CCXCIV.—*The Nature of the Alternating Effect in Carbon Chains. Part XXIX. Further Experiments bearing on the Problem of the Ortho-Para Ratio in Aromatic Substitution.*

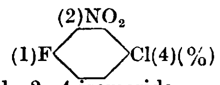
By Christopher Kelk Ingold and Charles Cyril Norrey Vass.

In a previous paper (this vol., p. 417) we developed the hypothesis that the principal polar orienting influence determining the ortho-para ratio in aromatic substitution arises from the external field of the substituent or substituents already present (direct effect, *D*), although steric inhibition and the occurrence of special mechanisms may modify the situation in certain cases (*Ann. Reports*, 1926, **23**, 140). The experimental test then applied consisted in a comparison of the orienting effects of fluorine and chlorine in *p*-fluorochlorobenzene and *o*-fluorochlorobenzene; for the (negative) direct effects due to fluorine and chlorine are expected to be large and in the order F$>$Cl. It followed that, whereas in the *p*-compound, in which the direct effect assists the other polar factors, the relative control of nitration by the two halogens should follow the order Cl$>$F (Found: Direction by Cl/Direction by F $= 72\%/28\%$), in the case of the *o*-compound, in which the direct effect acts in opposition to the other influences, the order might be reversed (Found: Direction by Cl/Direction by F $= 21\%/79\%$).

Since the difference between the direct effects of fluorine and bromine should be greater than that between fluorine and chlorine, our attention was attracted (*loc. cit.*, footnote) to some recent papers by Hove (*Bull. Acad. roy. Belg.*, 1926, **12**, 801, 823; *Bull. Soc. chim. Belg.*, 1927, 361) in which it is shown that *p*-fluorobromobenzene on nitration in a large excess of sulphuric acid or in fuming sulphuric acid gave (although not in good yield) a product containing more than 40% of the *o*-fluoronitro-isomeride. In spite of the unsatisfactory yields this proportion appears to be definitely too high to be adequately accounted for on the lines indicated in our previous paper; but, having regard to the conditions employed by Hove in his nitrations, the considerations advanced by Ingold and Ingold (preceding paper) relating to the influence of media on orienting effects appeared to offer a possible basis for the explanation of Hove's result. According to this view, the external fields of reagent and solvent molecules are assumed to effect some degree of polarisation of the directing atom, and, if the *o*-*p*-substitution of the halogenobenzenes be regarded as evidence of the affinity of the unshared halogen electrons for a positive charge (tautomeric effect, $+T$), there can be little doubt that it would be the positive ends of dipolar solvent molecules which would be oriented towards the halogen. It need not be supposed, even when concentrated sulphuric acid is in contact with a halogen compound, that the formation of a real salt takes place, for Baker has shown in an independent series of observations (this vol., p. 1586) that it is possible experimentally to draw a clear distinction between the electrostriction of acids by weak bases and actual salt-formation involving co-ordination of the proton; at the same time he has proved that the polarising effect of the condition which may be described as *incipient* salt-formation is very considerable. Furthermore, turning again to the tautomeric effect in the substitution of the halogenobenzenes and to the indications afforded by Ingold and Shaw's investigation of the relative velocity of these reactions (J., 1927, 2918), it is to be expected that the affinity of the unshared halogen electrons for a positive field will be in the order I>Br>Cl>F, and, *ceteris paribus*, that this order will therefore represent the effect of strong acids in polarising, and thus diminishing the *op*-orienting power of, halogen atoms. Finally, analogy with the nitration of acetanilide, in which the addition of sulphuric acid leads to the formation of appreciable quantities of the *m*-derivative, and also causes a marked rise in the ratio para/½ortho (Noelting and Collin, *Ber.*, 1884, **17**, 262; Holleman, Hartogs, and van der Linden, *Ber.*, 1911, **44**, 704), suggests that sulphuric acid produces particularly powerful medium-effects in substitutions oriented by substituent atoms containing unshared valency electrons.

