenzene with methoxide ions has been made.⁴

RESULTS AND DISCUSSION

We measured the rate of reaction of *o*- and *p*-fluoro-nitrobenzenes with methoxide in methanol and obtained an *ortho* : *para* ratio of 0.69 at 49.15° in good agreement with Bevan and Bye's² value of 0.68 at this temperature (0.70 at 25 °C).

Kinetic runs were carried with 2,4-difluoro-1-nitrobenzene and methoxide ions in methanol at 25 °C. In all cases when the methoxide : substrate ratio was greater than 2 : 1 the amount of methoxide consumed at infinity corresponded to the theoretical value calculated for the replacement of both fluorine atoms, and the expected product 2,4-dimethoxy-1-nitrobenzene was isolated from the solutions. When the initial concentration ratio was 1 : 1, the ¹⁹F n.m.r. spectra of the infinity solutions consisted of two peaks A and B, A being 12.3 p.p.m. downfield from B. Addition of 2,4-difluorobenzene to these solutions resulted in two additional peaks, hence A and B are due to the products of the reaction. Also when the runs were carried out with 2,4-difluoro-1-nitrobenzene in excess, the ¹⁹F spectrum consisted of four peaks, two identifiable as belonging to the substrate, the other two being in the same relative position as A and B. The position of absorption of B coincided with that of fluorobenzene. In all cases when the substrate was in excess, no 2,4-dimethoxy-1-nitrobenzene could be detected in the products by t.l.c. When the initial concentration of methoxide and substrate were 1 : 1 the ratio of the intensities of A and B was 1 : 0.815; when the

methoxide : substrate ratio was 1 : 1.5 the corresponding intensity ratio was 1 : 0.823.

3-Fluoro-4-nitroanisole (I) and 3-fluoro-6-nitroanisole (II), the products of replacement at the 4- and 2-positions in 2,4-difluoro-1-nitrobenzene were synthesised. Compound (I) had a ¹⁹F n.m.r. absorption which coincided with that of fluorobenzene and (II) absorbed 12.2 p.p.m. downfield from fluorobenzene. Hence the above intensity ratios indicate a value of 1.22 for the *ortho* : *para* ratio in 2,4-difluoro-1-nitrobenzene.

The apparent inconsistency of this result when compared with that obtained by individual measurements on *o*- and *p*-fluoronitrobenzenes arises primarily from the fact that the value of the *ortho* : *para* ratio derived from measurements on 2,4-difluoro-1-nitrobenzene is not a true measure of the relative activating powers of *ortho*- and *para*-nitro-groups. In aromatic nucleophilic substitution, the activating power of a group depends on the initial degree of activation of the parent system.^{5,6} In 2,4-difluoro-1-nitrobenzene the rate of replacement of the 2-fluorine atom reflects the influence of a *meta*-fluoro-substituent in an *ortho*-nitro-activated series while replacement at the 4-position includes the effect of *meta*-fluorine activation in a *para*-nitro-activated series, and the magnitude of *meta*-fluorine activation cannot be assumed to be the same in both series.

TABLE I

The reactions of 2,4-difluoro-1-nitrobenzene in some solvent-lyate systems at 25 °C

Solvent	MeOH	EtOH	Pr ⁱ OH
<i>ortho</i> : <i>para</i> Ratio	1.22	1.06	9.5
10 ³ k ₂ */l mol ⁻¹ s ⁻¹	5.88	36.1	164
10 ³ k _o */l mol ⁻¹ s ⁻¹	3.23	18.6	148
10 ³ k _p */l mol ⁻¹ s ⁻¹	2.65	17.2	15.6
k _o /k _H	25.1	22.4	20.9
k _p /k _H	14.8	29.7	47.2

* k₂ is the overall second-order rate constant for the reaction of 2,4-difluoro-1-nitrobenzene with alkoxide ions; k_o and k_p are the rate constants for the replacement of the 2- and 4-fluorine atoms.

