108. *The Cross-linking of Vinyl Polymers by Friedel–Crafts Catalysts. Part II.*

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The results of experiments on the Friedel–Crafts-catalysed cross-linking of various polymers, are discussed from the point of view of the electronic mechanisms of the reactions. The conclusions reached lend support to current theories of Friedel–Crafts reactions. It is shown that the cross-linking reaction probably involves unsaturated groupings in the polymer molecules, these groupings either being present normally in the polymer, or being introduced into it by the elimination of a simple molecule HX under the influence of the catalysts.

In a previous paper (Part I, *J.*, 1948, 771), a new method of cross-linking vinyl polymers was described. Polymers, such as polyvinyl chloride and polyvinyl acetate, dissolved in liquids of fairly high dielectric constant, for example nitrobenzene and tetrachloroethane, were treated with aluminium chloride or other Friedel–Crafts catalysts, and a coloured insoluble product was obtained.

Possible over-all equations were given without specifying the actual mechanism of the reactions involved. Further consideration of the problem has led to conclusions concerning the electronic mechanisms of the processes and it is the purpose of this communication to discuss them. The ideas developed give support to current theories concerning simple Friedel–Crafts reactions.

Experimental.

This paper is based on the observations recorded previously with the following additions :

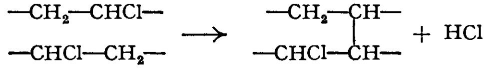
(i) poly*iso*butene dissolved in tetrachloroethane and treated with aluminium chloride is not cross-linked ; after chlorination, however, cross-linking can be introduced together with considerable darkening ;

(ii) the cross-linked products formed from polyvinyl chloride, polyvinyl acetate, and polymethyl methacrylate, by the action of Friedel–Crafts catalysts, are not made soluble by treatment with dilute acids or alkalis.

Discussion.

It was shown that besides introducing cross-linking into certain polymers, Friedel–Crafts catalysts can cause unsaturation to develop in these materials. The relevant equations written for polyvinyl chloride were :

(*a*)



$$\begin{array}{c}—CH_2—CHCl—\\ —CHCl—CH_2—\end{array} \longrightarrow \begin{array}{l}—CH_2—CH—\\ \qquad\quad |\\ —CHCl—CH—\end{array} + HCl$$

(*b*) $—CH_2—CHCl— \longrightarrow —CH{=}CH— + HCl$

It is generally accepted that when saturated hydrocarbons are involved in Friedel–Crafts reactions, unsaturation must be developed in them before reaction can occur (see, for example, Linstead, *Ann. Reports*, 1937, **34**, 251). It seems, therefore, that the two processes indicated above, are not completely separate and that the introduction of unsaturation may be an essential precursor to the formation of cross-linkages.

Fairbrother's work (*J.*, 1937, 503; *J.*, 1941, 293) showed that in a reaction involving an alkyl chloride, a hydrocarbon, and aluminium chloride, the primary step does not involve the hydrocarbon and can be represented as

$$R\cdot Cl + AlCl_3 \rightleftharpoons R^+ + [AlCl_4]^-$$

Taking polyvinyl chloride as the alkyl chloride, the equation $\cdot CH_2\cdot CHCl\cdot + AlCl_3 \rightleftharpoons \cdot CH_2\cdot \overset{+}{C}H\cdot + [AlCl_4]^-$ can be written. The loss of a proton from the carbonium ion thus:

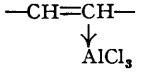
$$\cdot CH_2\cdot \overset{+}{C}H\cdot \longrightarrow \cdot CH{:}CH\cdot + H^+$$

would lead to unsaturation and to the possibility of colour (see, for example, Bowen, *Ann. Reports*, 1943, **40**, 12).

