519. *The Influence of the Nitro-group on the Reactivity of Aromatic Halogens. Part I.*

By C. W. L. Bevan.

Arrhenius parameters have been determined for the bimolecular substitution reaction of the *p*-halogenonitrobenzenes with sodium ethoxide in absolute ethyl alcohol, a reaction free from steric effects. A possible explanation of the order of reactivity is suggested.

The comparative rates of replacement of halogen atoms attached to a saturated carbon atom have been determined in a number of instances (*e.g.*, Polanyi *et al.*, *Trans. Faraday Soc.*, 1936, **32**, 843; Cooper and Hughes, *J.*, 1937, 1183; Miller and Bernstein, *J. Amer. Chem. Soc.*, 1948, **70**, 3600). In all cases the sequence of reactivity is RI > RBr > RCl > RF and the spread of reactivity of the order of 10^5—10^6. For the reactions of halogenobenzenes with sodium methoxide, and with pyridine (Tronow and Kruger, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1270; cf. *Chem. Zent.*, 1927, **2**, 1145), the rate sequence is PhI > PhBr > PhCl > PhF with a spread of reactivity less than 10^2 (cf. Bergstrom *et al.*, *J. Org. Chem.*, 1936, **1**, 170, 179). The presence of electron-attracting substituents in the halogenobenzenes and in halogenated heterocyclic molecules causes a reversal of this order of reactivity. For instance, the reactions of monohalogeno-2 : 4-dinitrobenzenes with ethoxide ions gave the relative rates: RCl, 3·26; RBr, 1·89; RI, 0·55 (Lulofs, *Rec. Trav. chim.*, 1901, **20**, 292). These reactions were found to be retarded by the addition of water and were established as bimolecular (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 627). Further, Holleman (*Rec. Trav. chim.*, 1904, **23**, 256) found that with methoxide ions 2 : 4-dinitrofluorobenzene reacts some 600 times as fast as the corresponding chlorobenzene (cf. Miller and Wrightson, Amer. Chem. Soc. Meeting, Sept. 17th, 1947, Abstr. of Papers, p. 16J; Chapman *et al.*, *Chem. and Ind.*, 1951, **8**, 148).

The results of the present investigation, which are free from possible complications due to *ortho*-substituents, are shown in Table I.

TABLE I.

k_2 (*in l. mol.*$^{-1}$ *sec.*$^{-1}$) *for* p-*halogenonitrobenzenes with* OEt^- *in absolute* EtOH.

p-Substituent : F.		Cl.		Br.		I.	
Temp.	k_2.	Temp.	k_2.	Temp.	k_2.	Temp.	k_2.
90·80°	$2·20 \times 10^{-1}$	90·80°	$9·63 \times 10^{-4}$	90·80°	$8·38 \times 10^{-4}$	90·80°	$7·09 \times 10^{-5}$
80·80	$1·04 \times 10^{-1}$	100·7	$2·00 \times 10^{-3}$	101·0	$1·80 \times 10^{-3}$	—	—
70·00	$4·73 \times 10^{-1}$	109·8	$3·82 \times 10^{-3}$	111·1	$3·73 \times 10^{-3}$	—	—
60·80	$2·08 \times 10^{-2}$	120·0	$7·60 \times 10^{-3}$	120·1	$6·87 \times 10^{-3}$	—	—
50·80	$8·56 \times 10^{-3}$	129·8	$1·42 \times 10^{-2}$	130·1	$1·31 \times 10^{-3}$	—	—

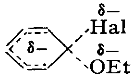
Arrhenius parameters.

p-Substituent	F	Cl	Br
$\log_{10} B$ (l. mol.$^{-1}$ sec.$^{-1}$)	10·7	9·0	9·2
E (kcals.)	19·0	20·1	20·3

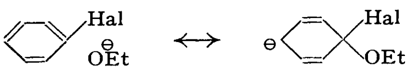
Arrhenius parameters were not determined for the iodide since the rate constants decreased rapidly after the first 10% of reaction and iodine was liberated, owing possibly to incursion of a free-radical reaction. The rate quoted is calculated from velocity constants determined over the first 10% of reaction.

