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

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The reactions of *p*-halogenonitrobenzenes with sodium methoxide in absolute methanol have been examined quantitatively, and are discussed as in Part III [Beckwith, Miller, and (in part) Leahy, *J.*, 1952, 3552] for the 1-halogeno-2 : 4-dinitrobenzenes.

By the method reported in Part I (Miller, *Rev. Pure Appl. Chem.*, 1951, **1**, 171) it was shown in Part III (*loc. cit.*) that the relative ease of replacement of halogens in nucleophilic substitutions is the resultant of opposing bond-strength and electronegativity factors, and that the reversal in their relative importance, as in alkyl halides on the one hand and activated aryl halides on the other, takes place between the halogeno- and halogenonitrobenzenes.

In the present work, the rates of attack by OMe^- in absolute methanol on the latter compounds, together with the Arrhenius parameters, are obtained. Bevan (*J.*, 1951, 2340) recently measured the rates of attack by OEt^- in ethanol on these compounds, though he did not discuss the Arrhenius parameters, and regarded his discussion as tentative. The kinetic difficulty with the iodo-compound, due to a side reaction forming free iodine, which he reported, was not encountered in this work. The kinetics for the chloro-compound have been determined less thoroughly by Holleman, de Mooy, and Ter Weel (*Rec. Trav. chim.*, 1916, **35**, 1).

Table 1.

Halogen in p-$NO_2{\cdot}C_6H_4{\cdot}Hal$	Temp.	Rate constants, 10^5k_2 (l. mole^{-1} sec.$^{-1}$)	Ratio, Cl = 1, at			E (cal.)	$\log_{10} B$
			0°	50°	100°		
Fluorine	0°	(0·626)	—	—	—	—	—
	$35{\cdot}5_5$	58·7	—	—	—	21,200 ± 100	11·75 ± 0·1
	40·2	104	—	—	—	—	—
	47·3	$187{\cdot}_5$	—	—	—	—	—
	$48{\cdot}0_5$	218	703	312	172	—	—
	50	(264)	—	—	—	—	—
	82·0	5,210	—	—	—	—	—
	100	(22,000)	—	—	—	—	—
Chlorine	0	$(0{\cdot}0_3890)$	—	—	—	—	—
	50	(0·847)	—	—	—	24,050 ± 150	11·2 ± 0·1
	71·0	8·42	—	—	—	—	—
	81·6	23·5	1	1	1	—	—
	100	(128)	—	—	—	—	—
	100·8	$137{\cdot}_5$	—	—	—	—	—
Bromine	0	$(0{\cdot}0_3634)$	—	—	—	—	—
	50	(0·716)	—	—	—	24,650 ± 100	11·5 ± 0·1
	82·0	$21{\cdot}8_5$	—	—	—	—	—
	100	(123)	0·612	0·745	0·961	—	—
	100·1	124	—	—	—	—	—
	120·4	680	—	—	—	—	—
Iodine	0	$(0{\cdot}0_3245)$	—	—	—	—	—
	50	(0·305)	—	—	—	25,000 ± 200	11·4 ± 0·1
	82·0	$11{\cdot}5_5$	—	—	—	—	—
	100	(56·4)	—	—	—	—	—
	100·1	56·9	0·275	0·361	0·441	—	—
	120·6	372	—	—	—	—	—
	138·5	1,360	—	—	—	—	—

The experimental results, given as Table 1, include, in parentheses, rate constants calculated from the Arrhenius parameters.

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Discussion of Results.—It is clear from the experimental measurements that the reversal in character from the halogenobenzenes is almost complete with the introduction of the first nitro-group in the *para*-position. Miller (*J.*, 1952, 3550) showed the *o*-nitro-group to be similar; even the *m*-group is effective to a smaller extent, as shown by comparison of *m*-fluoro- and *m*-chloro-nitrobenzene (unpublished work by Liveris, Lutz, and Miller, quoted by Heppolette and Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 4265) and Holleman and de Mooy, *Rec. Trav. chim.*, 1916, **35**, 17).

The differences between the mono- and the dinitro-series are small but in the right direction as shown in Table 2. If *A* is the difference in ionic resonance energy, *B* the difference in bond strength of the C–Hal bonds, and *C* the difference in activation energy (all in kcal.), the values being obtained as in Part III, then the equation, $0{\cdot}31B - 0{\cdot}48A = C$, fits well the experimental values relating fluorine, chlorine, and iodine, but does not in this series predict the correct value for bromine, as shown below :

TABLE 2.

	Halogen ratio at 50° :		Differences in activation energy (kcal.)	
Halogen	mononitro-series	dinitro-series	mononitro-series	dinitro-series
F	312	1200	−3·8	−4·6
Cl	1	1	$-0{\cdot}9_5$	$-1{\cdot}5_5$
Br	$0{\cdot}74_5$	$0{\cdot}62_5$	$-0{\cdot}3_5$	−1·9
I	0·36	0·24	0	0

	Halogen in *p*-halogenonitrobenzene			
	F	Cl	Br	I
C (actual)	−3·8	−0·95	−0·35	0
C (calc.)	−3·8	−0·95	$-1{\cdot}3_5$	0

The main feature, the marked difference between fluorine and the other halogens, is again clearly brought out. There is no obvious explanation for the divergence of bromine, but the forthcoming analysis of the simple halogenobenzenes should throw further light on this point.

The ratio of the electronegativity and the bond-strength factors in the mononitro-series bears a satisfactory relation to that in the dinitro-series, *viz.*, 1·55 as against 1·65 : a small but significant increase in the importance of the bond-strength factor is apparent.

As might be expected for simple *para*-substituents the values for $\log_{10} B$ are all very close, the whole range being only 0·55.

Experimental.—The runs were followed as in Part II (*loc. cit.*), but a graphical plot was used for k_2. Runs at each temperature were in duplicate except for those with fluorine at 47·3° and 48·05°. Probable errors in *E* and $\log_{10} B$ were determined by the method of least squares.

Materials. p-Fluoronitrobenzene, prepared from *p*-nitroaniline *via* the diazonium borofluoride in 54% overall yield, had m. p. 26°, b. p. 204—205° (lit. : 26°; 205°). *p*-Chloro-, *p*-bromo-, and *p*-iodo-nitrobenzene were commercial products crystallised to constant m. p. from ethanol and had m. p. 83° (lit., 83°), 124—125° (lit., 125°, 127°), and 172° (lit., 172°), respectively.

As a confirmation of the absence of the side reaction reported by Bevan (*loc. cit.*) several tubes of reaction mixture of the iodo-compound were held at 120·6° for 4 days. No free iodine could be detected.

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