Further evidence for this mechanism is provided by kinetic studies of the formation of olefins by the action of alkalis on certain alkyl halides (Hughes, Ingold, Masterman, and McNulty, *J.*, 1940, 899). The ionisation $H\cdot CR_2\cdot CR_2\cdot X \longrightarrow H\cdot CR_2\cdot \overset{+}{C}R_2 + X^-$ is thought to be followed by the step $H\cdot CR_2\cdot \overset{+}{C}R_2 \longrightarrow CR_2{:}CR_2 + H^+$ similar to the second stage in the scheme proposed above.

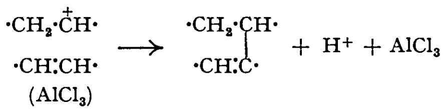
The bromination of alkyl bromides in the presence of ferric bromide leads to the substitution of a bromine atom on the carbon atom adjacent to the one already carrying a bromine atom (see Gilman, "Organic Chemistry", Wiley, New York, 2nd Edition, 1943, p. 180). This observation was explained by supposing that first the ferric bromide introduces unsaturation into the alkyl halide (as postulated above for polyvinyl chloride), $R\cdot CH_2\cdot CH_2Br \longrightarrow R\cdot CH{:}CH_2 + HBr$, and that bromine then adds across the double bond.

As mentioned already, when saturated hydrocarbons are involved in Friedel–Crafts reactions unsaturation must be developed in them before reaction can occur. It has been suggested that the double bond is involved in the formation of an unstable complex. In the case of polyvinyl chloride such unsaturation is developed and the mechanism proposed to explain its appearance is both simple and reasonable. The complex can be considered as resulting from the donation of electrons from a carbon atom to the electrophilic catalyst, thus



$$\begin{array}{c}-CH{=}CH-\\ \downarrow\\ AlCl_3\end{array}$$

There would be a marked tendency for such a complex to lose a proton in its reactions because electrons would be drawn away from a carbon–hydrogen bond, and it would effectively react as a negative grouping $\cdot CH{:}\overset{-}{C}$. If the complex interacts with the positive ion already described, cross-linking could occur by the reaction



$$\begin{array}{c}\cdot CH_2\cdot \overset{+}{C}H\cdot\\ \cdot CH{:}CH\cdot\\ (AlCl_3)\end{array} \longrightarrow \begin{array}{c}\cdot CH_2\cdot CH\cdot\\ |\\ \cdot CH{:}C\cdot\end{array} + H^+ + AlCl_3$$

The dependence of the speed of the whole reaction upon the dielectric constant of the solvent was described previously (Part I, *loc. cit.*). The effect is attributed in the main to the dependence of the primary formation of the positive ion on the dielectric constant; that process, involving the separation of oppositely charged entities, would be favoured in media of high dielectric constant where the electrostatic attraction between the charged bodies would be small. Subsequent steps in the sequence of reactions leading to cross-linking do not involve actual separation of charges, and are therefore likely not to be markedly affected by dielectric constant.

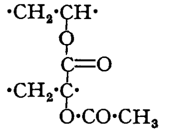
The equations developed to explain the cross-linking of polyvinyl chloride can equally well be applied to the other chlorine-containing polymers studied *viz.*, chlorinated polyvinyl chloride, halothene, chlorinated poly*iso*butene, and co-polymers containing vinyl chloride.

In the case of polyvinyl acetate, the preliminary ionisation is represented as:

$$\cdot CH_2\cdot CH(O\cdot CO\cdot CH_3)\cdot + AlCl_3 \rightleftharpoons \cdot CH_2\cdot \overset{+}{C}H\cdot + [CH_3\cdot CO_2\cdot AlCl_3]^-$$

being followed by the ejection of proton to give $\cdot CH{:}CH\cdot$. Subsequent reactions of the olefinic group and the positive ion can be formulated in the same manner as in the case of polymers containing chlorine. The cross-linkage is not of the type present in the product of the photochemical polymerisation of the vapour of vinyl acetate (Melville and Tuckett, *J.*, 1947, 1201);

that product is made soluble in water by treatment with potassium hydroxide and its structure is probably :



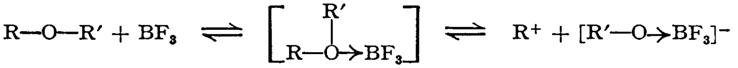
The resistance of the material formed by Friedel–Crafts catalysts to the action of acids and alkalis shows that it does not contain cross-linkages easily cleaved by hydrolysing agents, and that the separate polymer molecules are linked by carbon–carbon bonds.

