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

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Relative rates and Arrhenius parameters have been determined for the reactions with methoxide ion in " AnalaR " methanol of a series of mono- and di-nitrofluorobenzenes. The results permit a quantitative comparison of activation, in aromatic nucleophilic substitution, from the *meta*-position with that from other positions. The relative constancy of the non-exponential term of the Arrhenius equation over a very wide range of reaction rates is noted.

THE relative rates of electrophilic substitution at the three possible positions in mono-substituted benzenes have been extensively studied by Hughes, Ingold, and their collaborators (cf. Ferguson, *Chem. Reviews*, 1952, **50**, 47), but the corresponding nucleophilic substitution is by no means so extensively documented (cf. Bunnett and Zahler, *ibid.*, 1951, **49**, 273). Arrhenius parameters were therefore determined for an exchange reaction involving replacement of the fluorine atom of *o*-, *m*-, and *p*-fluoronitrobenzenes since data hitherto available do not permit quantitative comparison between activation, in such substitutions, from the *meta*-position with that from other positions.

The methoxide ion was chosen as the replacing entity since it is less likely than the ethoxide ion to cause steric complications and its reactions with halogenonitrobenzenes are less complex; the ethoxide ion can cause reduction of such compounds (Lobry de Bruyn, *Rec. Trav. chim.*, 1890, **9**, 197), whereas methoxide ion gives with *m*-fluoronitrobenzene a quantitative yield of *m*-nitroanisole (Holleman and Beekman, *ibid.*, 1904, **23**, 225).

It was also of interest to see whether *m*-fluoronitrobenzene gave a straightforward bimolecular reaction with methoxide ion since Kristjansen and Winkler (*Canad. J. Chem.*, 1951, **29**, 154) found the exchange reaction of sodium iodide with *m*-iodonitrobenzene in acetonitrile gave better first- than second-order rate constants.

Finally one of the basic assumptions on which theoretical calculations of such relative reactivities are based (cf. Dewar, *J.*, 1949, 463; Sixma, *Rec. Trav. chim.*, 1953, **72**, 4, 273) is that differences in reaction rates are due only to activation energy differences : this has not hitherto been tested for nucleophilic displacements at an aromatic carbon atom, in a series which includes unactivated and *meta*-activated cases. Thus Arrhenius parameters were also determined in the analogous reactions of 1-fluoro-2 : 4-dinitrobenzene, fluorobenzene, and 1-fluoro-3 : 5-dinitrobenzene.

Results.—Rate constants are assembled in Table 1. Comparative rate constants at 49·5° and Arrhenius parameters are shown in Table 2.

The results obtained in a typical run with *m*-fluoronitrobenzene are given in Table 3 and the influence of the initial concentration of reagents on k_2 in this run is shown in Table 4. The value of k_2 evidently depends in a simple manner on the concentration of the fluoride

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* Part I, *J.*, 1951, 2340.

and of the methoxide ion. The slight variation in rate constants is attributable to a salt effect.

The reaction of 1-fluoro-3 : 4-dinitrobenzene with methoxide ion in absolute methanol leads to the formation of 2 : 4-dimethoxynitrobenzene but an analysis of the four possible reactions involved has not yet been carried out.

By analogy with *m*-nitroanisole, the nitration of *m*-fluoronitrobenzene might have been expected to occur mainly in the 2-position (cf. Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 268). However the direction of substitution is controlled by the —*I* effect of fluorine as would be expected from the *ortho-para* ratio in the nitration of fluorobenzene (cf. Ingold, *op. cit.*, p. 261).

TABLE 1. k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *for 1-fluoronitrobenzenes with* OMe$^-$ *in* " *AnalaR* " *methanol.*

Substituent	Nil		2-nitro-			
Temp.	117·5°	149·1°	49·51°	38·98°	28·17°	17·90°
k_2	$6·20 \times 10^{-8}$	$2·07 \times 10^{-6}$	$1·60 \times 10^{-3}$	$5·66 \times 10^{-4}$	$1·78 \times 10^{-4}$	$5·62 \times 10^{-5}$

Substituent	3-nitro-				4-nitro-			
Temp.	97·87°	112·45°	119·92°	129·40°	49·54°	38·99°	28·52°	17·95°
k_2	$5·73 \times 10^{-5}$	$2·50 \times 10^{-4}$	$5·13 \times 10^{-4}$	$1·23 \times 10^{-3}$	$2·37 \times 10^{-3}$	$8·16 \times 10^{-4}$	$2·68 \times 10^{-4}$	$7·92 \times 10^{-5}$