Using initial methoxide : substrate concentrations in the ratio of 1 : 1.33 we obtained the overall second-order rate constant for the reaction of 2,4-difluoro-1-nitrobenzene with methoxide ions. Combination of this with the above product ratio enables the rate constants for substitution of the 2- and 4-fluorine atoms to be calculated and the results are in Table I. Division of

⁵ B. A. Balto, M. Liveris, and J. Miller, *J. Chem. Soc.*, 1955, 750.

⁶ C. W. L. Bevan, J. Hirst, and S. J. Una, *Nigerian J. Sci.*, 1966, 1, 27.

¹ J. F. Bunnett and R. J. Morath, *J. Amer. Chem. Soc.*, 1955, 77, 5051.

² C. W. L. Bevan and G. C. Bye, *J. Chem. Soc.*, 1954, 3091.

³ C. W. L. Bevan, *J. Chem. Soc.*, 1951, 2340; 1953, 655.

⁴ T. O. Bamkole and J. Hirst, *Chem. Comm.*, 1971, 69.

these individual rate constants by those for the methoxydefluorination of *o*- and *p*-fluoronitrobenzenes (Table 2) gives the relative activating power of a *meta*-fluorine substituent (k_F/k_H) as 25.1 in the *o*-fluoronitrobenzene series and 14.8 in the *p*-fluoronitrobenzene series.

TABLE 2

The reactions of *o*- and *p*-fluoronitrobenzenes in some solvent-lyate systems. Rates at 25 °C are calculated from the Arrhenius parameters

Solvent		MeOH	EtOH	Pr ^t OH
$10^4 k_2 / \text{l mol}^{-1} \text{ s}^{-1}$ at 25 °C	<i>ortho</i>	1.29 *	8.31	70.8
	<i>para</i>	1.79	5.89	3.47
	<i>o/p</i>	0.7	1.4	20.4
$E / \text{kcal mol}^{-1}$	<i>ortho</i>	19.9 *	20.4	17.7
	<i>para</i>	20.4	18.9	15.7
$\log A / \text{s}^{-1}$	<i>ortho</i>	10.7 *	11.88	10.83
	<i>para</i>	11.19	10.63	8.05

* Values by Bevan and Bye.²

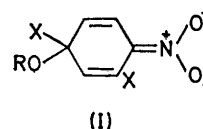
The activating effect of *meta*-substituents in the same parent compound should be, to a first approximation, independent of the nucleophile, particularly if the nucleophiles are very similar. We have measured the rates and product ratios of the reactions of 2,4-difluoronitrobenzene with ethoxide ions in ethanol and isopropoxide ions in propan-2-ol, using exactly the same techniques as in the methoxide-methanol system. In both systems, no 2,4-dialkoxy-1-nitrobenzene could be detected by t.l.c. when the substrate : alkoxide ratio was greater than unity. The results are in Table 1. We have also obtained the Arrhenius parameters for the alkoxydefluorination of *o*- and *p*-fluoronitrobenzenes in these systems and the results are in Table 2. From Table 1, the activating effect of a *meta*-fluorine substituent in the *o*-fluoronitrobenzene series (k_o/k_H) is, as expected, independent of the solvent-lyate system, but in the *p*-fluoronitrobenzene system the apparent activating power (k_p/k_H) increases steadily from methoxide to isopropoxide.

We have pointed out⁷ that for the alkoxydefluorination of *o*- and *p*-fluoronitrobenzenes, the *ortho* : *para* ratios increase from methoxide through ethoxide to isopropoxide. Models of the transition state for the reaction of *o*-fluoronitrobenzene show that although configurations are possible in which the nitro-group is planar to the benzene ring, the transition state is highly congested. We suggested that steric inhibition of solvation of the transition state of the *ortho*-isomer increases as the solvent is changed from methanol through ethanol to propan-2-ol. In principle, this could lead to either an increase or decrease in rate as both the entropy and enthalpy of activation are increased. In practice, the entropy term is dominant.

