# **72.** *The Influence of the Sulphur Atom on the Reactivity of Adjacent Atoms or Groups. Part VI. Aromatic Side-chain and Nuclear Reactivity.*

By George Baddeley and G. Macdonald Bennett.

In Part II (Bennett and Berry, J., 1927, 1676) the conclusion was reached that the reactions of an organic chloro-compound with an iodide (reaction I) and with water (reaction II) are of opposite polar types, being respectively accelerated and retarded by the introduction into the molecule of a nitro-group, and for each of these reactions deductions were made as to its mechanism. A contrast in variations of reactivity of this kind was first emphasised by Lapworth and Shoesmith (J., 1922, **121**, 1391), who explained it in terms of the alternating polarity rule.

Since the publication of our earlier paper the classification of side-chain reactions has been discussed thoroughly by Ingold and Patel (*J. Indian Chem. Soc.*, 1930, **7**, 95; *Ann. Reports*, 1927, **24**, 155) and by Williams (J., 1930, 35), whose two main groups of reactions are typified by the reactions we have studied.

The aim of the present investigation was in the first place to confirm the underlying principle for these two reactions with respect to the influence of a wide variety of substituent groups. At the same time it was anticipated that other indications of considerable significance might become evident, and this expectation has, in fact, been realised.

For a series of twelve aryl β-chloroethyl sulphides, in which the aryl group varies from mesityl and *p*-anisyl to dinitrophenyl, and for a few of the corresponding sulphoxides and sulphones the velocities of these two reactions in acetone have been determined at two temperatures; the results are in Table I.

The prepn. of the required substances has been described (this vol., p. 46).

The measurements of velocities of reaction I were carried out as described in Part II, and the coeffs. calculated by means of the formula for a bimolecular reaction there given. Control expts. showed that the values are independent of the mol. ratios of the reactants taken.

In the case of reaction II a preliminary survey showed that const. coeffs. could not be obtained with the formula for a unimolecular reaction unless the $H_2O$ present amounted to 50%, and the substance hydrolysed was in concn. not more than 0·01 mol. The values are not independent of the initial concn., but were all observed under comparable conditions. The method was as follows : 5 c.c. of a 0·01*M*-solution of the chloro-compound in acetone were placed in each of a series of tubes, 5 c.c. of $H_2O$ added, and the tubes sealed. The tubes were placed in the thermostat and shaken vigorously at first to complete the mixing. At intervals a tube was removed, cooled, opened, and the contents titrated with 0·01*N*-NaOH and phenol-red, the end-point being taken as that at which a red colour persisted for 30 sec.

The temp. of the thermostat was controlled to 0·05° and observed with a standardised thermometer.

An added volumetric refinement was achieved by the use of a simple device for filling the pipette. The latter was clamped vertically, and connected through a three-way tap on the one side to a tube to which suction could be applied (through a drying-tube), and on the other to a rubber bulb compressed by a screw clamp. The use and advantages of this in ease of working are obvious, and it gave a considerably increased accuracy.

*Reaction I for mesityl* β-*chloroethyl sulphide in acetone at* 55·1°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $t_2 - t_1$, hr. ...... | — | 0 | 2 | 10 | 19 | 22·5 | 26 | 30 |
| *A*, c.c. 0·003*M*-$KIO_3$ ......... | 31·70 ($A_0$) | 29·40 ($A_1$) | 28·55 | 25·60 | 22·70 | 21·35 | 20·40 | 19·30 |
| *k* .................. | — | — | 0·0774 | 0·0748 | 0·0745 | 0·0782 | 0·0775 | 0·0777 |

Mean 0·0766

*Reaction II for* 2 : 4-*dichlorophenyl* β-*chloroethyl sulphide at* 55·0°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *t*, min. ............... | 0 | 78 | 149 | 234 | 284 | 298 | 360 | 382 |
| *x*, c.c. ............... | 0·20 | 0·65 | 1·00 | 1·40 | 1·60 | 1·65 | 1·85 | 1·87 |
| *a* — *x*, c.c. ......... | 3·25 | 2·80 | 2·45 | 2·05 | 1·85 | 1·80 | 1·60 | 1·58 |
| *k* ..................... | — | 0·115 | 0·114 | 0·118 | 0·119 | 0·119 | 0·118 | 0·113 |

$a_\infty = 3·45$ Mean 0·116

TABLE I.