Substituent	2 : 4-dinitro-		3 : 5-dinitro-			
Temp.	−21·3°	−1·5°	49·56°	39·15°	29·00°	17·97°
k_2	$2·57 \times 10^{-1}$	$1·55 \times 10^{0}$	$4·19 \times 10^{-3}$	$1·36 \times 10^{-3}$	$4·21 \times 10^{-4}$	$1·07 \times 10^{-4}$

TABLE 2. k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *at* 49·55° *and Arrhenius parameters* ($k_2 = Be^{-E/RT}$).

Substituent	Nil	3-nitro	2-nitro	4-nitro	3 : 5-dinitro	2 : 4-dinitro
k_2	$3·38 \times 10^{-12}$	$1·59 \times 10^{-7}$	$1·60 \times 10^{-3}$	$2·37 \times 10^{-3}$	$4·19 \times 10^{-3}$	$5·66 \times 10^{1}$
log *B*	13·0	12·8	10·7	11·0	12·3	10·1
E (kcal.)	36·4	28·9(±0·3)	19·9(±0·2)	20·1(±0·2)	21·7(±0·2)	12·3(±0·3)

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

Reaction of *m*-fluoronitrobenzene with sodium methoxide in absolute methanol. Initially, [Halide], ≈ 0·03M and [NaOMe] ≈ 0·04M. Concn. are expressed in ml. of 0·0260N-NaOEt per 9·80 ml. of sample. Temp., 112·45°.

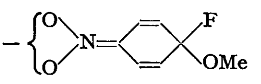
t (min.)		0	255	490	670	1395	1575	1942
NaOMe		13·32	12·07	11·17	10·58	8·72	8·37	7·77
Halide		11·36	10·11	9·21	8·62	6·76	6·41	5·81
10^4k_2		—	2·26	2·20	2·18	2·20	2·19	2·17
t (min.)	2118	2835	3095	3308	3570	4320	4615	∞
NaOMe	7·49	6·61	6·43	6·12	5·93	5·30	5·08	1·96
Halide	5·53	4·65	4·47	4·16	3·97	3·34	3·12	0·00
10^4k_2	2·19	2·18	2·12	2·20	2·17	2·25	2·28	—

Mean $k_2 = 2·20 \times 10^{-4}$; corrected value for solvent expansion (16—112°) $k_2 = 2·50 \times 10^{-4}$.

TABLE 4. *The effect of variation of concentration* (*mole l.*$^{-1}$) *of reagents on* k_2 (*Temp.*, 129·4°).

NaOMe	0·068	0·040	0·033	0·017	0·017
Fluoride	0·030	0·017	0·032	0·017	0·030
10^3k_2	1·12	1·24	1·22	1·33	1·32

Discussion.—The most striking point about the results shown in Table 2 is that the rate constants vary over a range of 10^{13} with a corresponding variation of activation energy between 12 and 36 kcal., while the non-exponential factor only varies by a factor of the order of 10^3. The figures justify the assumption that in the absence of steric effects substituent groups in aromatic substitution influence reaction rates at positions *ortho, meta,* and *para* to themselves mainly by their effect on activation energies. The non-exponential factors decrease in the same sequence as the activation energies but there does not appear to be a simple relationship between them. However, though interpretations of differences of this order on the basis of a few observations have limited significance, the non-exponential factor in the un- and two *meta*-activated cases (~12·5) is a couple of powers of ten greater than that of the *ortho*-, *para*-, and 2 : 4-di-substituted (~10·5). This may be attributable to a considerably greater contribution of quinonoid structures (*e.g.* as inset) in the transition states of the latter leading to more precise geometrical requirements with respect to entering and expelled groups than in the former, the transition states of which more closely resembling the aliphatic case, involve two less precisely defined partial bonds. Further, the charge on the transition state in the latter group is less dispersed than in the former compounds because of resonance involving structures such as that illustrated. The initial states of both are, to a first approximation, equally solvated and more so than the transition states where the charge on the methoxide ion is dispersed. Thus the exp ($\Delta S/\boldsymbol{R}$) term of the transition-state equation should be greater in the *meta*- and un-substituted compounds, leading to a higher probability factor, as is in fact observed (cf. Gripenberg, Hughes, and Ingold, *Nature*, 1948, **161**, 480).



