131. *Nucleophilic Displacement of Fluorine from Aromatic Compounds. Part I.*

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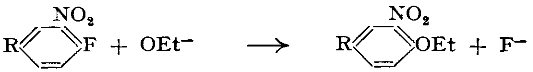
Arrhenius parameters have been determined over a range of temperatures for the reactions of a series of *o*-fluoronitrobenzenes substituted in the *para*-position to the fluorine with sodium ethoxide in absolute ethyl alcohol. An earlier tentative suggestion that the order of mesomeric release from the halogens is I>Br>Cl>F is invalidated by the results: these are briefly discussed in the light of those obtained recently in a similar reaction.

Bevan (*J.*, 1951, 2340) suggested that the sequence of halogen reactivity towards nucleophilic reagents, in the *p*-halogenonitrobenzenes, might be explained in terms of a mesomeric release from halogen atoms in the order I>Br>Cl>F. To test this, and to investigate the effect of both activating and deactivating substituents on nucleophilic replacement at an aromatic carbon atom, Arrhenius parameters have been determined, in absolute alcohol, for the reaction



where R is NH_2, H, F, Cl, Br, I, or NO_2. The effects of these and other substituents R on the reaction of analogous bromides with piperidine have been determined by Berliner and Monack (*J. Amer. Chem. Soc.*, 1952, **74**, 1574), who assumed, as is done in the present paper, that the effect of the *o*-nitro-group on the reaction rates is a constant factor. Rate constants are assembled in Table 1.

Table 1. *k_2 in l. sec.$^{-1}$ mole^{-1} for 4-substituted 1-fluoro-2-nitrobenzenes with* OEt^- *in absolute ethanol.*

R = NH_2		R = H		R = F	
Temp.	k_2	Temp.	k_2	Temp.	k_2
89·63°	$6·70 \times 10^{-3}$	60·98°	$2·86 \times 10^{-2}$	60·98°	$4·80 \times 10^{-2}$
69·30	$8·53 \times 10^{-4}$	49·62	$9·88 \times 10^{-3}$	50·98	$1·90 \times 10^{-2}$
49·56	$9·02 \times 10^{-5}$	40·36	$3·86 \times 10^{-3}$	40·98	$7·00 \times 10^{-3}$
		31·80	$1·55 \times 10^{-3}$	22·10	$8·71 \times 10^{-4}$
R = Cl		R = I		R = Br	
Temp.	k_2	Temp.	k_2	Temp.	k_2
51·05°	$1·39 \times 10^{-1}$	49·76°	$1·66 \times 10^{-1}$	50·98°	$1·90 \times 10^{-1}$
36·60	$3·68 \times 10^{-2}$	41·29	$8·02 \times 10^{-2}$	40·98	$7·99 \times 10^{-2}$
0·25	$7·49 \times 10^{-4}$	30·18	$2·91 \times 10^{-2}$	30·98	$3·24 \times 10^{-2}$
		20·83	$1·15 \times 10^{-2}$	22·10	$1·35 \times 10^{-2}$

For 1-fluoro-2 : 4-dinitrobenzene it was not possible to determine Arrhenius parameters because the reaction was too fast. The rate constant at −20·22° was 16·6 l. sec.$^{-1}$ mole^{-1}. Backwith, Miller, and Leahy (*J.*, 1952, 3552) estimate E for this reaction with OMe^- as 14·35 kcal.; Bevan (*loc. cit.*) gives E for reaction of *p*-fluoronitrobenzene with OEt^- as 19·0 kcal., and Bye (unpublished results) gives E for the reaction with OMe^- as 20·3 kcal.; it is therefore assumed that E for reaction of 1-fluoro-2 : 4-dinitrobenzene with OEt^- is $14·35 - (20·3 - 19·0) = 13$ kcal., giving k_2 at 49·6° = *ca.* $4·57 \times 10^3$ l. sec.$^{-1}$ mole^{-1}.

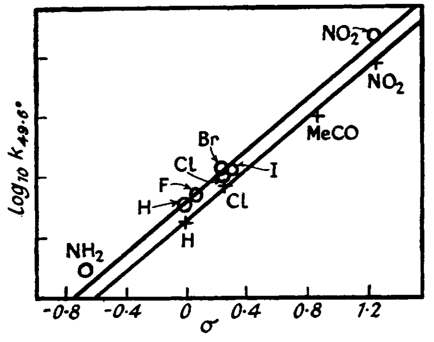
The sequence of rates in Table 2 shows that, as *para*-substituents in the reaction studied, all the halogens are activating with respect to hydrogen; *i.e.*, they withdraw aromatic electrons from the benzene ring and they do so in the order $I \sim Br > Cl \gg F$. Since the $(-I)$ effects of the halogens are undoubtedly in the order F>Cl>Br>I, the results indicate a mesomeric release in the order $F \gg Cl > Br \sim I$.

