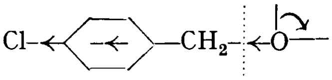
264. *The Relation of Electromeric Effects and Relative Polarisabilities of the Halogens.*

By Robert Robinson.

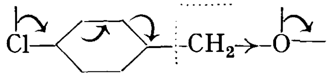
A paper by Baddeley and Bennett (this vol., p. 261) brings forward for discussion some matters of great general interest. Hitherto, the broad lines of the dual theory of inductive and electromeric effects have been found to be adequate without invoking special mechanisms, but now those authors, as the result of consideration of a reversal of anticipated orders of rates of reactions of certain halogen-substituted substances, have concluded that the electromeric effects of the halogens attached to the aromatic nucleus [or, in general, in heteroenoid systems $Hal(C{=}C)_n-$] are in the order $F>Cl>Br>I$, and, furthermore, that this electromeric effect arises from the repulsion of the electrons in the aromatic nucleus by the field of the outer electrons of the halogen atoms. First, then, we may discuss the evidence that the electromeric effects of the halogens (in such heteroenoid systems) in the series F, Cl, Br, I, diminish. It should be noted that Baddeley and Bennett do not put forward in support of their views a single example of a reaction in which the electromeric systems themselves take a direct part in the processes; that is, the unshared electrons produced in the electromeric displacements in these cases do not enter into new covalencies but exert their effects merely by initiating strains and a kind of relayed general electric effect.

A clear case of this kind was discussed in 1927 (Oxford and Robinson, J., 2240). It was found that the directive power of various benzyloxy-groups in benzyl and substituted benzyl ethers of guaiacol were the following (MeO, 100): $Ph{\cdot}CH_2{\cdot}O$, 113; *m*- also *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O$, 67; *m*-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}O$, 69; *p*-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}O$, 82; *m*-$MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}O$, 92. The explanations put forward depended on the recognition of inductive effects of Cl, NO_2, and even MeO operative in the same sense from the *m*-position to the reactive side chain, and in the case of the *p*-chlorobenzyloxy-group a partly compensating electromeric effect.

Inhibiting inductive effect: reaction-initiating displacement.



Accelerating electromeric effect: operative as inductive effect.



Baddeley and Bennett do not refer to this memoir, but their argument is on quite similar lines. They note that the effects of the different halogens in substances of the type *p*-$Hal{\cdot}C_6H_4{\cdot}$(side chain) on the reactivity of the side-chain centre are such as to place them in the polar series from Me to NO_2 in the inverted order of their generally assumed inductive effects; *i.e.*, Me . . . F, Cl, Br, I . . . NO_2 instead of Me . . . I, Br, Cl, F . . . NO_2. This was true for side-chain reactions facilitated either by accession of electrons to (anionoid) or by recession of electrons from (kationoid) the side chain. (Naturally the sequence is reversed in the latter case.)

We must be very grateful to Baddeley and Bennett for marshalling the available data in this admirable way, and one is not inclined to insist on the unsound features of the method of comparison of effects by means of reaction velocities; the general trend of the argument seems clear enough, and the deductions can be accepted up to a point.

This limit is reached by noting that it is only the permanent, static electromeric effect which is in question. No scope is given in any of these reactions for the full exercise of the electromeric potentialities of the halogen atoms.

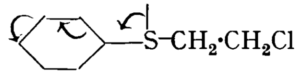
Now the order I>Br>Cl>F for the electromeric aptitude in heteroenoid systems has been derived from the results of experiments in which the electromeric systems themselves form the reactive centres, and this order may very well be the true one, even though the virtually static electromeric effect is F>Cl>Br>I.

The order I>Br>Cl>F is doubtless the order of the polarisability or deformability of the atoms, and thus an iodine atom should be able to accept both a greater negative charge *and* a greater positive charge than a fluorine atom.

It is unlikely that all the examples mentioned by Baddeley and Bennett will be found to conform to exactly the same type of explanation; questions of molecular association, including complex formation with the solvent, must undoubtedly affect the issue in many cases.

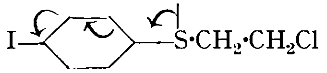
A whole group of the examples are easily brought into line without revolutionary conceptions by taking into consideration the greater polarisability of the heavier halogen atoms as compared with the lighter. The basic idea is that, where two electromeric processes are opposed and one of them is concerned with a heteroenoid system terminating in a halogen atom, then the resistance offered by the latter is not a question of the extent of its electromeric displacement under normal conditions, but will depend on the *deformability* of the halogen atom.

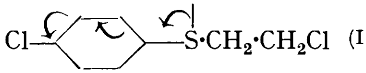
To take a specific example, Baddeley and Bennett have studied the hydrolysis of substances of the type $Ar{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$. It is clear that the essential thing here is the condition of the sulphur atom; if we give it a positive charge, as in the related sulphoxides and sulphones, we greatly diminish the speed of hydrolysis. Also, the effects of various substituents in the nucleus show that displacements of electrons towards the nucleus retard the reaction. But the chief effect of the nucleus on the sulphur atom is due to the activity of the conjugated heteroenoid system



and the greater the amplitude of this displacement the less readily will the substance be hydrolysed.

(I.)





(II.)

