*The S_N Mechanism in Aromatic Compounds. Part XIV.**

By BRIAN A. BOLTO, JOSEPH MILLER, and VINCENT A. WILLIAMS.

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The rate of replacement of halogen in 1-halogeno-2-nitrobenzenes by methoxide in methanol has been measured. The order F > Cl > Br > I is found, as with 1-halogeno-4-nitro- and 1-halogeno-2 : 4-dinitro-benzenes. The absence of steric factors in determining the order of the halogens is shown, and the *ortho*- and *para*-series are compared.

EARLIER papers [Beckwith, Miller, and (in part) Leahy, *J.*, 1952, 3552; Briner, Miller, and (in part) Liveris and Lutz, *J.*, 1954, 1265] were concerned with the replacement of halogens from aromatic compounds by S_N reactions. The present paper deals with the replacement of the halogens when the sole activating group is an *o*-nitro-group, the reagent being methoxide in absolute methanol as before. The experimental measurements and some derived quantities are given in Tables 1 and 2.

In view of other work by Miller *et al.* now proceeding, in extending variation of the replaced group beyond the halogen series, a group replacement factor (G.R.F.) is now defined, being the ratio of the rate constants for replacement of X in ArX and Cl in ArCl (*i.e.*, ArX/ArCl) at a given temperature. Other quantities already defined, and used here, are the substituent rate factor (S.R.F.) and steric index (S.I.) (Miller, *J.*, 1952, 3550; Miller and Williams, *J.*, 1953, 1475).

Discussion.—The now familiar pattern that fluorine is much more easily replaced than the other halogens in activated S_N reactions in the aromatic series is again shown. Apart from minor variations, discussed below, the pattern of the G.R.F.'s is almost the same in the *o*- as in the *p*-nitro-series. This shows clearly that the main pattern is not steric in origin.

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* Part XIII, *J. Org. Chem.*, 1955, **20**, 558.

TABLE 1. *Rate constants, etc., for 1-halogeno-2-nitrobenzenes.*

	Temp.	Rate constant * (10^5k_2; l. mole^{-1} sec.$^{-1}$)	Group replacement factor			E † (cal.)	$\log_{10} B$
			0°	50°	100°		
F ‡	0°	(0·658)	2210	722	317	19,700	10·4
	45·3	114					
	50·0	(181)					
	60·2	463					
	82·0	2860					
	100·0	$(11{,}0_{50})$					
Cl	0	(0·000297)	1	1	1	$23{,}6_{50}$	10·4
	50·0	(0·252)					
	75·3	3·62					
	81·6	6·82					
	100·0	(35·0)					
	100·8	37·4					
Br	0	(0·000121)	0·407	0·702	1·05	$25{,}5_{50}$	11·5
	50·0	(0·177)					
	81·8	6·23					
	100·0	(36·7)					
	100·1	36·9					
	113·7	123					
I	0	(0·0000429)	0·144	0·330	0·663	26,500	11·9
	50·0	(0·0829)					
	99·3	19·7					
	100·0	(21·1)					
	120·6	136					
	138·6	605					

* Values in parentheses obtained by using the Arrhenius parameters.

† Probable error in E is $\pm$ 1%, *i.e.*, approx. $\pm$ 200 cal. The fit to a straight line of the $\log_{10} k_2$ against reciprocal temperature plots is indicated by least-squares calculation of the "probable errors" of these plots; and these are in all cases within the figure given.

‡ For a recent similar study of this compound see Bevan and Bye, *J.*, 1954, 3091.

TABLE 2.

	Group replacement factor				S.I.		Difference of Arrhenius parameters for *ortho*- and *para*-series	
	ortho-series		*para*-series					
	50°	100°	50°	100°	50°	100°	E	$\log_{10} B$
F	722	317	312	172	1·46	2·00	−1500	$-1{\cdot}1_5$
Cl	1	1	1	1	3·36	3·66	− 400	−0·8
Br	0·702	1·05	0·745	0·961	4·04	3·35	+ 400	0
I	0·330	0·603	0·361	0·441	3·78	2·67	+1500	+0·5

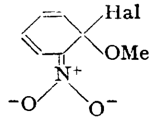
The order of replacement F $\gg$ Cl $>$ Br $>$ I has been ascribed (*locc. cit.*) to the inductive withdrawal by the halogen of the Ar–Hal bond electrons with consequent facilitation of attack by OMe^- on the ring carbon atom. An attempt was also made to correlate the activation energies with calculated electronegativity and conflicting bond strength factors, the latter being those of the Ar–Hal bonds. It was hoped that this treatment might be extended to the aliphatic series. While this gave fair agreement with experiment, the use of Ar–Hal bond strengths as a factor may not be justified if in the transition state the Ar–Hal bond is not yet broken, but merely changed to a bond of aliphatic type. If they were known, the differences between the Ar–Hal and Aliph–Hal bond strengths might be used. These differences will in any case parallel the C–Hal bond strengths; so both treatments should give similar results.