The transition states for alkoxydefluorinations are believed to be close to the Meisenheimer complex type intermediate, and for attack at the 4-position in 2,4-difluoro-1-nitrobenzene this has the structure (I; X = F).

⁷ C. W. L. Bevan, A. J. Foley, J. Hirst, and W. O. Uwamu, *J. Chem. Soc. (B)*, 1970, 794.

A considerable part of the transition-state solvation will be associated with the nitro-group, but this solvation



will be hindered by the presence of the neighbouring fluorine atom. No such hindrance is possible in the transition states for the alkoxydefluorination of *p*-fluoronitrobenzene; hence k_p/k_H will vary as the solvent-lyate system is varied. The transition states for the attack of alkoxide ions on *o*-fluoronitrobenzene and at the 2-position in 2,4-difluoronitrobenzene are very similar, so the presence of the 4-fluorine atom in the latter does not lead to any further impedance of solvation of the transition state, hence k_o/k_H is independent of the solvent-lyate system.

A similar investigation of 2,4-dichloro-1-nitrobenzene, and *o*- and *p*-chloronitrobenzenes in the three solvent-lyate systems, has also been made. Good rate constants for the reactions of 2,4-dichloro-1-nitrobenzene and *o*-chloronitrobenzene were obtained in all three systems. In the case of *o*-chloronitrobenzene in propan-2-ol the amount of alkali consumed and the amount of chloride liberated at infinity agreed with the calculated values. Prolonged immersion in thermostats at 70 °C and above however resulted in the slow formation of a yellow-brown colour. Rate constants could not be obtained for the reaction of *p*-chloronitrobenzene with isopropoxide ions. The rate of disappearance of alkali was much greater than the rate of appearance of chloride ion, and a yellowish-brown colour developed in the early stages of the reaction. It is probable that similar reactions are occurring here as in the reaction of *p*-chloronitrobenzene with potassium *t*-butoxide in *t*-butyl alcohol. Shein *et al.*⁸ have isolated *p*-nitrophenol and 4,4-dichloroazoxybenzene from this system. The Arrhenius parameters and other relevant data for the reaction of *o*- and *p*-chloronitrobenzenes in the three solvent-lyate systems are in Table 3.

TABLE 3

The reactions of *o*- and *p*-chloronitrobenzenes in some solvent-lyate systems. Rates at 90-85 °C are calculated from the Arrhenius parameters

Solvent		MeOH	EtOH	Pr ^t OH
$10^4 k_2 / \text{l mol}^{-1} \text{ s}^{-1}$ at 90-85 °C	<i>ortho</i>	1.70	5.37	10.5
	<i>para</i>	6.31	7.76	
	<i>o/p</i>	0.27	0.69	
$E / \text{kcal mol}^{-1}$	<i>ortho</i>	26.0	24.9	21.8
	<i>para</i>	23.9	20.2	
$\log A / \text{s}^{-1}$	<i>ortho</i>	11.85	11.68	10.11
	<i>para</i>	11.15	9.03	

The overall rate constants for the reactions of 2,4-dichloro-1-nitrobenzene in the three solvent-lyate

⁸ S. M. Shein, A. V. Yevstifeyev, and O. P. Krivopalova, *Organic Reactivity*, 1971, 8, 671.

systems were measured with an alkoxide : substrate ratio of 1 : 1.33. No 2,4-dialkoxy-1-nitrobenzene was detected by t.l.c. in any of the systems. *ortho* : *para* Ratios were determined from the integrated ^1H n.m.r. spectra of the material obtained after the reactions had gone to infinity. For the reaction with methoxide ions,

TABLE 4

The reactions of 2,4-dichloro-1-nitrobenzene in some solvent-lyate systems. Rates and *ortho* : *para* ratios measured at 90.85 °C