These results show that the inverted sequence of reactivity persists even in the absence of *ortho*-substituents, and that the large difference in rate between the fluoro- and the chloro-compound is reflected in both parameters of the Arrhenius equation.

The spread of reactivity is of the order 10^3—10^4 which is considerably less than in saturated halides. Formation of the transition state of aliphatic substitution, *viz.*, $\overset{\delta-}{\text{Hal}} \cdots\cdots \text{R} \cdots\cdots \overset{\delta-}{\text{OEt}}$, requires a stretching of the carbon–halogen bond in order partly to accommodate the electron pair of the attacking entity. In aromatic substitution (cf. Hughes and Ingold, *J.*, 1941, 608) the transition state may be pictured as

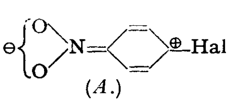


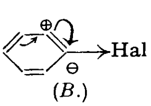
with canonical structures

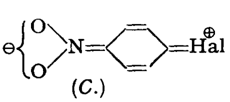


Here the electron pair of the attacking entity may resonate in part through the unsaturated system, so enabling the transition state to be formed without much stretching of the C–Hal bond. Changing the halogen should thus have a smaller effect on the reaction rate than in the aliphatic case.

The sequence of halogen reactivity in aliphatic systems is probably largely determined by bond strengths, and the inductomeric polarisability of the halogens which is believed to be in the order I > Br > Cl > F (cf. Baker and Hopkins, *J.*, 1949, 1089). However, in the aromatic case, the energetics of bond formation is likely to be the rate-determining factor. Exchange reactions of the phenyl halides are facilitated by electron-attracting substituents, and it has been pointed out by Catchpole, Hughes, and Ingold (*J.*, 1948, 10) that this must be correlated with the resulting reduction in π-electron screening of the reactive carbon atom, which is thus rendered more vulnerable to nucleophilic attack. The effects of the halogens may be considered on the following basis : in unsubstituted benzene there is one π-electron associated with each carbon atom, whereas in *p*-nitrohalogenobenzenes the nitro-group will tend, both by its tautomeric and by its inductive attraction, to reduce this to some fraction of unity by causing contributions from structures such as (*A*). The inductive effect of the halogen atoms, acting mainly on the electrons of the carbon–halogen bond, will increase the electronegativity of the reactive carbon atom and produce, in the π-electrons of the ring, displacements as in (*B*). This will tend to lower slightly the reduction in π-electron screening caused by the nitro- or other electron-attracting group. Moreover, mesomeric release by the halogen atom will produce a fractional π-electron at the reactive carbon atom by contributions from structures such as (*C*).


(*A*.)


(*B*.)


(*C*.)

Thus, both by its inductive and by its mesomeric effects the halogen atom will tend to oppose the reduction in π-electron screening caused by the nitro-group. The order of inductive attraction for the halogens is F > Cl > Br > I, so that, if the sequence of reactivity of the nitrohalogenobenzenes in the type of reaction under discussion, *viz.*, F > Cl > Br > I, is determined by the order in which they reduce the π-electron screening at the reactive carbon atom in the ground states of these molecules, then the order of mesomeric release leading to structures such as (*C*) would be I > Br > Cl > F. Such a sequence has been postulated by Evans and Walker (*Trans. Faraday Soc.*, 1944, **40**, 384), and Hurdis and Smythe (*J. Amer. Chem. Soc.*, 1942, **64**, 2212) have suggested from their measurements of the dipole moments of the *p*-nitrohalogenobenzenes that the nitro-group effects a greater increase in the double bond character of the C–Cl bond than of the C–F bond.

There is, however, a considerable weight of evidence summarised by Baker and Hopkins (*loc. cit.*) in favour of a mesomeric release by the halogens following the reverse order, and it must be stated that the combined influence of the effects discussed above is of too intricate a character to enable one to be emphatic regarding the conclusion of the analysis, which must, therefore, be regarded as tentative.

EXPERIMENTAL.