It may be noted that Berliner and Monack (*loc. cit.*) found a *p*-fluoro-atom to be deactivating in the reaction of *o*-bromonitrobenzene with piperidine, giving an activation energy ~1·2 kcal. higher than in the parent compound. However, in the closely similar case studied here over a range of temperatures, *p*-fluorine was slightly activating and led to a value of *E* the same as in the parent compound. Further, the difference in reactivity between the parent compound and the *p*-amino-compound is here of the order of 10^2 which shows a much smaller deviation from the behaviour in non-activated substitution (cf. Badger, Cook, and Vidal, *J.*, 1947, 1109) than was exhibited by a *p*-amino-group in the reaction studied by Berliner and Monack (*loc. cit.*).

TABLE 2. *k_2 in l. sec.$^{-1}$ mole^{-1} at 49·6° and Arrhenius parameters* ($k_2 = Be^{-E/RT}$).

p-Subst. :	NH_2	H	F	Cl	I	Br	NO_2
k_2	$9·02 \times 10^{-5}$	$9·88 \times 10^{-3}$	$1·66 \times 10^{-2}$	$1·15 \times 10^{-1}$	$1·65 \times 10^{-1}$	$1·68 \times 10^{-1}$	$4·6 \times 10^{3}$
$\log_{10} B$	10·7	11·7	11·9	11·4	11·0	11·0	—
E (± 0·15 kcal.)	25·0	20·1	20·1	18·2	17·4	17·4	[13·0]

The plot of $\log_{10} k$ at 49·6° against Hammett's σ values (Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, Chapter VIII) gives a line of slope ~3·3, indicating that this is a reaction which is considerably less susceptible to the influence of *p*-substituents than is the reaction between *o*-bromonitrobenzene and piperidine.



○, *Present investigation* ; +, *Bunnett* et al. (loc. cit.). *Plot of Hammett's σ against* $\log_{10}k_{49·6}$.

This is probably connected with the much greater nucleophilic power of OEt^- than of piperidine, and explains the greater effect of a *p*-amino-group in the latter case.

The figure further revealed that when the determined rate constant is used for 1-fluoro-2 : 4-dinitrobenzene and *E* is assumed to be 13·0 (see above), the *p*-nitro-compound falls close to the line if the phenolic constant of 1·27 is assumed. This is confirmed by a similar plot of the relative rates given by Bunnett *et al.* (*Chem. Reviews*, 1951, **49**, 309) and the results of Berliner and Monack (*loc. cit.*). The *p*-amino-group falls well off the line, as expected, and it is probably fortuitous that the *p*-nitro-group falls near the line since both these groups so powerfully perturb the benzene ring as to make it surprising that they should conform to a close log plot as they do in so many side-chain reactions.

EXPERIMENTAL

Materials.—All compounds used in rate measurements were crystallised to constant m. p. from the appropriate solvent.

4-*Amino*-1-*fluoro*-2-*nitrobenzene*. *p*-Fluoronitrobenzene obtained by nitration of fluorobenzene was reduced with iron dust and dilute hydrochloric acid. The resulting *p*-fluoraniline was nitrated (Holleman and Beekman, *Rec. Trav. chim.*, 1904, **23**, 237); the product had m. p. 98°.

Fluoronitrobenzene. Fluorobenzene was nitrated by Swarts's method (*Rec. Trav. chim.*, 1914, **33**, 263) and fractionated, to give a product, b. p. 112°/22 mm., m. p. −5·3°.

1 : 4-*Difluoro*-2-*nitrobenzene*. By Schiemann's method (*Ber.*, 1929, **62**, 3040) *p*-fluoroaniline was converted into *p*-difluorobenzene, which was nitrated by Swarts's method (*Bull. Acad. Roy. Belg.*, 1913, 241). The product had b. p. 103°/25 mm., m. p. −12°.

4-*Chloro*-1-*fluoro*-2-*nitrobenzene*. Prepared from 4-amino-1-fluoro-2-nitrobenzene (Swarts, *Rec. Trav. chim.*, 1916, **35**, 131), this had m. p. 10°.

