425. *The Polar Effects of the Halogens in Aromatic Combination.*

By G. Baddeley, G. M. Bennett, S. Glasstone, and Brynmor Jones.

In order to make clear the significance of the data recorded in the foregoing papers it is necessary to reconsider the question of the polar influences of the halogens in detail.

Inductive Effects.—The assumption has naturally been made, and is adopted here, that the halogens have inductive effects in aromatic compounds identical with those clearly indicated by the properties of aliphatic substances (strengths of the halogenoacetic acids : F>Cl>Br>I). It is instructive, however, to examine directly the evidence as to the inductive effects of the halogenophenyl groups. Since it is assumed that the inductive influence in a *p*-halogenophenyl compound may be modified by a permanent electromeric or " mesomeric " disturbance, it is clear that the data for *m*-substituted compounds will be the best indication of inductive strengths. Even in these substances some relayed modifying influence may be expected (compare, *e.g.*, Shoppee, J., 1932, 697), but it must be of a lower order of magnitude than that operating in the *p*-isomeride.

Data recorded by Kuhn and Wassermann (*Helv. Chim. Acta*, 1928, **11**, 31) for the strengths of the *m*-halogenobenzoic acids show little variation from one member to another of the halogen family, values of $-\log K_a$ being : *m*-F, 3·85; *m*-Cl, 3·81; *m*-Br, 3·86; *m*-I, 3·80.

The figures recorded in the preceding paper concerning the halogeno-anilines and -phenols indicate inductive effects for the halogenophenyl groups which are all of the same order but rise from fluorine to iodine and particularly between fluorine and chlorine :

	F.	Cl.	Br.	I.	
m-Halogenophenols, $10^{10} \times K_a$	1·51	4·90	4·37	3·89	in 30% ethyl alcohol
m-Halogenoanilines, $10^{12} \times K_b$	10·5	8·51	7·94	7·59	

A similar trend is apparent in the values of $K_a(\times 10^9)$ for the *m*-halogenophenylboric acids (Yabroff, Branch, and Bettmann, *J. Amer. Chem. Soc.*, 1934, **56**, 1850) : F, 1·10; Cl, 1·35; Br, 1·46; H, 0·197. The velocity coefficients of the two reactions studied for the *m*-halogenobenzyl chlorides (Bennett and Jones, this vol., p. 1815) also provide evidence on this point :

k for reaction	F.	Cl.	Br.	I.	H.
with iodide at 20°	1·84	2·17	2·47	2·34	1·32
with water at 70°	0·0159	0·0156	0·0132	0·0143	0·0671

The variations here are small, yet the drift for each reaction is in the sense of an inductive effect which increases in the order F<Cl<Br.

Again, the electromeric disturbances can at most have only a relayed secondary effect in the case of the *p*-halogenophenylethyl chlorides (Baddeley and Bennett, this vol., p. 1819), and here also the resultant observed velocities of reaction with iodide are approximately equal : F, 1·55; Cl, 1·65; Br, 1·63; I, 1·40; H, 0·735.

It is clear, then, from each of these sets of figures that the apparent inductive effects of the halogens attached to the phenyl group are almost equal. But this cannot be accepted as the whole truth, for the probability is admitted that some modification will have been introduced, even in the *m*-compounds, by the relayed influence of an electromeric or mesomeric disturbance. Moreover, there are numerous well-established facts which point to the familiar fall of inductive effects in the order F>Cl>Br>I in aromatic compounds. For instance, the velocities of reaction of the *p*-halogenophenyl β-chloroethyl sulphides with iodide (Baddeley and Bennett, J., 1933, 261) fell definitely in the order required by the usually accepted inductive effects (*p*-Cl, 0·197; *p*-Br, 0·150; *p*-I, 0·116), and the same is true of the mobilities in the tautomeric systems of the *p*-halogenated αγ-diphenylpropenes and the *m*- and *p*-halogenated αγ-diphenylmethyleneazomethines (Shoppee, J., 1930, 968; 1931, 1225; 1932, 696) :

$k_1 + k_2$ for		OMe.	I.	Br.	Cl.	NO_2.
diphenylpropenes	*p*-	0·058	0·39	0·64	1·02	—
diphenylmethylene-azomethines	*m*-	2·51	7·33	9·47	10·7	147
	p-	0·557	6·82	7·09	7·83	—

In these instances direct or relayed electromeric effects would not facilitate the reactions in question, and consequently do not operate. There are also several familiar features of nuclear substitution pointing in the same direction—such as the variation of the velocity of substitution of the halogenobenzenes, of the *o*/*p* ratio in these processes, and the percentages of *m*-derivative formed in nitrating the benzyl halides.