Preparation of Materials.—The *p*-chloro-, *p*-bromo-, and *p*-iodo-nitrobenzenes were commercial specimens recrystallised to constant m. p. from ligroin, giving respectively, m. p. 83·1°, 127·0°, 174·0°. *p*-Fluoronitrobenzene was prepared by Schiemann and Pillarsky's method (*Ber.*, 1929, **62**, 6040), b. p. 80·5°/9·5 mm., m. p. 27·5°.

Commercial absolute alcohol was dried by Smith's method (*J.*, 1927, 1288) as modified by Manske (*J. Amer. Chem. Soc.*, 1931, **53**, 1106) and fractionated. It was stored under oxygen-free nitrogen and delivered for use under pressure.

Kinetic Measurements.—Thermostat temperatures below 100° were steady to within ±0·01° ; those above 100° to within ±0·05°. The method of sealed tubes was used at all temperatures. Aliquots of approx. 0·02M-solutions of the halides and of an approx. 0·04M-solution of sodium ethoxide in absolute ethyl alcohol were mixed (at −80° in the case of the fluoride), sealed, and immersed in a thermostat for definite periods of time. Zero readings were obtained from tubes immersed for 5 minutes. The reaction was stopped by rapidly cooling and then opening the tubes under a few ml. of 2N-nitric acid ; the halide ion produced in reaction was determined by titration with 0·02M-silver nitrate solution, a valve potentiometer being used. In the case of the fluoride, the tubes were opened under an aliquot of standard acid, and excess of acid determined by back-titration with standard carbon-dioxide-free alkali, with bromothymol-blue as indicator.

Rate constants were calculated from the formula :

$$k_2 = \frac{1}{(a - b)t} \log_e \left[\frac{b(a - x)}{a(b - x)}\right]$$

where a and b are the initial concentrations of sodium ethoxide and alkyl halide respectively, and x is the decrease in concentration after time t. The results of typical experiments are shown in detail in Table II. A correction for solvent expansion between the temperature at which the tubes were filled and that at which the rate was measured was applied. Rate constants could be duplicated to within ±1%.

TABLE II.

Determination of rate constants, k_2, *in sec.*$^{-1}$ *g.-mol.*$^{-1}$. *Reaction of* p-*fluoronitrobenzene with sodium ethoxide in absolute ethyl alcohol.*

Initially, [Halide] ~ 0·01M. and [NaOEt] ~ 0·02M.

Concns. are expressed in ml. of 0·01190N-NaOH per 9·65 ml. sample. Temp. = 80·80°.

t (min.)	0	4	5	6	7	8	10	13	16	20	25
[NaOEt]	14·14	12·09	11·72	11·43	11·18	10·79	10·41	9·77	9·41	8·89	8·58
[Halide]	6·60	4·55	4·18	3·89	3·64	3·25	2·87	2·23	1·87	1·35	1·01
10^2k_2	—	9·64	9·64	9·45	9·22	9·81	9·44	9·87	9·56	10·10	9·67

Mean $k_2 = 9{\cdot}63 \times 10^{-2}$; corrected for solvent expansion (16—81°), $k_2 = 1{\cdot}04 \times 10^{-1}$.

Reaction of p-*chloronitrobenzene with sodium ethoxide in absolute ethyl alcohol.*

Initially [Halide] ~ 0·01M. and [NaOEt] ~ 0·02M.

Concns. are expressed in ml. of 0·0200N-AgNO$_3$ per 9·65 ml. sample. Temp. = 129·8°.

t (min.)	0	5	10	15	25	35	40	65	70	116	145
[NaOEt]	10·20	9·87	9·57	9·30	8·77	8·34	8·20	7·61	7·48	6·64	6·48
[Halide]	4·62	4·29	3·99	3·72	3·19	2·76	2·62	2·03	1·90	1·06	0·90
10^2k_2	—	1·18	1·19	1·20	1·24	1·29	1·26	1·17	1·19	1·30	1·18

Mean $k_2 = 1{\cdot}22 \times 10^{-2}$; corrected for solvent expansion (18—130°), $k_2 = 1{\cdot}42 \times 10^{-2}$.

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