

## 112. *Electrolytic Dissociation Processes. Part II. The Friedel-Crafts Reaction.*

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A TRANSITION from a covalent binding to an ionic binding can be brought about in several ways. In Part I (J., 1936, 847) it was shown that, on the dissolution of iodine monochloride in carbon tetrachloride or cyclohexane, an augmentation of the dipole moment occurred, and that, as the polarisability of the solvent was increased, the solutions gradually became conducting. A similar augmentation of the dipole moment under the influence of solvation was shown in the case of the hydrogen halides (Fairbrother, J., 1932, 43; 1933, 1541; *Trans. Faraday Soc.*, 1934, 30, 862).

In addition to the action of solvation in bringing about such a transition, it is to be expected that a similar effect will be produced by the proximity to the dipole in question, of molecules which possess the power of forming complexes with the outer end of the dipole. In the case of simple solvation we may be dealing chiefly with coulombic forces between the ions and the solvent molecules; these lead to ionisation (as distinct from electrolytic dissociation, which it precedes) only of such molecules in which the potential energies of the covalent and ionic states are not widely separated. In the case of complex formation we have also the formation of a chemical bond between one of the potential ions and a part of its environment, resulting effectively in the formation of an ion of larger radius and the same charge, which is consequently less tightly bound to its fellow. Thus, Lowry (*Chem. and Ind.*, 1923, 42, 1048) and Brønsted (*Rec. trav. chim.*, 1923, 42, 718) have pointed out that a hydracid only gives rise to hydrogen ions in the presence of molecules (e.g., water) which can combine with the proton, and Lowry (*Phil. Mag.*, 1923, 46, 964) has discussed at length the process of "intramolecular ionisation" as a precursor to many organic reactions. Also, Meerwein (*Annalen*, 1927, 455, 227) has shown that many weak electrolytes are increased in strength by the formation of complex ions.

A transition of a covalent carbon-chlorine bond into an ionic bond, through complex formation, appears to occur as the first step in the well-known Friedel-Crafts synthesis. This reaction, of which there are many forms, has been studied in the present work in its application to the synthesis of acetophenone from benzene and acetyl chloride and of  $\beta$ -phenyl- $\beta$ -methylpropane from benzene and *tert.*-butyl chloride.

Friedel and Crafts expressed the opinion (*Compt. rend.*, 1877, 85, 74) that the first step in the reaction was the formation of a double compound between the benzene and the aluminium chloride, with the elimination of hydrogen chloride,  $C_6H_6 + Al_2Cl_6 = C_6H_5 \cdot Al_2Cl_5 + HCl$ , and the subsequent reaction of the double compound with the aliphatic chloride and the regeneration of the aluminium chloride. They explained the apparent

absence of reaction between the aluminium chloride and the benzene on the assumption that the double compound was unstable and was formed only in small quantities at a time. The view that some kind of double compound is formed between the aluminium chloride and one or other of the reactants as the first step in the reaction, has been generally held for a long time, and Perrier (*Compt. rend.*, 1893, **116**, 1298; *Ber.*, 1900, **33**, 815) and Böeseken (*Rec. trav. chim.*, 1900, **19**, 19; 1901, **20**, 102) isolated crystalline compounds of aluminium chloride with acid chlorides. But the fact that some Friedel-Crafts reactions could be carried out with much less than the molecular proportion of aluminium chloride led Böeseken (*ibid.*, 1904, **23**, 1904) to suggest that the intermediate-compound theory should be replaced by a catalytic hypothesis according to which the molecules were activated by the catalyst, combination then occurring between these activated molecules with the subsequent evolution of hydrogen chloride. Later (*ibid.*, 1910, **29**, 85), he suggested that the action of the aluminium chloride was due to a "dislocating influence" on the molecules, this influence being exerted where the molecules were weakest: "in organic chlorides it is probably the chlorine atom which is thus activated."

A new aspect has been given to the intermediate-compound hypothesis by Meerwein (*Annalen*, 1927, **455**, 227) and Hückel ("Theoretische Grundlagen der Organischen Chemie," 1931, Vol. 1, p. 351), who regard the complexes which are formed as co-ordination compounds containing the complex anion  $[\text{AlCl}_4]^-$ , thus:  $\text{CH}_3\cdot\text{COCl} + \text{AlCl}_3 \longrightarrow (\text{CH}_3\cdot\text{CO})^+ + [\text{AlCl}_4]^-$ . Such a process would constitute effectively a conversion of the covalent carbon-chlorine bond into an ionic bond.