It may, therefore, be concluded that the halogens have inductive effects in aromatic compounds which vary in the same order as in aliphatic compounds, but that these are frequently modified by other factors so as to be either reduced to equality or inverted in order.

Mesomeric Effects.—When it was pointed out recently (J., 1933, 261, 1112) that a number of recorded data indicated a " permanent electromeric effect " of the halogens substituted in aromatic compounds diminishing in the order F> Cl> Br> I, the need for a new designation for this effect was emphasised, since the electromeric effect had originally been defined by English authors as arising only in reaction and therefore not permanent. The new term " mesomeric " was introduced at that time by Ingold (*ibid.*, p. 1120) and has been generally adopted. The nature of this effect is open to question and will be referred to later.

The magnitudes of the mesomeric effects of the halogens must diminish in the order F> Cl> Br> I. This supposition is necessary in the first place to account for the approximate equality in the *apparent* inductive effects of the halogens shown by the evidence reviewed above—it being taken into account that the true inductive effects fall from fluorine to iodine. It is still more necessary to explain the much larger variations among the data relating to similar properties among the *p*-halogenated substances. Thus the dissociation constants of the *p*-halogenated benzoic acids and phenylacetic acids have quite recently been cited in this sense by Dippy, Watson, and Williams (this vol., p. 346), together with the figures for the *p*-halogenated phenylboric acids (Yabroff, Branch, and Bettmann, *loc. cit.*). Our constants for the halogenated anilines and phenols show this point in a more striking fashion :

	F.	Cl.	Br.	I.	H.	
p-Halogenoanilines, $10^{12} \times K_b$	120	28·8	21·9	15·1	126	in 30% ethyl alcohol
p-Halogenophenols, $10^{10} \times K_a$	0·26	1·32	1·55	2·19	0·32	

In an earlier discussion of this problem, the fact that *p*-chloro- is a stronger base than *p*-bromo-aniline was explained by Robinson (J., 1933, 1116) as a consequence of the greater deformability of the bromine atom in face of the electromeric process originating from the nitrogen atom. Provided that the inductive effects of the substituents could be dismissed as a negligible factor, this suggestion appeared to provide a sufficient explanation of the small observed difference of strength for the chloro- and bromo-aniline and for the similar difference in the case of *p*-chloro- and *p*-bromo-phenols. The argument might be further extended to account for the similar small differences in strength of the *p*-halogeno-benzoic and -phenylboric acids. It is true that in these compounds there is no atom such as nitrogen capable of conjugation with the nucleus; but the negative ion of the halogeno-acids might nevertheless, from this point of view, gain stability, increasingly as the substituent varied from fluorine to iodine, by reason of the increasing accommodation allowed to a polarisation of the nucleus in the field of the negative pole.

The dissociation constants of the fluoro-anilines and -phenols show, however, that there is an important factor not to be explained away in this manner. Although the introduction of the fluorine atom into the *m*-position of aniline and of phenol reveals a large inductive effect of fluorine ($10^{11} . K_b$ for aniline,* 400; for *m*-fluoroaniline,* 25·7. $10^{10} . K_a$ for phenol,* 1·2; for *m*-fluorophenol,* 5·25), yet the *p*-fluoro-compounds are equal in strength to the parent substances (*p*-fluoroaniline,* 444; *p*-fluorophenol,* 1·12). It follows that the inductive effects of the halogens are by no means negligible in this connexion, and that a large mesomeric effect is revealed for fluorine much in excess of that for chlorine.