The primary step in the cross-linking of polymers of *n*-butyl vinyl ether is written as

$$\cdot CH_2\cdot CH(O\cdot C_4H_9)\cdot + AlCl_3 \rightleftharpoons \cdot CH_2\cdot \overset{+}{C}H\cdot + [C_4H_9\cdot O\cdot AlCl_3]^-$$

followed by the formation of olefinic groupings, which would account for the darkening observed when polymerising the monomer with Friedel–Crafts catalysts (Chalmers, *Canadian J. Res.*, 1932, **7**, 472). Cross-linking is developed by the interaction of the carbonium ion and the olefinic grouping in the manner described already.

The equations given for the initial ionisation of polyvinyl acetate and polyvinyl ether are analogous with the general equation proposed by Price and Ciskowski (*J. Amer. Chem. Soc.*, 1938, **60**, 2499) to represent the primary step in Friedel–Crafts reactions involving alcohols, esters, and ethers, *viz.*,



$$R{-}O{-}R' + BF_3 \rightleftharpoons \left[\begin{array}{c} R' \\ | \\ R{-}O{\rightarrow}BF_3 \end{array}\right] \rightleftharpoons R^+ + [R'{-}O{\rightarrow}BF_3]^-$$

where R′ can be a hydrogen atom, an acyl group, or an alkyl group.

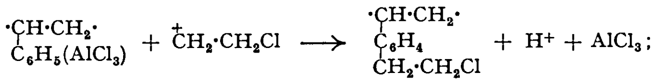
Polystyrene cannot be cross-linked in nitrobenzene solution because the polymer does not contain reactive groups, the removal of which would yield positive ions. The polymer can be cross-linked in solvents containing more than one chlorine atom per molecule, presumably by a composite reaction involving the solvent.

Taking ethylene dichloride as the solvent, it is visualised that cross-limking takes place by the following series of reactions :

(i) the formation of a positive ion from a molecule of solvent :

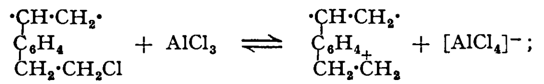
$$Cl\cdot CH_2\cdot CH_2\cdot Cl + AlCl_3 \rightleftharpoons Cl\cdot CH_2\cdot CH_2^+ + [AlCl_4]^- ;$$

(ii) the substitution of the chloroethyl group into the phenyl group of a polymer, by the interaction of the positive ions shown in (i) with the complex formed between the catalyst and the polymer :



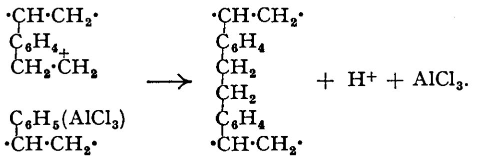
$$\begin{array}{l}\cdot CH\cdot CH_2\cdot \\ C_6H_5(AlCl_3)\end{array} + \overset{+}{C}H_2\cdot CH_2Cl \longrightarrow \begin{array}{l}\cdot CH\cdot CH_2\cdot \\ C_6H_4 \\ CH_2\cdot CH_2Cl\end{array} + H^+ + AlCl_3 ;$$

(iii) ionisation of the substituted polymer formed in (ii), under the influence of the catalyst :



$$\begin{array}{l}\cdot CH\cdot CH_2\cdot \\ C_6H_4 \\ CH_2\cdot CH_2Cl\end{array} + AlCl_3 \rightleftharpoons \begin{array}{l}\cdot CH\cdot CH_2\cdot \\ C_6H_4 \\ CH_2\cdot \overset{+}{C}H_2\end{array} + [AlCl_4]^- ;$$