	MeOH	EtOH	Pr ^t OH
<i>ortho</i> : <i>para</i> Ratio	1.98	2.55	
$10^3 k_2$ */l mol ⁻¹ s ⁻¹	9.12	17.4	26.9
$10^3 k_o$ */l mol ⁻¹ s ⁻¹	6.06	12.5	26.9
$10^3 k_p$ */l mol ⁻¹ s ⁻¹	3.06	4.90	
k_o/k_H	35.6	23.2	25.7
k_p/k_H	4.8	6.3	

* k_2 is the overall second-order rate constant for the reaction of 2,4-dichloronitrobenzene with alkoxide ions. k_o and k_p are the rate constants for replacement of the 2- and 4-chlorine atoms.

the n.m.r. spectrum of the product contained two well separated signals due to the methoxymethyl hydrogen atoms at δ -3.88 and -3.95 p.p.m. Synthesis of the two methyl ethers formed during the reaction identified

spectrum due to the aromatic protons also showed that only one product was present in addition to unchanged substrate and that these two were present in the relative proportions of 3 : 1, as would be expected from the initial reactant concentrations of isopropoxide (0.06M) and substrate (0.08M). T.l.c. gave only one spot in addition to that due to the unchanged substrate. The product was identified as 4-chloro-2-isopropoxy-1-nitrobenzene by comparison of its n.m.r. spectra with the spectra of authentic 4-chloro-2-isopropoxy- and 2-chloro-4-isopropoxy-1-nitrobenzene. Details of the comparison are given in Table 5. The kinetic results and *ortho* : *para* ratios, together with the individual rates for substitution at the 2- (k_o) and 4- (k_p) positions, and the k_o/k_H and k_p/k_H ratios are given in Table 4.

The interpretation of the results for the chloro-compounds is complicated by the fact that in the ground state, and possibly in the transition state, the plane of a nitro-group *ortho* to a chlorine atom is rotated considerably from the plane of the benzene ring. Watson,⁹ from an X-ray crystallographic study of 1-chloro-2,4-dinitrobenzene, has shown that the plane of the 2-nitro-group is rotated 39° from the plane of the benzene ring. Bunnett¹⁰ has cited this non-coplanarity as a factor

TABLE 5

A comparison of the n.m.r. spectra of the product obtained from the reaction of isopropoxide ions with 2,4-dichloro-1-nitrobenzene with the spectra of authentic samples of 4-chloro-2-isopropoxy- and 2-chloro-4-isopropoxy-1-nitrobenzene

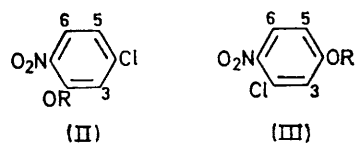
Protons	Peak description	- δ /p.p.m.			J/Hz		
		(II)	(III)	Product	(II)	(III)	Product
6-H *	Doublet	7.75	7.98	7.75	8.5	9	8.5
5-H *	Doublet of doublet	6.94	6.80	6.93	(a) † 8.5 (b) ‡ 2	(a) † 9 (b) ‡ 2.5	(a) † 8.5 (b) ‡ 2
3-H *	Doublet	7.03	7.02	7.03	2	2.5	2
Me ₂ -C-O C(H)O	Doublet	1.40	1.39	1.40	6	6	6
>	Septet	4.68	4.64	4.68	6	6	6

* The δ and J values quoted are the same for the methyl, ethyl, and isopropyl ethers. † Splitting due to 6-H. ‡ Splitting due to 3-H.

these as being due to 2-chloro-4-methoxy-1-nitrobenzene (*para*-substitution) and 4-chloro-2-methoxy-1-nitrobenzene (*ortho*-substitution) respectively. The products of the reaction with ethoxide ions gave a spectrum in which the peaks due to the hydrogen atoms of the ethyl groups were less well resolved. This part of the spectrum showed a major product [δ -4.18 (q) and -1.45 (t) p.p.m.] together with a minor component whose absorbance appeared as side peaks to that of the major component [δ -4.10 (q) and -1.42 (t) p.p.m.]. Both of the possible ethers were synthesised and the major component identified as 4-chloro-2-ethoxy-1-nitrobenzene (*ortho*-substitution).