The ability of aluminium chloride to form complexes was explained by Lewis ("Valence and the Structure of Atoms and Molecules," New York, 1923, p. 99) on the basis that "aluminium, like boron, frequently completes its group of 8 (electrons) by attaching to itself a lone pair belonging to another atom." Thus, it forms the stable compound  $\text{AlCl}_4\text{K}$ , which would presumably have the anion  $[\text{AlCl}_4]^-$  in the fused state (Hildebrand, "Solubility," New York, 1936, p. 115).

There are, therefore, three main possibilities in the Friedel-Crafts mechanism: (1) the formation of an intermediate compound between the benzene and the aluminium chloride, as suggested by Friedel and Crafts, (2) a physical catalysis wherein the molecules of the reactants are "activated," (3) the formation of a co-ordination compound between the aliphatic chloride and the aluminium chloride, in which the organic chlorine atoms leave the carbon atoms completely and enter a complex anion  $[\text{AlCl}_4]^-$  which is able to rotate relatively to the carbonium ion prior to the evolution of hydrogen chloride. [The formation of a complex molecule, *e.g.*,  $\text{R}\cdot\text{COCl}\cdot\text{AlCl}_3$ , in which each aluminium atom is found at the end of the reaction to be combined with the same chlorine atoms with which it started, is hardly to be differentiated from (2).]

The use of aluminium chloride in which part of the chlorine atoms are unstable isotopes, *i.e.*, radioactive, offers a means of deciding between these possibilities. If the mechanism were as (1), the evolved hydrogen chloride would be more radioactive than an equivalent amount of the final reaction mixture, since the organic chloride would act as a diluent of the latter: if it were as (2), then the hydrogen chloride when first formed would be wholly inactive. If the mechanism were as (3), then, since all the chlorine atoms concerned in the reaction would have an equal chance of escaping as hydrogen chloride, a complete interchange between the active and inactive chlorine atoms would take place. A complete interchange of this character has now been found experimentally.

This, however, does not, by itself, entirely eliminate the possibility that the interchange of chlorine atoms may have taken place, subsequent to the actual reaction, between the hydrogen chloride and the catalyst, though complex formation does not appear to take place readily between the hydrogen chloride and the aluminium chloride, and every hydrogen chloride molecule would have to form an  $\text{AlCl}_4\text{H}$  complex and be re-evolved as hydrogen chloride for equality of interchange by such a process. Also, there is some indication that, in the Friedel-Crafts synthesis of ketones, the combined aluminium chloride is not immediately liberated but remains as part of a double compound with the ketone, and interchange with the uncombined aluminium chloride could only occur as a heterogeneous reaction.

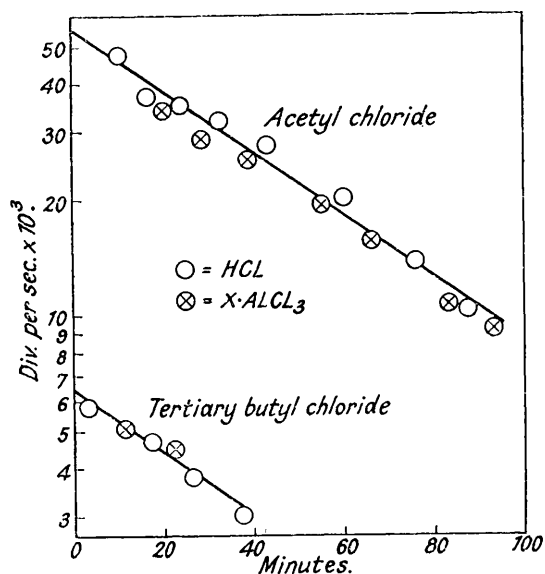
It has also been shown experimentally by the use of radioactive aluminium chloride, however, that an interchange of chlorine atoms takes place between acetyl chloride and aluminium chloride,  $\text{CH}_3\cdot\text{COCl} + \text{AlCl}_3 \longrightarrow (\text{CH}_3\cdot\text{CO})^+ + [\text{AlCl}_4]^-$ , in the absence of any third reactant or evolution of hydrogen chloride.

## EXPERIMENTAL.

*Materials.*—Merck's thiophen-free benzene was dried over phosphoric oxide and distilled. Acetyl chloride of C.P. quality was fractionated before use. *tert.*-Butyl chloride (Eastman Kodak) was dried over phosphoric oxide and distilled. The aluminium chloride was taken from a new bottle of "Reagent" quality.