*Velocity Coefficients,* k, *for Reactions I and II and Activation Energies,* E, *of Substances of the Types* Ar·S·$CH_2$·$CH_2$Cl, Ar·SO·$C_2H_4$Cl, *and* Ar·$SO_2$·$C_2H_4$Cl.

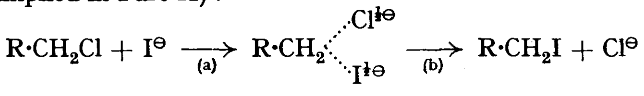
| | | Reaction I. | | | Reaction II. | | |
|---|---|---|---|---|---|---|---|
| | Ar. | $k_{55·0°}$. | $k_{75·0°}$. | *E*. | $k_{55·0°}$. | $k_{75·0°}$. | *E*. |
| | *s*-$C_6H_2Me_3$ ............... | 0·076 | 0·428 | 19·8 | 3·92 | (0·194 at 25°) | 19·6 |
| β-Chloro-sulphides. | *p*-$C_6H_4Me$ ................... | 0·077 | 0·454 | 20·3 | 1·83 | (0·102 at 25°) | 18·8 |
| | β-$C_{10}H_7$ ..................... | — | 0·663 | — | — | — | — |
| | *p*-$C_6H_4$·OMe .................. | — | 0·433 | — | 2·60 | — | — |
| | $C_6H_5$ ........................ | 0·091 | (see Part II) | | — | — | — |
| | *p*-$C_6H_4Cl$ .................. | 0·197 | 1·25 | 21·0 | 0·613 | 2·61 | 16·2 |
| | *p*-$C_6H_4Br$ .................. | 0·150 | 0·953 | 21·1 | 0·507 | 1·99 | 15·6 |
| | *p*-$C_6H_4I$ .................. | 0·116 | 0·787 | 21·9 | 0·426 | 2·14 | 18·4 |
| | 2 : 5-$C_6H_3Cl_2$ ........... | 0·187 | 1·11 | 20·3 | 0·063 | 0·277 | 16·9 |
| | 2 : 4-$C_6H_3Cl_2$ ........... | 0·207 | 1·20 | 20·0 | 0·116 | 0·493 | 16·5 |
| | *s*-$C_6H_2Cl_3$ ................. | 0·153 | 0·922 | 20·5 | 0·032 | 0·198 | 20·8 |
| | *p*-$C_6H_4$·$NO_2$ ................. | 0·298 | (redetermined) | — | 0·045 | 0·250 | 19·8 |
| | 2 : 4-$C_6H_3(NO_2)_2$ ......... | 0·600 | 4·15 | 21·5 | — | — | — |
| β-Chloro-sulph-oxides. | *s*-$C_6H_2Me_3$ ............... | 0·527 | 3·48 | 21·5 | Zero reactivity in hydrolysis | | |
| | 2 : 5-$C_6H_3Cl_2$ ........... | 0·562 | 3·18 | 19·8 | | | |
| | 2 : 4-$C_6H_3Cl_2$ ........... | 0·484 | 2·61 | 19·2 | | | |
| | *p*-$C_6H_4$·$NO_2$ ................. | 0·790 | — | — | | | |
| β-Chloro-sulphones. | $C_6H_5$ ........................ | — | 0·300 | — | Zero reactivity in hydrolysis | | |
| | *s*-$C_6H_2Me_3$ ............... | — | 0·370 | — | | | |
| | *a*-$C_{10}H_7$ ..................... | — | 0·294 | — | | | |
| | β-$C_{10}H_7$ ..................... | — | 0·354 | — | | | |
| | *p*-$C_6H_4Cl$ .................. | 0·0714 | 0·518 | 22·7 | | | |
| | *p*-$C_6H_4Br$ .................. | — | 0·462 | — | | | |
| | *p*-$C_6H_4$·$NO_2$ ................. | — | 0·960 | — | | | |