The comparative data for the velocities of hydrolysis of the halogenated benzyl chlorides also bear on this point : the figures for the *m*-substituted compounds show the presence of

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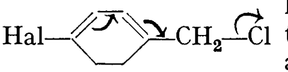
* In aqueous solution.

the retarding inductive effects, as described above; but, in addition, there is an influence which facilitates the reaction for the *p*-halogenated benzyl chlorides, relatively in all cases, and absolutely in comparison with the parent benzyl chloride itself in the case of the fluoro-compound :

Velocity coefficients, k_{70°, for hydrolysis of halogenobenzyl chlorides.

	F.	Cl.	Br.	I.	H.
m-	0·0159	0·0156	0·0132	0·0143	0·0671
p-	0·114	0·0394	0·0310	0·0296	

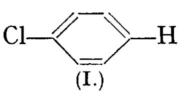
This influence falls in a pronounced manner from fluorine to iodine (*p*/*m* velocity ratios : F, 7·17; Cl, 2·53; Br, 2·35; I, 2·07).* The process of hydrolysis might, according to the commonly accepted view, be expected to be promoted by the influence of the nuclear halogen atom on the extended allyloid system (inset) (whether this involves the complete conjugation of the nuclear halogen atom with the nucleus by an increase of its covalency or not), and consequently these data point to a mesomeric or an electromeric effect, or both, for the halogens falling in magnitude from fluorine to iodine. This conclusion appears to be inevitable, and it may be noted that no special explanation seems to be available here, since there is no process which can be formulated as proceeding from the CH_2Cl group back across the nucleus towards the nuclear halogen atom. Moreover these conclusions, which have been derived from the data for the *p*-substituted amines, phenols, and benzyl chlorides, would still be valid if the figures for the *m*-isomerides had been taken at their face value as indicating a slight increase of inductive effect from fluorine towards iodine.



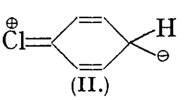
The order of the halogens with respect to the permanent electromeric (mesomeric) effect was stated by Baddeley and Bennett to be in diminishing intensity from fluorine to iodine (*loc. cit.*, p. 265), and the evidence now reviewed is supplementary to that originally collected in the earlier paper. The order I>Br>Cl>F for this effect is given by Ingold (*Chem. Rev.*, 1934, **15**, 244), presumably because he regards this as more probable. Yabroff, Branch, and Bettmann (*loc. cit.*), on the other hand, have since independently arrived at the opposite (correct) order as previously put forward from this laboratory.

The order of the mesomeric effect in the halogen family may thus be taken as established. The effect is clearly of the nature of a static polarisation, for its permanence has repeatedly been stressed. The mesomeric effect is, moreover, detected when the dipole moments of aromatic substances are analysed (Sutton, *Proc. Roy. Soc.*, 1931, **133**, *A*, 668; Bennett and Glasstone, *ibid.*, 1934, **145**, *A*, 71), but it should be noted that such evidence gives no indication as to which atoms are concerned in the polarisation in question.

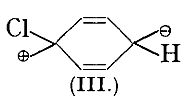
If this polarisation be regarded as involving an actual increase of covalency in the bond between halogen and nuclear carbon atoms (as has been held by various chemists), its diminution from fluorine to iodine is difficult to explain, the opposite tendency being the natural expectation. On the other hand, if it has its origin in the controlling field of the halogen atom (as suggested by Baddeley and Bennett), the observed order is exactly that which would be expected. This view has recently been supported by Watson and others (*loc. cit.*).



(I.)



(II.)



(III.)