Comparing (I) and (II), it is suggested that even if the $\overset{|\curvearrowright}{\mathrm{I}}$——$C_6H_5$ effect is greater than $\overset{|\curvearrowright}{\mathrm{Cl}}$——$C_6H_5$ in those simple examples, yet, in such a heterogeneous arrangement, the greater plasticity of the iodine atom (as compared with Cl) must result in an apparent reversal of the order of the electromeric *or* of the inductive effects of these halogen atoms. This latter point is to be emphasised. Most of the difficulties raised by Baddeley and Bennett disappear if it is the *inductive* effect which is reversed in the aromatic types.

Obviously the explanation based on relative deformabilities fits the facts in all those cases in which the electromeric *or* the inductive effect is opposed to some other effect or process more directly concerned with the reaction. And this is true whether the reaction is promoted by electron accession to, or recession from, the side chain.

It must be remembered, too, that in all the cases discussed by Baddeley and Bennett, we are dealing with second-order effects, and that the halogens as a whole take their proper place in the polar series. If there remains a residuum of data which demands the order F>Cl>Br>I for the *static* part of the electromeric effect in some heteroenoid systems, it is nevertheless not at all clear that this would require as a corollary a new mechanism for such a process. We know too little about this matter to enable us to say what the extent of covalency changes should be from a purely theoretical standpoint.

In any case, it is surely desirable to gain information about the electromeric systems from a study of reactions in which they directly participate, rather than from a study of those in which they exert what is virtually a relayed general or inductive effect. In many of Baddeley and Bennett's cases we cannot be sure that it is the order of the electromeric effects of the halogens that is reversed; it may perhaps better be described as the total inductive effect of the whole system.

Secondly, the new mechanism proposed by Baddeley and Bennett for the electromeric effect in heteroenoid systems is unacceptable for a variety of reasons. It breaks the series $>$N–, $\overset{|}{\underset{|}{\mathrm{O}}}$, halogens. Why should the last term acquire a new specific mechanism which most certainly cannot apply to $>$N–Ar?

Again, the mechanism, if operative, should apply to other compounds, such as $PhCF_3$, which are, however, substituted in the *m*-position by kationoid reagents. This difficulty is not overcome by reference to the dipole, because this is not located or isolated between the carbon and fluorine atoms, but is a property of the molecule. Also there is a dipole in PhCl, the positive end of which should be even more effective in holding the electrons of the nucleus.

This new view of the genesis of the electromeric effect of the halogens affords no explanation of the stability of the aryl halides towards hydrolytic agents, and the usual theory would appear to have an advantage in this respect.

Again, if the activations of toluene and chlorobenzene are attributed to similar electrostatic repulsion from the methyl and the chlorine atom respectively, we would expect some *m*-substitution in chlorobenzene.

In passing, it should be noted that the cases of *o*- and *p*-chlorofluorobenzenes, cited by Baddeley and Bennett in support of their views, offer no difficulties along the usual lines. The *p*/*o* ratio for fluorobenzene is much higher than for chlorobenzene (nitration). Therefore, electromeric and inductive effects conspire to produce the observed result for the *p*-isomeride; *i.e.*, predominating substitution *o*- to chlorine. In the *o*-isomeride, the *p*/*o* ratio favours substitution *p*- to fluorine, and the discriminating influence of the general effect suffers partial cancellation as the result of the operation of factors first discussed by Allan, Oxford, Robinson, and Smith in the cases of the guaiacol ethers. This explanation is either identical with or analogous to that proposed by Ingold and Vass, and it is greatly to be preferred to the suggestion of Baddeley and Bennett. The phenomenon of contrast between relative directive powers of groups situated in *o*- and *p*-positions is not confined to halogen atoms. Allan, Oxford, Robinson, and Smith noted the same thing in less degree in the alkyloxy-series.

Are we then to apply Baddeley and Bennett's theory to oxygen as well as to the halogens, and if so, why do the four unshared electrons of oxygen initiate so much more powerful an electromeric effect than the six similar electrons of the halogens?

Finally, the two criticisms of the covalency-increase hypothesis by Baddeley and Bennett may be mentioned. The statement that there is no tendency for halogenobenzenes to pass into quinonoid derivatives is difficult to comprehend. What could the constitution of such derivatives be, and under what experimental conditions could they be recognised?

The remark that " it is not easy to understand how the deactivating inductive effect of a halogen atom can persist unchanged at the moment when the nature of the carbon–halogen bond is radically altered by the postulated change of covalency of the halogen," is the result of a failure to realise that the inductive effect is not supposed to modify sharing; it displaces electrons, but does not produce unshared electrons. In the case of chlorobenzene, the carbon atoms are under the influence of the strong positive field of the nucleus of the chlorine atom. The electromeric displacement has quite a different character, and involves variations in the sharing of quantised electrons; some become unshared. These unshared electrons are alone capable of forming new covalencies with atoms of reagents, and therefore their position orients a substitution process. But they may all the time be situated in a powerful deactivating positive field, and therefore the rate of reaction is greatly reduced. There is really no theoretical difficulty in the simultaneous operation of the inductive and the electromeric effect in such substances as chlorobenzene on the basis of the theory that the electromeric effect or process depends on an increase of covalency between halogen and nucleus.

Actually, the view of Baddeley and Bennett seems to be the more vulnerable on this ground, as it does postulate that a single atom exerts both an electrostatic attraction and at the same time an electrostatic repulsion on the electrons of the aromatic nucleus.

These criticisms and replies to criticism must not be concluded without an acknowledgment that the importance of the closely argued memoir of Baddeley and Bennett is not dependent on the validity of the views put forward; it contains many generalisations and comparisons which will be of the greatest value, whatever the verdict of future xperimenters may be on the mechanisms advanced to explain them.