$C_6H_5$·$SO_2$·$(CH_2)_3$·Cl ......... $k_{55°} = 0·490$

## DISCUSSION.

*Mechanism of the Reactions.*—In interpreting the data given in Table I it will be well to state for each of the reactions studied the mechanism which we attribute to it, and which the new experiments tend to confirm.

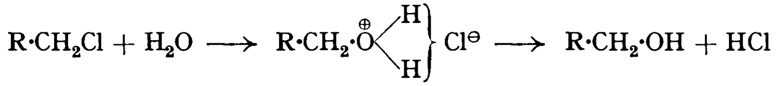
Reaction I between organic chloro-compounds and an iodide appears to involve the following steps (implied in Part II):



$$R{\cdot}CH_2Cl + I^{\ominus} \xrightarrow[(a)]{} R{\cdot}CH_2\overset{\cdot\cdot Cl^{\frac{1}{2}\ominus}}{\underset{\cdot\cdot I^{\frac{1}{2}\ominus}}{}} \xrightarrow[(b)]{} R{\cdot}CH_2I + Cl^{\ominus}$$

of which process (a) is the rate-determining stage, the essential capture of an iodine ion by the reacting carbon atom being facilitated by electron-recession from the $CH_2Cl$ group (the presence of electron-attracting substituents in R).

The hydrolysis of chlorides by water, reaction II, may on the other hand be formulated thus:



$$R{\cdot}CH_2Cl + H_2O \longrightarrow R{\cdot}CH_2{\cdot}\overset{\oplus}{O}\left<\begin{matrix}H\\H\end{matrix}\right\}Cl^{\ominus} \longrightarrow R{\cdot}CH_2{\cdot}OH + HCl$$

The critical factor here is the separation of $Cl^{\ominus}$ from the carbon atom, and its first stage, an incipient ionisation of chlorine, must be assisted by electron-accession to the $CH_2Cl$ group (the presence of electron-repelling groups in R). This course reversed must be ascribed to the reaction III (Br in place of Cl) used for the study of reactivities of hydroxy-compounds in Part V (J., 1931, 296), the formation of the intermediate complex being again facilitated by electron-accession.

The variations observed in Parts II—V in the behaviour of hydroxy- and chloro-compounds with respect to these opposed reactions are adequately explained as the result of two influences: an electron-attracting inductive effect of the sulphur atom transmitted along the chain and clearly apparent in the depressed reactivities for reactions II and III of the γ-substituted sulphides; and a special activating mechanism due to the intermittent close approach or contact of the sulphur atom with the $CH_2{\cdot}OH$ group, which causes a high reactivity to appear in those cases where this approach is sterically easy—in particular in the β-, δ-, and ε-substituted sulphides (cf. *Chem. and Ind.*, 1932, **51**, 776). In the δ- and ε-chloro-compounds ring-closure takes precedence of the hydrolytic reaction, but the essential mechanism may be regarded as identical.

*General Order of the Reactivity Values.*—The variation of the velocities in reaction I for the series of substituted chloro-sulphides is in the order: *p*-anisyl<*p*-tolyl<phenyl<*p*-halogenophenyl<*p*-nitrophenyl<dinitrophenyl. The order for reaction II for this series is exactly the reverse. This confirms the generalisation of our original suggestion.

At the same time, when some of the individual values are considered in detail, one or two slight deviations are noticed from the exact inversion of order which might at first sight have been expected. Thus, when due allowance has been made for the inductive effects, the substitution of chlorine, methyl or nitro-groups in the ortho-position affects reaction I in the opposite sense from their effect when in the para-position; the reactivities of sulphones, when compared with those of the sulphides and sulphoxides in reaction I, appear anomalous; and the effects on the reactivity for reaction II of the three halogens inserted in the *p*-position are in an order which is the opposite of that anticipated. These three points will now be discussed in turn.