The sharp peaks observed for the isopropyl group in the n.m.r. spectrum of the product obtained from the reaction of 2,4-dichloro-1-nitrobenzene with isopropoxide ions indicated that only one ether was present. The

reducing the activating power of an *ortho*-nitro-group relative to that of a *para*-nitro-group in the alkoxy-dehalogenation of *o*- and *p*-halogenonitrobenzenes. Miller *et al.*¹¹ however pointed out that in the formation



of the transition state, the compressions of the initial state in the *ortho*-series are released to a considerable extent and they concluded that reduction of activating power due to the absence of coplanarity in the transition state is not likely to be important. Whether this conclusion is correct or not, it cannot operate in the transition state for replacement of the 4-chlorine atom

⁹ K. J. Watson, *Nature*, 1960, **188**, 1102.

¹⁰ J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.

¹¹ B. A. Balto, J. Miller, and V. A. Williams, *J. Chem. Soc.*, 1955, 2926.

in 2,4-dichloro-1-nitrobenzene, hence the activating effect of the nitro-group for this substitution will be less than in the replacement reactions of *p*-chloronitrobenzene. A consequence of this is that *ortho*:*para* ratios obtained from measurements of 2,4-dichloro-1-nitrobenzene would be expected to be higher than those obtained from rate measurements on *o*- and *p*-chloronitrobenzenes. Tables 3 and 4 show this to be the case; the *ortho*:*para* ratios obtained from measurements on *o*- and *p*-chloronitrobenzene are less than unity and those obtained from 2,4-dichloro-1-nitrobenzene are greater than unity. This contrasts with the behaviour of the fluoro-substrates (Tables 1 and 2). With the exception of the reaction with methoxide ions, *ortho*:*para* ratios derived from measurements on *o*- and *p*-fluoronitrobenzene are greater than those obtained from 2,4-difluoro-1-nitrobenzene; moreover the values of the *ortho*:*para* ratios obtained from this substrate are only approximately half those recorded for 2,4-dichloro-1-nitrobenzene.

The rotation of the nitro-group with respect to the benzene ring will allow it to become more accessible to solvent molecules, and steric exclusion of solvation in the transition state for substitution at the 4-position should be of less importance in 2,4-dichloro-1-nitrobenzene than in 2,4-difluoro-1-nitrobenzene. The results in Table 4 show that there is only a small change in k_p/k_H in changing from the methanol solvent-lyate system to the ethanol one.

EXPERIMENTAL

Materials.—*p*-Fluoronitrobenzene was commercial, m.p. 26.4 °C. Commercial *o*-fluoronitrobenzene was fractionally frozen several times to constant f.p. -5.9 °C. *o*-Chloronitrobenzene, m.p. 33 °C, *p*-chloronitrobenzene, m.p. 83 °C, and 2,4-dichloro-1-nitrobenzene, m.p. 34 °C, were recrystallised commercial samples. 2,4-Difluoro-1-nitrobenzene, a commercial sample, was distilled. 2,4-Dimethoxy-1-nitrobenzene was obtained by the action of excess of sodium methoxide on 2,4-difluoro-1-nitrobenzene and had m.p. 74 °C (lit.,¹² 73 °C).

3-Fluoro-4-nitroanisole and 3-fluoro-6-nitroanisole. Nitration of 3-fluorophenol by the method of Hodgson and Nixon¹³ gave 3-fluoro-4-nitrophenol, m.p. 42 °C (lit.,¹³ 42 °C), and 3-fluoro-6-nitrophenol, m.p. 32 °C (lit.,¹³ 32 °C). Methylation of the phenols by Hodgson and Nicholson's procedure gave 3-fluoro-4-nitroanisole, m.p. 56 °C (lit.,¹⁴ 56.5 °C), and 3-fluoro-6-nitroanisole, m.p. 52 °C (lit.,¹⁴ 52 °C).

