263. *The Influence of Nuclear Halogens on Aromatic Side-chain Reactivity.*

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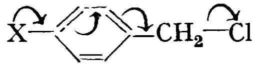
A study has recently been made (Baddeley and Bennett, this vol., p. 261) of the velocities of reaction of a series of substituted aryl β-chlorosulphides of the type $X\cdot C_6H_4\cdot S\cdot C_2H_4Cl$ with (*a*) water: $RCl + H_2O \longrightarrow R\cdot OH + HCl$, and (*b*) an iodide: $RCl + I' \longrightarrow RI + Cl'$. When the various nuclear substituents X are arranged in the order of their influence on the observed reactivities, they form two series in which there is for reaction (*a*) a continuous rise, and for reaction (*b*) a continuous fall of inductive effect of X, the reactions being, in fact, of types *A* and *B* respectively (Ingold and Rothstein, J., 1928, 1217). The order of the reactivities in reaction (*a*) is as follows: *p*-anisyl>*p*-tolyl>phenyl>*p*-halogenophenyl>*p*-nitrophenyl>dinitrophenyl, and that for reaction (*b*) is the exact opposite. The halogens as a group fall into their correct place in each series, and for reaction (*b*) the order of the halogens within the group is normal, but for reaction (*a*) it is completely inverted:

p-Substituent X	Me.	H.	I.	Br.	Cl.	NO_2.
Velocity of reaction (*a*)	1·83	—	*0·426*	*0·507*	*0·613*	0·045
Velocity of reaction (*b*)	0·077	0·091	0·116	0·150	0·197	0·298

An anomaly of this kind in the order of the halogens occurs in many other cases, and attention was first directed to it by Ingold (*Ann. Reports*, 1927, **24**, 156; see also Shoppee, J., 1930, 974; 1932, 696). A few of the data in some representative cases are given in the following table of relative reaction velocities:

	p-Substituent, X.						
Relative velocity of:	Me.	H.	I.	Br.	Cl.	F.	NO_2.
Hydrolysis of benzyl chlorides (Olivier)	164	15·5	*7·4*	*7·8*	*9·6*	—	1·15
Alcoholysis of benzhydryl chlorides (Norris)	413	1·0	—	*0·331*	*0·421*	—	*ca.* 0·0
Hydrolysis of benzyl bromides (Shoesmith and Slater)	—	0·67	—	*1·43*	*1·8*	*4·0*	0·29
Hydrolysis of benzoic esters (McCombie and Scarborough)	0·275	0·543	*2·58*	*2·34*	*2·08*	—	v. large

The direction in which these figures should vary as a consequence of the inductive effects (− *I*) of the halogens (which diminish in the order F>Cl>Br>I) is in each case clear from the data for other substituents. The observed order within the halogen group indicates that some other factor is here at work in opposition to these inductive effects. For the halogenobenzyl halides this is clearly the electromeric effect (+ *T*) usually written as in inset. In the hydrolysis of the benzoic esters, however, the effect in question does not assist but retards the reaction, which is in this instance favoured by large inductive effects. The additional effect here appears to resemble the electromeric effect (+ *T*) in sign, but to be a permanent polarisation rather than a potential or temporary electronic displacement which would await the demand of the reagent to become apparent.



The possibility that there is a permanent component of the electromeric effect, or a polarisation of some kind associated with it, was first considered by Ingold (Ingold and Ingold, J., 1926, 1312; *Ann. Reports*, 1926, **23**, 149). The presence of such an effect in permanent form was made clear by the results of measurements of dipole moments (Höjendahl, *Physikal. Z.*, 1929, **30**, 391; cf. Bennett, *Ann. Reports*, 1929, **26**, 132), and this line of evidence has since been developed very successfully by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 668). (The term " permanent *electromeric* effect " and the use of the curved arrow notation in this connexion are, strictly speaking, inappropriate, but they are adopted here in conformity with current usage, and because it appears that the true electromeric effect and the polarisation which is associated with it may be of common origin.)