*Effect of the External Field of Groups in the Ortho-position.*—It has been pointed out (Part IV; J., 1930, 2364) that a polar group possesses an electrical field outside it of opposite sign from that of its usual inductive effect exercised along the line of attachment to the rest of the molecule. In the data now under consideration for reaction I the influence of such fields of the methyl, chlorine and nitro-groups is clearly revealed, a simple explanation being thus provided for the first of the apparent anomalies referred to above. The velocity coefficient of phenyl β-chloroethyl sulphide (at 55°, 0·091) is reduced by inserting a *p*-methyl group in accordance with the general order of polar effects (0·077), yet the introduction of two additional methyl groups in the ortho-positions in the mesityl chloro-sulphide gives a figure no lower (0·076). The corresponding β-chloroethyl sulphones show the same point in a more striking manner, the mesityl sulphone having actually a higher reactivity (0·390 at 75°) than the phenyl sulphone (0·300).

A chlorine atom in the *p*-position more than doubles the speed of reaction of the parent sulphide (at 55°; 0·091, 0·197), yet the values for the di- and tri-chlorophenyl chloro-sulphides show that the *o*-chlorine atoms depress the reactivity (2 : 4-dichlorophenyl, 0·207; 2 : 5-dichlorophenyl, 0·187; *s*-trichlorophenyl, 0·153). According to our view, the inductive effects of the nuclear chlorine atoms in the trichlorophenyl sulphide must give the side-chain chlorine atom an extremely high reactivity with iodide ions, but the fields of the chlorine atoms in the ortho-positions hinder the approach of the negative ions, and so depress the observed speed of reaction. The corresponding effect does not appear, and was not to be expected, in the velocities of reaction II. The inductive effects of the substituents here alone operate, the ortho-groups having no marked influence on the speed of the reaction with water molecules, which, being uncharged, can approach unhindered by the outer field.

A similar trend is apparent to a minor degree in the results for the *o*- and *p*-nitrophenyl chloro-sulphides (Part II; phenyl 0·091, *p*-$NO_2$ 0·257, *o*-$NO_2$ 0·180). The *o*-nitro-group might have been expected to have a larger inductive influence than the *p*-.

It must be pointed out that a simple steric hindrance is out of the question in all these cases: the complete inhibition of esterification by Fischer's method observed with *o*-di-substituted benzoic acids is absent in the *o*-disubstituted phenylacetic and phenylglyoxylic acids, in which there is one extra carbon atom between nucleus and reacting group (V. Meyer, *Ber.*, 1895, **28**, 1254), so that our reaction at the terminal group of a four-atom chain must be even more free from any such simple blocking effect. Moreover, the diminution of rates of *both* reactions I and II caused by a chlorine atom introduced into the ortho-position might have seemed evidence of simple steric hindrance, were it not for the fact that methyl groups inserted in the ortho-position *increase* the velocity of both reactions.

*Comparative Influences of Sulphide, Sulphoxide, and Sulphone Groups.*—With respect to reaction II the sulphoxides and sulphones have no measurable reactivity. This was to be expected, for the positive charges on the sulphur atoms must cause a high inductive depression of the hydrolysis, and at the same time activation by the mechanism described above for sulphides (p. 263) cannot occur with a positively charged sulphur atom.

It had seemed possible that this activating process might nevertheless have operated between the oxygen atoms of the sulphone group and the $CH_2Cl$ group of the $\gamma$-chloro-propylsulphone. This was not, in fact, detected, a result which might be taken as pointing to an actual electronic interaction between the activating atom and the reacting group rather than mere close spatial proximity as being necessary in such reactions.

