XLVII.—*The Mechanism of Activation of Halogen Atoms by a Nitro-group Present in the Same Aromatic Nucleus.*

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As a result of some experiments on the relative reactivities of various halogenonitro-compounds (preceding paper), we have been led to consider afresh the general problem of reactivity among such compounds.

Different reagents give very different comparative reactivities for a series of halogenonitro-compounds. Some reagents appear to act only in so far as they are ionised. For instance, Lulofs (*Rec. trav. chim.*, 1901, **20**, 292) showed that the rate of interaction of 1-bromo-2 : 4-dinitrobenzene and sodium ethoxide in alcoholic solution was decreased either by increasing the concentration or by adding sodium bromide or sodium acetate (compare also Segaller, J., 1913, **103**, 1154; Shroder and Acree, J., 1914, **105**, 2582; Baudet, *Rec. trav. chim.*, 1924, **43**, 758). In other cases, it is not definitely ascertainable whether the reactions are ionic or not.

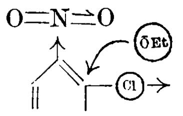
The nitro-group is the only group which in the absence of other groups is known to cause really pronounced activation of halogen atoms. It is, therefore, not only because the nitro-group is a meta-directing group that it exerts so powerful an activating influence. That is, it is not the dipolar structure of the nitro-group that produces the activation, since the sulphone, carboxyl, and sulphoxyl groups produce only feeble activating effects by themselves.

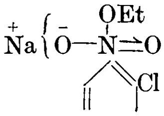
It seems probable, therefore, that the activating effect of the nitro-group depends on the presence of the nitroso-group, O:N, containing apolar oxygen. Moreover, it is known that the nitroso-group (although it is ortho-para directing) exerts a very powerful influence by itself on substituents in the para-position. For example, *p*-nitrosodimethylaniline reacts with alkali to give *p*-nitrosophenol under conditions which leave *p*-nitrodimethylaniline unchanged, and a second nitro-group is necessary before the dimethylamino-group is readily replaced by hydroxyl (2 : 4-dinitrodimethylaniline). Similarly, as Fischer and Hepp (*Ber.*, 1887, **20**, 2475; 1888, **21**, 684) have shown, *p*-nitrosophenol reacts even at 100° with ammonium acetate, ammonium carbonate, and ammonium chloride to give *p*-nitrosoaniline. *p*-Nitrophenol, on the other hand, is unaffected even by piperidine at the same temperature (Le Fèvre and Turner, J., 1927, 1113).

On first considering the matter it appeared to us that reactions involving alkali alkyloxides were of the direct interaction type, whereas those involving bases were indirect, additive compounds being formed intermediately. On the other hand, coloured additive compounds are certainly formed in both cases, and there seems no reason to assume that the additive compounds are unessential in one case and essential in the other. It is conceivable that the formation of additive compounds could actually hinder the main reaction (compare the Friedel–Crafts reaction, as studied by Olivier, *Rec. trav. chim.*, 1926, **45**, 817).

In the typical case of *o*-chloronitrobenzene, according to modern theories, the nitro-group seeks to acquire more than its due half-share in the pair of N–C_α co-valency electrons, and does so at the expense of C_β to which chlorine is attached. This carbon atom therefore tends to gain control over an electron and it can do this in one of three ways (see I): (1) by taking more than its due

(I.)





(II.)

half-share of the C_β–Cl pair, (2) by tentative borrowing from the $C_\beta C_\gamma$ electrons, or (3) by attaching an electron outside the molecule. Now chlorine cannot be regarded as willing to relinquish its share in an electron with which, as we know, it separates from C_β as a result of the completion of the process under discussion. Process (2) must occur to some extent, otherwise *p*-chloronitrobenzene would not be reactive, but (3) is also probable in many cases. For instance, when the reagent is sodium ethoxide, C_β endeavours to acquire an electron from the negative ethoxyl ion, and, at this moment, chlorine, which has a great tendency to become an ion, takes entire charge of the original C_β–Cl pair. As a result, the already adjacent ethoxyl group becomes attached to C_β.