4-*Bromo*-1-*fluoro*-2-*nitrobenzene*. Prepared from 4-amino-1-fluoro-2-nitrobenzene (Hove, *Bull. Acad. Roy. Belg.*, 1927, **1**, 372), this had m. p. 19°.

1-*Fluoro*-4-*iodo*-2-*nitrofluorobenzene*. Prepared from 4-amino-1-fluoro-2-nitrobenzene (Hove, *ibid.*, p. 1), this had m. p. 35·5°.

1-*Fluoro*-2 : 4-*dinitrobenzene*. A commercial specimen, recrystallised from ether, had m. p. 26°.

Ethyl alcohol was dried and stored, as described previously (Bevan, *loc. cit.*).

Product Analyses.—Aliquots of reaction mixture which had been allowed to go to completion were concentrated and acidified with hydrochloric acid, and the crystals deposited were washed with a little water and dried, giving the corresponding 4-halogeno-2-nitrophenetoles. 4-Fluoro-, m. p. 33° (lit., 33·7°), 4-chloro-, m. p. 60° (lit., 61°), 4-bromo-, m. p. 57°, and 4-iodo-derivatives, m. p. 77° (lit., 80°), were identified. The reactions followed a second-order rate law and gave good constants over 5% to 95% reaction; therefore from the above figures the product was evidently the corresponding phenetole.

Kinetic Measurements.—In all cases, except that of 1-fluoro-2 : 4-dinitrobenzene, sodium ethoxide was ~0·033M and halide ~0·025M. In the exceptional case both concentrations were reduced by a factor of 10. For 4-amino-1-fluoro-2-nitrobenzene sealed tubes were used. Otherwise 50 ml. of a solution of the halide, to be 0·025M on dilution with 25 ml. of sodium ethoxide (~0·1M), were brought to the thermostat temperature in a stoppered flask. The sodium ethoxide, also at thermostat temperature, was added from a fast-delivery pipette stored at this temperature. The time of half addition was taken as the time of initial reaction. Aliquots were transferred, by means of a pipette stored at thermostat temperature, into excess of standard hydrochloric acid and back-titrated with standard carbon-dioxide-free alkali in nitrogen, with bromothymol-blue as indicator. Rate constants were calculated from the usual formula for a bimolecular reaction. The results of typical experiments are shown in Table 3. A correction was applied for solvent expansion. Rate constants could be duplicated within 1%.

TABLE 3. *Determination of rate constants k_2 (l. sec.$^{-1}$ mole^{-1}).*

Reaction of 4-*amino*-1-*fluoro*-2-*nitrobenzene with sodium ethoxide in absolute ethyl alcohol.*

Initially, [Halide] ~0·025M and [NaOEt] ~0·033M. Concns. are expressed in ml. of 0·00893N-NaOH per 4·90-ml. sample. Temp., 89·63°.

t (min.)	0	25	32	35	41	45	51	56	65	80	91	105	119
[NaOEt]......	16·67	14·25	13·65	13·41	13·01	12·91	12·55	12·31	11·84	11·18	10·71	10·38	9·90
[Halide]......	10·72	8·30	7·70	7·46	7·06	6·96	6·60	6·36	5·89	5·23	4·76	4·43	3·95
10^3k_2	—	6·15	6·34	6·41	6·40	6·06	6·08	6·03	6·10	6·13	6·26	6·01	6·18

Mean 6·18; duplicate 6·12; $k_2 = 6·15 \times 10^{-3}$; corr. for solvent expansion (20—90°), $k_2 = 6·69 \times 10^{-3}$.

Reaction of 1 : 4-*difluoro*-2-*nitrobenzene with sodium ethoxide in absolute ethyl alcohol.*

Initially, [Halide] ~0·025M and [NaOEt] ~0·033M. Concns. are expressed in ml. of 0·01048N-NaOH per 5·00-ml. sample. Temp., 60·98°.

t (min.)	0	3	5	7·4	10·3	13·28	16	18·87	23·95	27·89	32·8	38·5
[NaOEt]............	17·11	14·11	12·68	11·27	10·17	9·24	8·59	8·09	7·37	6·95	6·52	6·19
[Halide]............	12·57	9·57	8·06	6·73	5·63	4·70	4·05	3·55	2·83	2·41	1·98	1·65
10^2k_2	—	4·67	4·86	4·90	4·81	4·96	4·86	4·67	4·75	4·83	4·83	4·61

Mean 4·80; duplicate 4·79; $k_2 = 4·80 \times 10^{-2}$.

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