The behaviour of these compounds in reaction I requires more detailed consideration. The inductive effects of sulphoxide and sulphone groups should increase in strength owing to the presence of one and two dipoles respectively. As far as the sulphoxides are concerned, the increase of reactivity thus deduced is found, the values being each about three times those of the parent sulphide. Yet the figures for the six $\beta$-chloroethyl sulphones examined are not higher, but actually lower (about half) than those of their parent sulphides. Compared with butyl chloride, moreover, phenyl $\beta$-chloroethyl sulphide itself has a low reactivity (0·56 : 1·0; Kirner and Richter, *J. Amer. Chem. Soc.*, 1929, **51**, 3409). The possibility that a sulphone is deactivated as a consequence of the extreme intensity of its inductive factor is excluded by the fact that the introduction of a nitro-group into the phenyl sulphone raises the reactivity considerably.

We attribute the low values for the phenyl $\beta$-chloro-sulphide and its sulphone to the influence of a field which, by repelling iodine ions, reduces the collision number and so masks what would otherwise be a high reactivity. This deactivating field is due to the groups $C_6H_5{\cdot}S{\cdot}$ and $C_6H_5{\cdot}SO_2{\cdot}$ in which the polarised and positively charged nuclei constitute the positive end in each case of an effective dipole, the negative end of which is directed towards the seat of reaction. Two other points support this: the variation of reactivity in sulphones with different substituents shows their modification of this nuclear polarisation; and the absence of the aromatic nucleus in methyl $\beta$-chloroethyl sulphide makes the screening field of its sulphur atom less intense, so that the reactivity is higher (Kirner and Richter, *loc. cit.*) notwithstanding the fact that the inductive effect must be lower. With the extra length of chain in the corresponding phenyl γ-chloropropyl compounds the seat of reaction is removed far enough from these groups to make the screening effect of minor importance, the γ-chloro-sulphide (Part II; and Kirner and Richter, *loc. cit.*) being consequently highly reactive and its sulphone still more so. The inductive effect, it may be remarked, has to pass across only two saturated carbon atoms to reach the reacting $CH_2Cl$ group in the γ-chloropropyl compounds and is still potent, whereas the deactivating field must surround that group to be effective.

A consideration of the steric arrangement of the sulphoxide and sulphone groups makes it clear that the negative field of the latter occupies more than half the adjacent space, whereas the single dipole of the former must have a more symmetrical field. This difference suffices to explain the comparative importance of the screening in the sulphoxides and the sulphones.

*The Influence of Halogens on Aromatic Reactivity.*—The influence of a single halogen atom substituted in the *p*-position of phenyl β-chloroethyl sulphide is in descending order Cl>Br>I for reaction I (*p*-Cl, 0·197; *p*-Br, 0·150; *p*-I, 0·116), which follows, as would be expected, the order of the strengths of the halogenoacetic acids (F>Cl>Br>I). Yet the rates of hydrolysis (reaction II) for these same substances follow the *same* and not the opposite order (*p*-Cl, 0·613; *p*-Br, 0·507; *p*-I, 0·426).

In seeking an explanation of this we have found much other evidence in the literature involving a similar anomaly, but hitherto unexplained. A reconsideration of these and other points has led us to a modification of the current view of the influence of halogens on aromatic reactivity which brings all these facts into a satisfactory scheme. It will appear, moreover, that the underlying explanation is an almost inevitable corollary of our view of the external reversed field of atoms.

The evidence bearing on this question concerns the influence of halogens (a) on side-chain reactions and (b) on nuclear substitution. We find that the former data all point unmistakably to an order of diminishing electromeric effect among the halogens of F>Cl>Br>I, while the facts under the latter heading also allow of an alternative explanation on similar lines, and in certain respects definitely require it. The order given above is admittedly the opposite of that hitherto accepted, and demands a new view of the origin of the electromeric effect in the halogenobenzenes, since it is inconsistent with the covalency change $\overset{\curvearrowright}{\mathrm{X}}{-}\mathrm{C}$. Iodine would be the most prone to such a change and in fluorine it should be almost or quite impossible.