A further point emerges when one considers the additive effects of substituents. Thus the introduction of a *m*-nitro-group into fluorobenzene reduces the activation energy for the replacement considered here by 7 kcal., and the introduction of a second *m*-nitro-group, to give 1-fluoro-3 : 5-dinitrobenzene, causes a further reduction by 7 kcal., while in all three reactions the non-exponential factor is sensibly constant. However this additivity does not obtain as between the independent facilitation by *o*- and *p*-nitro-groups (~16 kcal.) and that effected by both simultaneously in 1-fluoro-2 : 4-dinitrobenzene (~24 kcal.). This is a further example of an apparent limit to the capacity of the benzene ring for transmission of the electrical influences from powerfully perturbing groups to the seat of reaction (cf. Newton, Stubbs, and Hinshelwood, *J.*, 1953, 3384).

EXPERIMENTAL

Materials.—Fluorobenzene. A commercial specimen after fractionation had b. p. 85·0° (uncorr.).

1-*Fluoro*-3 : 4-*dinitrobenzene.* This was prepared in about 70% yield by nitration of 1-fluoro-3-nitrobenzene in nitric–sulphuric acid. After repeated recrystallisation from ethanol the product had m. p. 49·5°. Reaction with methoxide ion in absolute methanol (two equivalents of sodium methoxide were used in 12 hr. at 80·6°) gave a product, m. p. 74·5°; 3 : 4-dinitroanisole, prepared as described by Vermuelen (*Rec. Trav. chim.*, 1906, **25**, 30), had m. p. 74·1°. The identity is confirmed by the work of Suschitzky (*J.*, 1953, 3042).

1-*Fluoro*-3-*nitrobenzene and* -4-*nitrobenzene.* These were prepared by Schiemann's method (*Ber.*, 1929, **62**, 3041) from the corresponding nitroanilines. The former was fractionated and had b. p. 198·0° (uncorr.); the latter was recrystallised from absolute ethyl alcohol to constant m. p. 26·8°.

1-*Fluoro*-2-*nitrobenzene.* This was prepared from fluorobenzene by Swarts's method (*Rec. Trav. chim.*, 1913, **33**, 263) and fractionated at 22 mm.; it had m. p. −5·3°.

1-*Fluoro*-3 : 5-*dinitrobenzene.* 3 : 5-Dinitroaniline, made from 3 : 5-dinitrobenzoyl chloride by the method of Blanksma and Verberg (*ibid.*, 1934, **53**, 988), was converted by Schiemann's method (*loc. cit.*) into 1-fluoro-3 : 5-dinitrobenzene, which was recrystallised from light petroleum (b. p. 80—100°) to a constant m. p. of 43·6°.

1-*Fluoro*-2 : 4-*dinitrobenzene.* A commercial specimen was crystallised from ether to constant m. p. 26·0°.

Methanol. Magnesium (10 g.) and iodine (0·5 g.) were dissolved in "'AnalaR" methanol (2 l.) which was then refluxed for ½ hr. and distilled.

Kinetic Measurements.—Thermostat temperatures below 100° were steady to within ±0·02°, those above 100° to within ±0·05°. The reactions were carried out in well-stoppered flasks below 50°, and above this temperature in sealed tubes. In all solutions except those of fluorobenzene and 1-fluoro-2 : 4-dinitrobenzene, sodium methoxide was ~0·03M and the halide ~0·02M. With fluorobenzene both concentrations were raised by a factor of 5 and with the 1-fluoro-2 : 4-dinitro-compound both concentrations were 0·002M. The reactions were followed by the procedure used by Bevan (*J.*, 1953, 655) except in the case of fluorobenzene where the reaction was very slow and, since the possibility of side reactions cannot be excluded, the initial rate of production of fluoride ion was measured by Rowley and Churchill's method (*Ind. Eng. Chem. Anal.*, 1937, **9**, 551) and was assumed to be due to replacement by methoxide ion. Rate constants in this case decreased as reaction proceeded so that in order to get an estimate of the Arrhenius parameters, rate constants were used which had been calculated after the same percentage reaction at two temperatures.

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