(iv) this ionised polymer molecule reacts with a polymer–catalyst complex as shown in (ii) :



$$\begin{array}{l}\cdot CH\cdot CH_2\cdot \\ C_6H_4 \\ CH_2\cdot \overset{+}{C}H_2 \\ \\ C_6H_5(AlCl_3) \\ \cdot CH\cdot CH_2\cdot\end{array} \longrightarrow \begin{array}{l}\cdot CH\cdot CH_2\cdot \\ C_6H_4 \\ CH_2 \\ CH_2 \\ C_6H_4 \\ \cdot CH\cdot CH_2\cdot\end{array} + H^+ + AlCl_3.$$

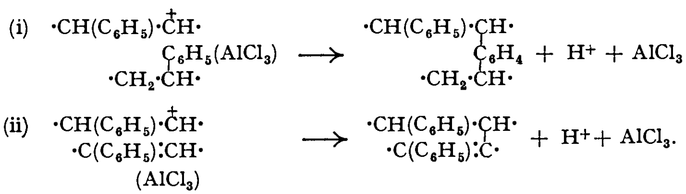
Fairbrother showed (*J.*, 1941, **293**) that the carbon–halogen bonds in halogenated benzenes show no tendency to undergo heteropolar fission according to the scheme :

$$C_6H_5\cdot X + AlCl_3 \rightleftharpoons C_6H_5^+ + [AlCl_3X]^- ;$$

consequently polystyrenes chlorinated in benzene rings would behave, from the point of view of Friedel–Crafts-catalysed cross-linking, just as unsubstituted polystyrene. Polymers of α- or β-chlorostyrene would be expected to undergo cross-linking in nitrobenzene, because the preliminary ionisation

$$\cdot CH(C_6H_5)\cdot CHCl\cdot + AlCl_3 \rightleftharpoons \cdot CH(C_6H_5)\cdot\overset{+}{C}H\cdot + [AlCl_4]^-$$

can occur. The phenomenon is actually observed. Cross-linking could take place according to two equations; in the first, the positive ion reacts with a complex of aluminium chloride and a phenyl group in the polymer. In the second equation cross-linking results from the interaction of the positive ion with a complex involving a double bond in the straight chain of the polymer, as in the case of polyvinyl chloride:

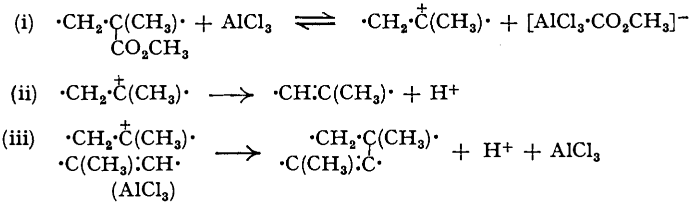


$$\text{(i)}\quad \begin{array}{l}\cdot CH(C_6H_5)\cdot\overset{+}{C}H\cdot \\ \qquad C_6H_5(AlCl_3) \\ \cdot CH_2\cdot CH\cdot\end{array} \longrightarrow \begin{array}{l}\cdot CH(C_6H_5)\cdot CH\cdot \\ \qquad C_6H_4 \\ \cdot CH_2\cdot CH\cdot\end{array} + H^+ + AlCl_3$$

$$\text{(ii)}\quad \begin{array}{l}\cdot CH(C_6H_5)\cdot\overset{+}{C}H\cdot \\ \cdot C(C_6H_5)\colon CH\cdot \\ \quad (AlCl_3)\end{array} \longrightarrow \begin{array}{l}\cdot CH(C_6H_5)\cdot CH\cdot \\ \cdot C(C_6H_5)\colon C\cdot\end{array} + H^+ + AlCl_3.$$

Even in suitable chlorinated solvents, cross-linking can occur only if (i) the polymer normally contains double bonds (as in polymers containing the benzene nucleus), or (ii) if unsaturation can be induced in it by the two-stage elimination of a fairly simple molecule HX. Unlike polystyrene, another hydrocarbon polymer, poly*iso*butene, cannot be cross-linked even when dissolved in tetrachloroethane, because it cannot satisfy either of the conditions given above.