(*A*) *Side-chain Reactions.*—The view is now widely held that nuclear electromeric effects involve, to a certain extent at least, redistributions of charge which persist whether a reaction is in progress or not (*e.g.*, Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; Shoppee, J., 1932, 696), and it appears inevitable that such disturbances should consequently be able to retard as well as to accelerate reactions. This view has already been adopted by Shoppee (*loc. cit.*, p. 698; but compare J., 1930, 969, 974), and there are many examples which point to its occurrence. Thus the insertion of the *p*-methoxy-group into phenyl β-chloroethyl sulphide results in a velocity for reaction I which is much less than that of the parent substance (Table I). This indicates an electromeric depression of the speed of the reaction large enough to outweigh the accelerating inductive effect of methoxyl. The same point is still more clearly apparent in the classical observations of Lapworth and Shoesmith (*loc. cit.* and J., 1926, 214) on the methoxybenzyl bromides. The order of speeds of hydrolysis, *p*-MeO>*o*-MeO>unsubstituted>*m*-MeO, illustrates activation by the electromeric effects of *o*- and *p*-methoxyl and deactivation by the inductive effect of *m*-methoxyl. In the velocities of reduction (comparable with our reaction I) the order found was *m*-MeO>*o*-MeO>*p*-MeO and unsubstituted, pointing to a definite electromeric retardation by *o*- and *p*-methoxyl.

In reactions of type A (Ingold and Patel, *loc. cit.*) the inductive effects of halogens must retard, and their electromeric effects should accelerate, the reaction for the *p*-isomeride. In the *m*-isomeride, on the other hand, the inductive effect is weaker and the electromeric almost or quite inoperative. Consequently the relative forces of the electromeric effects of the halogens are indicated by the variation of the ratio of velocities *p*/*m*, or by the order of velocities of the *p*-isomerides. In Table II we have summarised the evidence on this particular point. Our new figures for reaction II and four other sets of data for reactions of type A all show *p*-halogenated compounds with reactivities in the descending order Cl>Br>I. The inductive influences would produce the opposite order, so that this result must arise from an electromeric effect falling markedly in the order F>Cl>Br>I. The case of *p*-fluorobenzyl bromide is particularly striking (Shoesmith and Slater, J., 1926, 214), for it has a higher reactivity than benzyl bromide itself. In three instances the *p*/*m* ratios (column 4) are available and support the same conclusion.

TABLE II.

*The Influence of Halogens on Side-chain Reactions.*

| Reaction. Type A. | Authors. | Order of velocities of *p*-halogenated compounds. | *p*/*m* Velocity ratio. |
|---|---|---|---|
| Hydrolysis of $Ar{\cdot}S{\cdot}C_2H_4Cl$ .................. | Baddeley and Bennett | Cl>Br>I | |
| Hydrolysis of $Ar{\cdot}CH_2Cl$ ..................... | Olivier | Cl>Br>I | Cl>Br>I |
| Hydrolysis of $Ar_2CHCl$ ........................ | Norris | Cl>Br | |
| Hydrolysis of $Ar{\cdot}CH_2Br$ ..................... | Shoesmith and Slater | F>Cl>Br | |
| Action of $Ar{\cdot}NH_2$ on chloronitrobenzenes | Linke | Cl>Br>I | Cl>Br>I |
| Reduction of $Ar{\cdot}NH{\cdot}NH_2$ .................. | Franzen | Cl = Br | Cl>Br |
| Reaction. Type B. | | | *m*/*p* Velocity ratio. |
| Hydrolysis of $Ar{\cdot}CO_2R$ ........................ | Kellas | Cl<Br<I | Cl>Br |
| | McCombie and Scarborough | Cl<Br<I | Cl>Br>I |
| | Kindler | Cl<Br<I | Cl>Br |
| Hydrolysis of phthalides ..................... | Tasman | Cl<Br<I | |
| Action of $R{\cdot}CN$ with $H_2S$ ..................... | Kindler | Cl<I | |
| Benzoylation of $Ar{\cdot}OH$ ........................ | Bernoulli | Cl<Br | |
| Tautomerism of $Ar{\cdot}CH_2{\cdot}N{:}CH{\cdot}Ar'$ ......... | Shoppee | Cl>Br>I | Cl>Br>I |
| Hydrolysis of aryl succinimides ............ | Sanna | Cl<Br | Br>Cl (?) |
| Reduction of $Ar{\cdot}CH_2Br$ ..................... | Shoesmith and Slater | F<Cl | |