3-Chloro-4-nitro- and 3-chloro-6-nitro-phenyl ethers. 3-Chlorophenol, b.p. 62 °C at 0.2 mmHg, was obtained from 3-chloroaniline by Koelsch's procedure.¹⁵ Nitration of the phenol by Hodgson and Moore's method¹⁶ gave 3-chloro-6-nitrophenol, m.p. 39 °C (lit.,¹⁶ 41 °C), and 3-chloro-4-nitrophenol, m.p. 121 °C (lit.,¹⁶ 121–122 °C). Methylation of the phenols by Ungnade and Ortega's procedure¹⁷ gave 3-

chloro-6-nitroanisole, m.p. 70.5–71 °C (lit.,¹⁸ 71 °C), and 3-chloro-4-nitroanisole, m.p. 54–55 °C (lit.,¹⁷ 53–55 °C). 3-Chloro-4-nitrophenetole, m.p. 38.5–39 °C (lit.,¹⁹ 39–40 °C), was obtained from the corresponding phenol and diethyl sulphate by a similar procedure. Attempts to prepare the 6-nitrophenetole by the same procedure were unsuccessful. 3-Chloro-6-nitrophenetole, m.p. 63–63.5 °C (lit.,²⁰ 63 °C), was obtained from the reaction of equimolar proportions of 2,4-dichloro-1-nitrobenzene and sodium ethoxide in a sealed tube at 90 °C for 3 h.

4-Chloro-2-isopropoxy-1-nitrobenzene. The procedure of Wilson *et al.*²¹ for the preparation of 3-chloro-4-isopropoxy-1-nitrobenzene was used. 3-Chloro-6-nitrophenol (1.74 g) was added to sodium (0.25 g) in methanol (5 cm³). The solution was added to dimethylformamide (13.5 cm³), followed by the slow addition of isopropyl bromide (1.42 g). The mixture was heated in a sealed tube at 90 °C for 24 h and then poured into water and extracted with toluene. The toluene extract was washed with 2*N*-NaOH and water, and dried (Na₂SO₄). Distillation of the residue from the toluene extract gave 4-chloro-2-isopropoxy-1-nitrobenzene, b.p. 62–64 °C at 0.2 mmHg, $n_D^{23.3}$ 1.5427 (Found: C, 49.9; H, 4.5; Cl, 16.8; N, 6.8%; M^+ , 215. C₉H₁₀ClNO₃ requires C, 50.1; H, 4.7; Cl, 16.4; N, 6.5%; M^+ , 215). 2-Chloro-4-isopropoxy-1-nitrobenzene, b.p. 140–145 °C at 0.4 mmHg, $n_D^{23.3}$ 1.5589, was prepared in a similar fashion (Found: C, 49.8; H, 4.8; Cl, 16.4; N, 6.8%; M^+ , 215).

Solvents.—Methanol, ethanol, and propan-2-ol were dried as previously described.^{7,22}

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%. In the case of the chloro-compounds, the values of the rate constants at at least two temperatures were checked by potentiometric titration with silver nitrate of the chloride ion liberated. In all cases infinity titres agreed with the

TABLE 6

Determination of k_2 for the reaction of *p*-chloronitrobenzene with ethoxide ions in absolute ethanol at 79–60 °C

Initially [Halide] = 0.0300*M*, [OEt⁻] = 0.0646*M*. 5 cm³ samples titrated with 0.2495*N*-HCl

Time/min	0	60	120	180	240	260	360
Titre	12.92	12.50	12.15	11.80	11.49	11.40	10.96
10 ⁴ k_2 /l mol ⁻¹ s ⁻¹		3.20	3.07	3.14	3.15	3.13	3.13
Time/min	425	480	540	600	660	720	∞
Titre	10.70	10.48	10.30	10.14	9.97	9.80	6.97
10 ⁴ k_2 /l mol ⁻¹ s ⁻¹	3.14	3.18	3.15	3.07	3.09	3.11	