As reported before, polymethyl methacrylate is cross-linked with only slight accompanying discolouration, which suggests that little, if any, unsaturation is introduced during treatment with Friedel–Crafts catalysts. Consequently the mechanism shown below, involving steps analogous with those proposed for the case of polyvinyl chloride, is rejected:

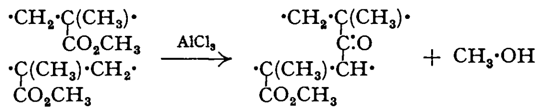


$$\text{(i)}\quad \begin{array}{l}\cdot CH_2\cdot C(CH_3)\cdot \\ \quad CO_2CH_3\end{array} + AlCl_3 \rightleftharpoons \cdot CH_2\cdot\overset{+}{C}(CH_3)\cdot + [AlCl_3\cdot CO_2CH_3]^-$$

$$\text{(ii)}\quad \cdot CH_2\cdot\overset{+}{C}(CH_3)\cdot \longrightarrow \cdot CH\colon C(CH_3)\cdot + H^+$$

$$\text{(iii)}\quad \begin{array}{l}\cdot CH_2\cdot\overset{+}{C}(CH_3)\cdot \\ \cdot C(CH_3)\colon CH\cdot \\ \quad (AlCl_3)\end{array} \longrightarrow \begin{array}{l}\cdot CH_2\cdot C(CH_3)\cdot \\ \cdot C(CH_3)\colon C\cdot\end{array} + H^+ + AlCl_3$$

Various *ad hoc* hypotheses can be made about the mechanism of the reaction; for example it seems feasible that if the carbonyl group donates electrons to the catalyst, it would be unnecessary to introduce further unsaturation into the molecule. The over-all equation could therefore be



$$\begin{array}{l}\cdot CH_2\cdot C(CH_3)\cdot \\ \quad CO_2CH_3 \\ \cdot C(CH_3)\cdot CH_2\cdot \\ \quad CO_2CH_3\end{array} \xrightarrow{AlCl_3} \begin{array}{l}\cdot CH_2\cdot C(CH_3)\cdot \\ \qquad C\colon O \\ \cdot C(CH_3)\cdot CH\cdot \\ \quad CO_2CH_3\end{array} + CH_3\cdot OH$$

giving a cross-linkage stable to acids and alkalis, as observed.*

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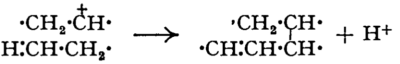
* *Added in Proof.*—We are grateful to Dr. E. H. Farmer for pointing out that the group $\cdot CH\colon CH\cdot CH_2\cdot$ is more likely to react as $\cdot CH\colon CH\cdot\overline{C}H\cdot$ or $\cdot\overline{C}H\cdot CH\colon CH\cdot$ than as $\cdot CH\colon\overline{C}\cdot CH_2\cdot$. The overall equation for the final step in the cross-linking of polyvinyl chloride should therefore be written:



$$\begin{array}{l}\cdot CH_2\cdot\overset{+}{C}H\cdot \\ \cdot CH\colon CH\cdot CH_2\cdot\end{array} \longrightarrow \begin{array}{l}\cdot CH_2\cdot CH\cdot \\ \cdot CH\colon CH\cdot CH\cdot\end{array} + H^+$$

This reaction may depend upon the formation of a complex between the olefinic group and the catalyst as suggested above, or alternatively it might occur without the participation of a catalyst molecule. In the second case, the reaction would be similar to that proposed for the primary formation of the olefinic group, with the ejection of the proton occurring intermolecularly instead of intramolecularly; the catalyst would be involved only once in the whole process of cross-linking. Slight revision is necessary in the equations proposed to explain the cross-linking of other polymers; the cross-linkage should be shown as involving a carbon atom adjacent to the group $\cdot CH\colon CH\cdot$ and not an atom of the group itself.