References for the above reactions will be found in the paper by Williams (*loc. cit.*), except that of Shoppee (J., 1931, 1225; 1932, 696). The latter's values for equilibrium composition in the three-carbon system (J., 1930, 974) provide a still further similar anomaly, which falls into line.

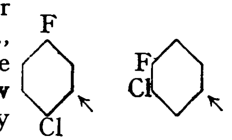
For reactions of type B a *p*-halogen atom must conversely cause acceleration by its inductive and retardation by its electromeric effect, and indications of the order of the latter are obtained from the *m*/*p* ratios and the velocities for *p*-isomerides. In Table II seven separate studies of such reactions are cited which give the order of falling velocity Cl<Br<I. As the inductive acceleration must be in the opposite sense, Cl>Br>I, these facts once again point to electromeric effects falling from chlorine to iodine and large enough to reverse the final order of velocities. The order in the single case of the methylene-azomethine tautomerism (Shoppee) differs in that it is not reversed, but the operation of the electromeric effect is nevertheless clear from column 4. The *m*/*p* ratio is in this, as in the other instances, in agreement with the general conclusion.

The relatively high values of reactivity for *m*-halogenated compounds in such reactions as the hydrolysis of esters (*m*>*p*) indicate a large depression by electromeric influence in the *p*-position, which may, perhaps, be due to a capacity for the carbonyl group to sustain this effect and so increase its weight.

A further relevant point is a comparison of the strengths of *p*-chloro- and *p*-bromo-anilines. The inductive effects (Cl>Br) should make the chloro-base the weaker. The electromeric disturbance should appear as a partial negative charge on the carbon atom carrying the amino-group, and should strengthen the base. If the electromeric effects are in the order Br>Cl, as usually assumed, this will further tend to make the chloro-base the weaker : but if the order of the latter effects is the reverse (Cl>Br), they must counteract and may outweigh the inductive effects. This is in fact the case : the chloro-base is the stronger of the two (*p*-chloroaniline, *k* $1{\cdot}49 \times 10^{-10}$; *p*-bromoaniline, $1{\cdot}04 \times 10^{-10}$ : Farmer and Warth, J., 1904, **85**, 1726).

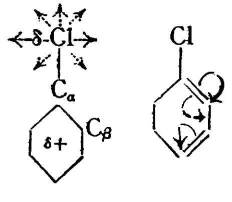
(*B*) *Nuclear Substitution.*—The interpretation of the results of nuclear substitution of halogenobenzenes involves a question as to which of two effects is principally responsible for each feature of the result. It has been stated, for instance, that the fall in the *p*/*o* ratio of products in nitrating the various halogenobenzenes in the series F, Cl, Br, I is due rather to the increasing electromeric effects of the halogens than to the known fall in their inductive effects (Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, 49). It does not appear clear to us why an electromeric effect should favour substitution in the *o*- rather than the *p*-position : moreover, the varying inductive effects are adequate to explain this series and we now adopt this view, as it can be reconciled with the variation of an electromeric effect in the order F>Cl>Br>I. The *p*/*o* ratios of products of nitrating benzyl fluoride (1·92; Ingold and Ingold, J., 1928, 2262) and benzyl chloride (1·34; Holleman, *Rec. trav. chim.*, 1914, **33**, 1) show a similar tendency, in a case where the intervening methylene group makes an electromeric directive effect from halogen to nucleus impossible.