Mean $k_2 = 3.13 \pm 0.07 \times 10^{-4}$ l mol⁻¹ s⁻¹. Duplicate 3.17 ± 0.06 × 10⁻⁴ l mol⁻¹ s⁻¹. Mean k_2 corrected for solvent expansion 3.55 × 10⁻⁴ l mol⁻¹ s⁻¹.

theoretical values. Details of the experimental procedure have been given;⁷ for runs above 45 °C sealed tubes were used. Table 6 illustrates the determination of rate constants at a particular temperature. The results at different temperatures are in Table 7.

¹⁸ A. F. Holleman and W. J. De Mooy, *Rec. Trav. chim.*, 1915, **35**, 5.

¹⁹ H. H. Hodgson and H. Clay, *J. Chem. Soc.*, 1930, 963.

²⁰ F. Beilstein and A. Kurbatow, *Annalen*, 1876, **182**, 94.

²¹ H. F. Wilson, D. H. McRae, and B. M. Vittimberga, U.S.P., 3,238,223; *Chem. Abs.*, 1966, **64**, 14,170b.

²² M. A. Adeniran, C. W. L. Bevan, and J. Hirst, *J. Chem. Soc.*, 1963, 5868.

¹² F. Swarts, *Rec. Trav. chim.*, 1915, **35**, 154.

¹³ H. H. Hodgson and J. Nixon, *J. Chem. Soc.*, 1928, 1879.

¹⁴ H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 1940, 1268.

¹⁵ C. F. Koelsch, *J. Amer. Chem. Soc.*, 1939, **61**, 969.

¹⁶ H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, 1925, 1599.

¹⁷ H. E. Ungnade and I. Ortega, *J. Org. Chem.*, 1952, **17**, 1475.

TABLE 7

Rate constants for the reactions of *o*- and *p*-fluoro- and -chloro-nitrobenzenes with alkoxide ions at various temperatures

Substrate	MeO ⁻		EtO ⁻		PriO ⁻	
	<i>t</i> /°C	$\frac{10^4 k_2}{\text{l mol}^{-1} \text{s}^{-1}}$	<i>t</i> /°C	$\frac{10^4 k_2}{\text{l mol}^{-1} \text{s}^{-1}}$	<i>t</i> /°C	$\frac{10^4 k_2}{\text{l mol}^{-1} \text{s}^{-1}}$
<i>o</i> -Fluoronitrobenzene			14.70	2.45	2.60	6.25
			25.00	8.32	10.00	14.7
			35.50	27.2	20.00	42.8
			44.80	71.5	30.00	116.00
<i>p</i> -Fluoronitrobenzene	28.80	2.59	15.00	1.96	15.3	1.43
	39.00	7.80	25.40	6.22	25.10	3.47
	49.49	22.8	35.50	17.5	35.0	8.17
<i>o</i> -Chloronitrobenzene			44.90	43.7	45.0	18.7
	110.05	10.15	90.72	5.09	70.35	1.74
	120.00	24.4	100.02	12.0	80.45	4.28
	129.10	52.1	109.68	28.1	90.40	9.94
<i>p</i> -Chloronitrobenzene	138.80	111.0	120.80	70.6	102.80	27.1
	100.00	14.1	79.60	3.35		
	110.00	32.8	90.08	7.65		
	120.80	77.0	100.65	16.9		
	173.0	108.70	30.0			
		120.70	67.7			

Product Analyses.—Run solutions were allowed to go to infinity at the required temperature. The solvent was removed under slightly reduced pressure and the residue dried in a desiccator. The ¹⁹F (fluorobenzene as internal

reference) and ¹H (Me₄Si as internal reference) n.m.r. spectra of CDCl₃ solutions of the residue were determined with a Varian Associates 56/60 spectrometer.

[2/1127 Received, 18th May, 1972]