The existence of such permanent polarisations is now generally admitted, but since it is doubtful whether the basis of comparison of aliphatic and aromatic dipole moments by reference to analogous phenyl and *tert.*-butyl derivatives is entirely justifiable, the relative magnitudes of the difference M(ar.) $- M$(al.) arrived at by this method for various substituents must be regarded as still uncertain.

When the data listed above are considered from this point of view, the order among the halogens requires the operation in all cases of an effect $(+T)$ which varies markedly in intensity in the order F>Cl>Br>I. The extreme case is that of *p*-fluorobenzyl bromide, which is not only hydrolysed faster than the corresponding chlorobenzyl bromide, but approximately twice as fast as the parent benzyl bromide itself.

The following figures for the relative strengths of substituted anilines lead to a similar conclusion :

Substituent	*p*-Me.	H.	*m*-Br.	*p*-Br.	*m*-Cl.	*p*-Cl.	*p*-NO_2.
$10^{11} \times K_b$	150	46	3·82	8·8	3·45	9·9	0·1

Here again the position of the halogens as a group is as expected. The fact that *m*-halogenated anilines are weaker than the *p*-isomerides (Flürscheim, J., 1910, **97**, 84) reveals an electromeric effect $(+T)$, but the relative strengths of the *p*-chloro- and *p*-bromo-amines show this effect to be greater for chlorine than for bromine.

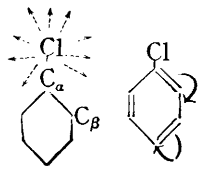
In the case of the substituted benzoic acids the general order of strengths is again normal :

p-Substituent	Me.	H.	Cl.	CN.	NO_2.
$10^5 \times K_a$	4·3	6	9	31	40

yet the recent measurements of Kuhn and Wassermann in aqueous methyl alcohol (*Helv. Chim. Acta*, 1928, **11**, 31) show that the *p*-halogenobenzoic acids vary but slightly in strength among themselves, the small variations being in the inverted order (values of $10^6 K_a$: *p*-I, 10; *p*-Br, 9·3; *p*-Cl, 10; *p*-F, 8·3). These figures also indicate an influence $+T$ increasing in magnitude from iodine to fluorine, and it may be pointed out that, when the large differences in the inductive effects of the halogens, revealed by the strengths of the halogenoacetic acids, are taken into consideration, a mere equality in the above figures would have sufficed to demonstrate the point.

The order hitherto accepted for the electromeric effects of the halogens is : I>Br>Cl>F. The evidence as to the velocity of substitution in halogenobenzenes and the comparative directive powers of the halogens is not, however, conclusive on this point. Variations in velocities of substitution and in the observed *o*/*p*-ratio may be regarded as determined entirely by the inductive effects. As regards the comparative directive powers the facts are also inconclusive, but in some cases they may be held to point to a higher directive power for fluorine than for chlorine.

It is therefore now proposed to accept the view that the electromeric effects of the halogens vary in intensity in the inverted order : F>Cl>Br>I, and since this order is inconceivable if the effect arises from an increase of covalency between the halogen atom and the nuclear carbon atom to which it is attached, as commonly supposed, a new view of its origin is required. (Such a covalency increase between halogen and carbon seems, moreover, to be at variance with the chemistry of the halogens, since it appears to imply the possibility of a double bond between carbon and chlorine or fluorine.)



The electromeric effects of halogens may be regarded as ethenoid or butadienoid polarisations in the nucleus promoted by the electron-repelling outer field of the halogen atom—of which independent evidence has been obtained in other ways. This field, acting outside the bond C_α—C_β, may give rise to a permanent polarisation and also it may initiate completed electromeric changes in the nucleus when these can lead to reaction. This suggestion has two advantages. It provides a simple explanation of the common origin of the electromeric effect and of the permanent polarisation associated with it; and it accounts for the inverted order of intensity of this effect among the halogens. For the order of the strengths of the outer fields of the halogens should be the same as the order of their inductive effects and the same must consequently be the order of intensity of the electromeric effects which these fields promote.