The mode of substitution of *o*- and *p*-dihalogenobenzenes presents an anomaly which has already aroused special interest. When two different halogen atoms are in the *p*-position they direct substitution *o*- to themselves in the order Br>Cl and Cl>F, yet when they are situated *o*- to each other the precedence in directive power appears reversed so that Cl>Br and F>Cl. Ingold and Vass (J., 1928, 417, 2262), in discussing this, invoke in addition to the inductive and electromeric effects a direct effect, which is assumed to follow the inductive effect in sign and magnitude. On this basis they account for the above results, the electromeric effects of the halogens being relegated to a secondary place in the consideration of the case of the *o*-dihalogenobenzenes. Once again the difficulty vanishes if the electromeric effects are taken as varying in the order F>Cl>Br. In the *p*-dihalogeno-compounds the inductive effect of each halogen will tend to prevent substitution in the *o*-position to it, and the resulting substitution is greater near to chlorine than to fluorine; but with the *o*-dihalogenobenzenes the inductive effects will co-operate and the electromeric effects display their directive powers in the respective *p*-positions in the order F>Cl. This interpretation is simpler than that of Ingold and Vass, and is therefore to be preferred.



*Genesis of Electromeric Effect of Halogens.*—The current view of an increase of covalency between halogen and nuclear carbon as the origin of the electromeric effect, we reject as unsatisfactory for the reasons elaborated above. The circumstance that there is no apparent tendency for halogenobenzenes to pass into quinonoid derivatives under any conditions moreover makes this conception inherently less probable than the similar view of the activated forms of phenol and aniline. Nor is it 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. The alternative possibility, which we now advance, is that the electromeric effects of the halogens are ethenoid and butadienoid changes in the nucleus promoted by the electrical fields of the halogen atoms—opposite in sign but parallel in magnitude with their inductive effects, varying therefore in the order we have deduced, namely, F>Cl>Br>I.

It is out of the question to prove in detail that an activation of $C_\beta$ will be promoted by the outer field of a halogen atom attached to $C_\alpha$; but careful consideration of the origin of the inductive effect shows that the halogen atom must have an electron-repelling direct effect around it and that this operates in every direction in space. The net negative charge (δ-) which the halogen appropriates must have a positive equivalent, but this will be largely distributed throughout the nucleus (hence the deactivation) and the electron-repelling field may control at least the outer electrons of the bond $C_\alpha C_\beta$ to the point of initiating the electromeric change.



This view represents the directive effects of methyl and the halogens as both due to nuclear changes encouraged by the substituent, the former acting, however, by means of its inductive, the latter by means of a direct effect.

It may be pointed out that substituents such as the nitro- and carboxyl-groups, which, like halogen atoms, have electron-attracting inductive effects do not cause *op*-nuclear substitution because they differ from the halogens in that they contain complete and fractional dipoles respectively ($\overset{\oplus}{N}$—$\overset{\ominus}{O}$, $\overset{\delta+}{C}$—$\overset{\delta-}{O}$), the positive ends of which are directed towards the nucleus, whereas the halogen atom is more correctly regarded as a partial negative pole. The case of benzotrichloride may be explained in a similar manner.

*Activation Energies of the Reactions.*—A striking feature of our data, particularly for reaction I, is the uniformity of the activation energies of the various substances. This no doubt reflects the fact that whatever may be the variations in structure (and consequently in reaction velocity) the activation energy remains a constant property of the $CH_2$—Cl bond.

This constancy is remarkable, but not unique. The values of activation energy for a wide range of alkyl iodides in reaction with alkali phenoxide found by Segaller (J., 1914, **105**, 110) were, for example, practically constant.

The conclusion may be drawn that, if velocity of reaction be expressed by the formula $k = \alpha e^{-E/RT}$, the influence on these reactions of the various factors above discussed is represented in the value of the constant $\alpha$ rather than in the activation energy $E$.

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