Thus in Hove's experiments all the conditions calculated to produce an anomalous result are present, but it appeared impossible directly to test this view of the situation by further study of the nitration of *p*-fluorobromobenzene because Hove was unable to establish satisfactory conditions for this reaction in the absence of an excess of sulphuric acid. We have therefore sought for evidence of the medium-effect in the analogous case of *p*-fluorochlorobenzene and have studied the effect of varying quantities of sulphuric and fuming sulphuric acids on the proportions in which the isomerides are formed. In the nitration of this substance the effect of the medium would be expected to be smaller than in *p*-fluorobromobenzene; nevertheless, it should be in the same direction and the addition of excess of acid should increase the proportion of the *o*-fluoronitro-compound (Cl>F).

That this is indeed the case is evident from the following figures:

	Mols. H_2SO_4 per mol. HNO_3.					Mols. "free" SO_3 per mol. H_2SO_4.		
	0·00	0·67	0·86	3·00	6·00	0·33	0·64	1·87
	20·8	24·1	24·5	25·0	25·5	27·8	28·9	30·0
$\frac{1:2:4\text{-isomeride}}{1:3:4\text{-isomeride}} \times 100$	26·2	31·8	32·5	33·3	34·2	38·4	40·6	42·9

It will be seen that by the addition of sulphuric acid the proportion of 1 : 2 : 4-compound relatively to its isomeride has been increased by 31%, and that the addition of fuming sulphuric acid caused an increase of 64%. These results not only furnish a sufficient explanation of Hove's observations, but also suggest that in the nitration of the monohalogenobenzenes the addition of sulphuric acid should increase the ratio para/½ortho, and that this combined illustration of the operation of the direct effect and the polarising influence of solvent molecules should become increasingly marked with increasing atomic weight of the halogen. It is proposed to test these deductions.

EXPERIMENTAL.

p-*Fluorochlorobenzene and its Nitro-derivatives*.—*p*-Fluoroaniline (25 g.), prepared from *p*-fluoronitrobenzene (Ingold and Vass, *loc. cit.*), was diazotised at – 5° to 0° in solution in hydrochloric acid (175 c.c. of *d* 1·15; ice, 50 g.) with a concentrated solution of sodium nitrite. The solution was saturated with hydrogen chloride at 0°, treated with precipitated copper (20 g.) under reflux, and distilled in steam. The *p*-fluorochlorobenzene (yield, 66%), which was extracted with ether from the basified distillate and dried with phosphoric oxide, had b. p. 129—130° (compare Swarts, *Rec. trav. chim.*, 1915, **36**, 131).

2-Fluoro-5-chloronitrobenzene was prepared from *p*-fluoroaniline by nitration in sulphuric acid solution (Holleman, *Rec. trav. chim.*, 1905, **24**, 29) and subsequent replacement of the amino-group by chlorine (Swarts, *loc. cit.*). 5-Fluoro-2-chloronitrobenzene was prepared by an analogous series of reactions from *p*-fluoroacetanilide (Swarts, *loc. cit.*).

Nitration of p-*fluorochlorobenzene*. The nitration of this substance in nitric acid alone was studied by Swarts, whose quantitative results differ to some extent from those obtained by us. Swarts analysed his nitration product by two methods. First, ordinary thermal analysis indicated the presence of 27·75% of the *o*-fluoronitro-compound (Found by us, 20·8%); but a re-plot of Swarts's data connecting the f. p.'s of mixtures of the isomerides shows a marked deflexion in the neighbourhood of the composition of the nitration mixture. Since this deflexion depends only on one observation by Swarts, and since, furthermore, we have been quite unable to confirm it, it is probable that Swarts's figures require revision. Secondly, Swarts treated his nitration mixture with sodium methoxide under conditions in which, according to his observations, the *o*-fluoronitro-compound reacts completely and the *o*-chloronitro-compound is unaffected; the figure obtained by this method, namely, 27·78% of *o*-fluoronitro-compound, is in remarkably good agreement with the result of thermoanalysis. Our observations show, on the contrary, that neither under the conditions described by Swarts nor under any others that we have been able to discover is it possible to obtain a quantitative decomposition of one isomeride and a complete absence of any decomposition of the other; *e.g.*, under the conditions described by Swarts, 5-fluoro-2-chloronitrobenzene underwent hydrolysis to the extent of 11·6—12·3% (see Table IV). From these observations it appears that it is impossible to analyse the nitration product by this method, and that the agreement obtained by Swarts was fortuitous.