The mesomeric effect is regarded by Ingold and by Branch (*locc. cit.*) as due to a resonance between two forms such as (I) and (II). According to current views, all such polarisations of the aromatic nucleus are to be regarded as due to resonance (compare Sidgwick, *Ann. Reports*, 1934, **31**, 40). The question, in this instance, as to whether the second of the

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* It may be pointed out that, although caution may be necessary in making close comparisons of the velocities of reaction of different molecules with a given reagent (compare Conant and others, *J. Amer. Chem. Soc.*, 1925, **47**, 480; Lapworth, J., 1931, 1964), yet the similarity of substances such as *p*-fluoro- and *p*-chloro-benzyl chlorides in physical properties and molecular weight may give significance to even a small difference in their reactivities, and it will be evident that a comparison of the *p*/*m* velocity ratios for the fluoro- and chloro-benzyl chlorides is not open to criticism from this point of view.

resonance forms involves an actual increase of covalency between halogen and nuclear carbon is a minor one—a resonance between two forms in the sense of a nuclear butadienoid polarisation (the second form being III) is equally possible and would be consistent with the suggestion we have made. A decision between these two possibilities may be left to the calculations of wave-mechanics if and when these can be made with certainty, but meanwhile it may be pointed out that the latter conception appears to have a reasonable chemical basis whereas the other meets with difficulties.

The Electromeric Effect.—The mesomeric effect was conceived as a permanent electromeric effect. From this point of view these effects are intimately related and have a common origin; it is therefore reasonable that the order of the electromeric effects for the halogens should be the same as for the mesomeric effect, *i.e.*, F>Cl>Br>I. Moreover, the relationship between the two effects implies that a mesomeric effect in a substance such as *p*-fluorobenzyl chloride must, if it facilitates a reaction the substance is undergoing, at once develop on demand in the reaction into a true electromeric effect. Consequently, the observation that *p*-fluorobenzyl chloride has the highest velocity of hydrolysis among halogenobenzyl chlorides (in spite of the retarded reaction observed for *m*-fluorobenzyl chloride) must be regarded as indicating that not only the mesomeric but also the electromeric effect is in fact at its highest for fluorine among the halogens.*

This point requires careful consideration, because it seems likely that any conflict of statement as to the order of the electromeric effects of the halogens may be essentially a question of the use of the terms involved. According to our view, any evidence which might be advanced to support the opposite order (falling from iodine to fluorine) for the electromeric effects may be explained as relating to the different factor of bond polarisability discussed below.

The Polarisability Factor.—There is also another influence of the halogens (in common with many other substituents, X) which must affect the orientation and other features of aromatic substitution reactions, *viz.*, the polarisability of the C–X bond. This polarisability affords an explanation of the *o*-*p*-directive power of groups such as CH_3, CH_2Cl, $CH_2{\cdot}CN$, etc., and might in itself suffice to account for the *o*-*p*-directive power of the halogens. It has been customary to ascribe the *o*-*p*-directive power of the methyl group in toluene to its electron-repelling inductive effect, but this view cannot account for the similar orientation caused by such a substituent as the $CH_2{\cdot}CN$ group, which must have an electron-attracting inductive effect.

In the halogen family, the familiar variation of the velocity of substitution in halogenobenzenes may be contributed to by the variation we must expect in the polarisability of the carbon–halogen bond (the assumption of a covalency increase being unnecessary). From the point of view of aromatic substitution it may well be that this factor is *permissive*, whereas the mesomeric (and electromeric) effect is *forcibly directive* in action. The combined operation of these two factors—the mesomeric effect and the polarisability factor—will suffice to account for the substitution of *o*-chlorofluorobenzene predominantly *para* to the fluorine atom whereas the *o*-bromoiodobenzene is substituted to the greater extent *para* to iodine (Ingold and Vass, J., 1928, 417; Holleman, *Rec. trav. chim.*, 1915, **34**, 228).

In brief, therefore, we take the view that the known facts can be accounted for consistently and satisfactorily by the following factors: (1) the mesomeric polarisation varying for the halogens in the order F>Cl>Br>I, (2)the electromeric effect (if any) in the same order, (3) the inductive effect and field effects varying also in the order F>Cl>Br>I, and (4) a polarisability effect (presumably identical with Ingold's "inductomeric polarisability," *loc. cit.*, p. 263) which varies in the order: I>Br>Cl>F.

THE UNIVERSITY, SHEFFIELD.

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* The data admittedly do not give an independent proof that the electromeric effect varies in the order stated. The possibility remains that the electromeric effect is negligible in these cases. A true electromeric effect might be held to occur only in systems terminated by atoms such as O, N, or S.