*Procedure.*—About 0.5 g. of coarsely powdered aluminium chloride was placed in a shallow aluminium tray, covered with thin aluminium foil, and exposed to a beam of deuterons of about 5 million volts energy, produced by the Cyclotron described by Lawrence and Cooksey (*Physical Rev.*, 1936, 50, 1131), for about 30 microampère-minutes. The irradiation was carried out in air, and the target was water-cooled to avoid volatilisation of the aluminium chloride. The active sample was then mixed with excess of inactive aluminium chloride (about 10 g. in all), quickly ground to a fine powder, and placed in a 200-c.c. flask attached to a ground-in reflux condenser and dropping funnel. The aluminium chloride was immediately covered with 8 c.c. of dry benzene, and 6–7 g. of acetyl chloride were slowly added from the dropping-funnel, the residue in the funnel being washed into the reaction mixture with a further 5 c.c. of dry benzene. The evolved hydrogen chloride was passed through a 10-cm. plug of glass-wool to catch any spray, and absorbed by 5*N*-potassium hydroxide. When apparent reaction had ceased, the mixture was gently boiled under reflux for 15 minutes, and the hydrogen chloride in the flask blown out by a gentle stream of air dried by phosphoric oxide. The residue in the flask was poured slowly into cold water, a little nitric acid added, and the organic matter extracted with ether. The chloride in the aqueous portion was precipitated with silver nitrate, and the silver chloride washed and dried. The potassium chloride produced in the absorption of the hydrogen chloride was also converted into dry silver chloride. Equal weights of the two samples of silver chloride were then dissolved in equal volumes of concentrated aqueous ammonia, and placed in thin glass test-tubes (1 cm. diam.) which could be introduced directly in a fixed position inside the case of a sensitive quartz-fibre electroscop. The glass tubes were lightly coated on the outside with "Aqua-dag" graphite to form a conducting layer and prevent electrostatic disturbance of the electroscop needle. Readings were then taken alternately of the activities of the two samples of chloride. The use of an ammoniacal solution of the silver chloride, instead of the solid, permits, as shown by Olson, Libby, Long, and Halford (*J. Amer. Chem. Soc.*, 1936, 58, 1313), a better reproducibility of the geometry of the system. The total time taken from the removal of the sample from the Cyclotron to the commencement of readings was slightly under 2 hours, or about 3 half-lives of the radio-chlorine. In the process of activation a radioactive isotope of aluminium  $^{28}\text{Al}$  would also be obtained (Lawrence, *Physical Rev.*, 1934, 46, 746), but as this has a half-life of only 153 secs. it would not interfere with the measurements, and in any case, most of it would be removed in the precipitation with silver nitrate.

The results are shown in the figure, in which the movement of the quartz fibre, in divisions per sec.  $\times 10^3$  (minus the background drift), is plotted logarithmically against the time of observation. The results for the two samples of silver chloride—from the hydrogen chloride and from the reaction residue,  $\text{X}\cdot\text{AlCl}_3$ —are suitably differentiated. The lines drawn across the diagram correspond to a half-life of 37 minutes (Olson *et al.*, *loc. cit.*). The activities of the



two samples of silver chloride do not differ by more than about 10%, which is probably due to accumulated experimental errors, and the interchange may therefore be regarded as complete. A similar result was obtained with *tert.*-butyl chloride and benzene except that, the sample of aluminium chloride not being so active as in the first case, it was not possible to follow the decay curves for so long.

In order to show that the interchange can take place between acetyl chloride itself and the aluminium chloride, 5 g. of a similar mixture of active and inactive aluminium chloride were placed in a glass tube attached to a vacuum distillation apparatus, and 3 g. of acetyl chloride were added slowly with cooling. The mixture was kept for a few minutes at room temperature, and then the pressure was reduced: very little acetyl chloride (condensed in liquid air) distilled over at a pressure of about  $10^{-4}$  mm.; the mixture was then heated externally with water to about  $50^{\circ}$ , and a little more distilled at the same pressure. The distillate was examined directly, since the amount was insufficient for a quantitative treatment by the above procedure, and was found to possess a strong radioactivity, decaying with the half-life of 37 minutes characteristic of radio-chlorine. The distillation was carried out through a 10-cm. plug of tightly packed glass-wool to catch any spray.

It is therefore to be concluded that the first stage in the Friedel-Crafts reaction, for the synthesis of ketones or hydrocarbons, is the "ionisation" under the influence of the aluminium chloride, of the covalent aliphatic carbon-chlorine bond, with the formation of the ion  $[\text{AlCl}_4]^-$  and a positive carbonium ion. Such a process constitutes, in a sense, "activation" of the aliphatic chloride, in that the ion pair in question is more reactive than the un-ionised chloride, and unless a stable complex is formed between the aluminium chloride and the final product, a small amount of aluminium chloride will serve to "activate" a large amount of organic chloride. The Friedel-Crafts synthesis includes a variety of reactions and the use of several different metallic chlorides as catalysts: whether the above considerations apply quite generally is a matter for further investigation.

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