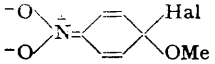
It should be noted that, if the Ar–Hal bond is to any extent weaker than a full bond in the transition state, then solvation of the partially formed halide ion will also favour replacement in the order F $>$ Cl $>$ Br $>$ I, the difference between fluorine and the others being largest.

Another point is that the operation of the $+M$ effect is one of the factors favouring the opposite order to that found experimentally. It operates effectively only in the initial state of the Ar–Hal molecule.

Inasmuch as the bonding of halogen in the transition state is not known, though usually approximated to a full Aliph–Hal bond, it is thought unprofitable at present to attempt further analysis of the activation energies.

The comparatively small differences between the two mononitro-series are significant: the spread of E and $\log_{10} B$ is bigger in the *ortho*-series—6800 and 1·3, compared with 3800 and $0{\cdot}5_5$; in comparing the individual E and $\log B$ values, there is a smooth transition in going from fluorine (*ortho*-values lower) to iodine (*ortho*-values higher). The structure of the transition states, in line with aromatic S_E reactions, and the discussion by Miller (*Rev. Pure Appl. Chem.*, 1951, **1**, 171), is regarded as approximating to the structures (I) and (II).

(I) 

 (II)

The delocalisation energy of (I) might be expected to be greater than that of (II) with its cross-conjugation, though the apparently greater stability of *p*- than of *o*-quinones indicates that this may not be fully justified. In formation of (I) the compressions of the initial state in the *ortho*-series are released to a considerable extent; no such factor applied to the *para*-series. In the *ortho*-series, the nitro-group is not coplanar with the ring in the initial state but can be so in the transition state: reduction in activating power due to absence of coplanarity is therefore not likely to be important. This is confirmed by examination of the steric indices, for while that for the fluoro-compounds is smaller than the others, those for chlorine, bromine, and iodine are approximately equal, and only slightly bigger than that for fluorine.

The various factors above are consistent with the experimental values of E and B.

Comparison of the *o*- and *p*-halogenonitrobenzenes with the 1-halogeno-2 : 4-dinitrobenzenes shows that the S.R.F.'s of the *o*- and the *p*-nitro-group are not greatly affected by variation of the replaced group when another activating group is already present; the range of S.R.F. for *o*-NO_2 being $1{\cdot}26$ to $9{\cdot}69 \times 10^5$ at 0°, and for *p*-NO_2 from $6{\cdot}73 \times 10^5$ to $1{\cdot}14 \times 10^6$ at 0°.

While the comparative unimportance of steric effects in series where only the one *ortho*-group is present has been shown, a definite steric effect is to be expected when both *ortho*-positions are occupied and this has already been demonstrated for groups *ortho* to chlorine (Miller, *J.*, 1952, 3550; Miller and Williams, *J.*, 1953, 1475).

EXPERIMENTAL

Runs were followed as in Part II (Miller, *J.*, 1952, 3550), except that graphical plots were used for k_2. Runs were made at least in duplicate at each of three temperatures.

Materials.—*o*-Fluoronitrobenzene, prepared from *o*-nitroaniline by the Schiemann reaction, had b. p. 217°/764 mm., 117·5°/34 mm. (lit., 214·6°/761 mm.).

TABLE 3.

Titration value ...	7·82	8·33	8·70	9·10	9·49	9·77	10·12	10·50
log term	0·3336	3539	3701	3897	4174	4278	4511	4799
Time (min.)	0	4	8	12	16	20	26	32
Titration value ...	10·90	11·33	11·67	12·08	12·45	12·80	14·09	
log term	5149	5595	6043	6634	7341	8209	—	
Time (min.)	40	50	60	75	90	110	∞	

$k_2 = 4{\cdot}59_4 \pm 0{\cdot}03_0 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$.

o-Chloro- and *o*-bromo-nitrobenzene were commercial products, crystallised to constant m. p. from methanol and aqueous methanol respectively and had m. p. 32·5° (lit., 32°) and 43° (lit., 43°), respectively.

o-Iodonitrobenzene, prepared from *o*-nitroaniline (Ullmann, *Ber.*, 1896, **29**, 1878) and recrystallised from aqueous methanol, had m. p. 50° (lit., 49·5°, 54°).

TABLE 4.

Temperature		45·3°		60·2°		82·0°	
Rate constants	113	114	115	462	464	2840	2870
($10^5 k_2$)		(av. 114)		(av. 463)		(av. 2860)	

$E = 19{,}6_{60} \pm 30$ cal.

Typical Kinetic Values.—A typical run (for *o*-fluoronitrobenzene at 60·2°) is given as Table 3, while the full set of rate constants for the same compound used for calculation of " probable error " by least squares is given as Table 4.

UNIVERSITY OF WESTERN AUSTRALIA,
NEDLANDS, WESTERN AUSTRALIA.

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