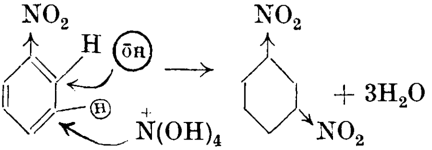
A similar process may be assumed to occur in reactions involving bases, the basic residue being substituted for the ethoxyl group. It is also clear that the above process of electron drift produces an alternating effect, so that *m*-chloronitrobenzene is not reactive.

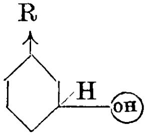
On the other hand, this theory, without modification, requires that other meta-directing groups should cause ortho-para activation, and that ortho-para-directing groups, at any rate in so far as they are definitely polar (*e.g.*, $\overset{-}{O}$ in phenoxides), should cause meta activation. Since these activations are only observed to a slight extent, we must adopt the view, originally due to Kenner and others, that the nitro-group is activating because it forms additive compounds. Now the additive compound with sodium ethoxide would probably be (II), in which the ethoxyl radical would be expected to undergo ortho-para wandering either of the inter- or of the intra-molecular type (compare Ingold, J., 1927, 1245). It will naturally be attracted to C_β for reasons already given. Elimination of chlorine as the ion is a necessary subsequent process for the attainment of electrical neutrality (separation of solid sodium chloride, frequently insoluble in the reaction mixture, etc.), and it should be noted that the additive compound is formed without destruction of the positive charge on the nitrogen atom, and with the actual attachment of a negative charge to the originally neutral oxygen atom.

In a similar way, a base NHR_2 would form the intermediate additive compound in which H replaces Na and NR_2 replaces OEt. Activation of substituents (*e.g.*, nitro-groups) other than halogen atoms can be discussed in the same manner.

On similar lines, the nitration of nitrobenzene (or other compound undergoing *m*-substitution) is capable of explanation. In the case of nitrobenzene, C_β can acquire control of one of the electrons of the negative hydroxyl ion present in the nitrating solution (see below). The simultaneous electron shift from the $C_\gamma C_\delta$ bond to C_γ causes attraction of the positive NO_2 ion, and there is formed the Obermiller type of additive compound (III), which then changes to *m*-dinitrobenzene owing to the driving force of water elimination.

(III.)





(IV.)

The preliminary addition of the elements of the reagent to the nitro-group is here unnecessary, and it is known that nitrobenzene nitrates less rapidly than benzoic acid, showing that the unique characteristics of the nitro-group as regards activating effects do not come into play in this case.

Although, as Wieland and Sakellarios (*Ber.*, 1920, **53**, 201) have shown, nitric acid combines with ethylene to give β-nitroethyl alcohol, that is, it reacts as if it had separated into OH^- and NO_2^+ ions, objection may be taken to the assumption usually made that aromatic nitration involves these ions. This difficulty can be surmounted if it be assumed that orthonitric acid is the actual nitrating agent, and that this compound is represented by $[\overset{+}{N}(OH)_4]\overset{-}{O}H$. This substance could supply hydroxyl ions, and instead of a nitro-group one must assume addition of $N(OH)_4$, which is equivalent in effect to that group.

If the above theory accounts for the *m*-nitration of nitrobenzene, etc., then with an ortho-para directing group it will be C_γ which will attract an OH^- ion, giving (IV). The $[\overset{+}{N}(OH)_4]$ ion can then add either to C_β or to C_δ, and the proportions of these will depend particularly on the bulk of R; for instance, one would expect *tert.*-butylbenzene to nitrate mainly in the para-position, as it does. Previous theories, not involving the prior attachment of hydroxyl in the meta-position, do not explain so simply why a bulky group has a low ortho-para directive ratio.

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