The conditions under which the various nitrations were carried out are recorded in Table I. In all experiments the temperature was − 15° to −10°. The isolation of the product was effected by the method previously described for *o*-fluorochlorobenzene (Ingold and Vass, *loc. cit.*). The synthesised isomerides were isolated and purified by a similar process. The freezing points recorded in Tables I, II, and III are uncorrected, but were determined under identical conditions with the same apparatus. In order to control possible changes of composition during isolation, the material, after the f.-p. determination, was redissolved in nitric acid and the isolation repeated, with the result that the f. p. remained unaltered to within 0·1°. Furthermore, as a check on the binary character of the nitration products, some of these were mixed with known proportions of the pure isomerides and the f. p.'s of the mixtures were compared with the f. p.–composition curve.

Table I.

Thermal Analysis of Nitration Products.

Expt.	Yield of nitration product (%).	Yield of 4-chloro-2-nitrophenol (%).	HNO_3 (mols. excess).	H_2SO_4 (mols.).	"Free" SO_3 (mols.).	F. p.	2-Fluoro-5-chloro-nitrobenzene (%).
1, 2	92	1·4	3·5	—	—	26·8°	20·7
3, 4	94	2·6	2·2	—	—	26·6	21·0
8	95	0·4	1·7	1·8	—	25·0	24·1
7	95	0·5	2·5	3·0	—	24·85	24·5
5	99	—	—	3·0	—	24·6	25·0
6	100	—	—	6·0	—	24·3	25·5
9	100	—	—	2·6	0·85	23·2	27·6
10	90 *	—	—	5·2	1·7	23·0	28·0
14	100	—	—	3·3	2·1	22·6	28·9
11, 12, 13	100	—	—	1·5	2·8	22·0	30·0

* Accidental mechanical loss.

Table II.

Freezing Points of Mixtures of 2-Fluoro-5-chloronitrobenzene (*p*) *and 5-Fluoro-2-chloronitrobenzene.*

p (%)	0·00	19·80	22·29	22·78	24·52	24·79	26·21
F. p.	35·90°	27·30°	26·00°	26·20°	24·70°	24·60°	24·20°
p (%)	27·16	28·53	29·26	32·53	33·65	35·77	37·94
F. p.	23·90°	22·50°	22·20°	20·80°	19·00°	19·00°	18·00°
p (%)	38·14	42·80	61·47	89·40	100·00		
F. p.	16·10°	13·20°	1·80°	3·00°	8·00°		

TABLE III,

Illustrating Binary Character of Nitration Mixtures.

a = composition from f.-p. curve. Percentage of 2-fluoro-5-chloronitrobenzene.
b = new compositions calc. from original f. p. and weights of isomerides added. Percentage of 2-fluoro-5-chloronitrobenzene.

Expt.	Original f. p.	*a*.	*b*.	New f. p. found.	New f. p. from curve.
2	26·8°	20·7	17·8	28·1°	28·2°
6	24·3	25·5	29·2	22·5	22·5
,,	,,	,,	36·3	18·3	18·6

TABLE IV.

Decomposition of the Fluorochloronitrobenzenes with Methyl-alcoholic Sodium Methoxide.

Isomeride or mixture.	Weight (g.).	Temp.	Conditions.	Total halide ions formed.*	Chloride ions formed.†
5-Fluoro-2-chloronitrobenzene	5·8662	25°	Swarts‡	12·13	Not determined
,, ,,	3·0196	,,	,,	11·57	
,, ,,	4·4123	,,	,,	12·30	
2-Fluoro-5-chloronitrobenzene	4·2242	,,	,,	100·3	0·0
Nitration product. Expt. 3	5·1744	,,	,,	33·16	Not determined
,, ,, Expt. 4	3·7192	,,	,,	36·11	
,, ,, Expt. 2	2·7317	,,	,,	35·8	
5-Fluoro-2-chloronitrobenzene	0·2655	100	Ingold‡ and Vass	Not determined	85·6
2-Fluoro-5-chloronitrobenzene	0·2011	,,			5·66
Nitration product. Expt. 2	0·2385	,,			70·5

* Measured by loss in alkalinity. † Directly estimated.
‡ *Loc. cit.*

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THE UNIVERSITY, LEEDS.

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