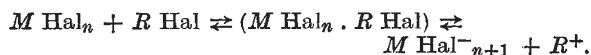


FRIEDEL-CRAFTS CATALYSTS AND POLYMERIZATION

A CONFERENCE on "Friedel-Crafts Catalysts and Polymerisation" was held on Saturday, September 15, in the Chemistry Department of the University of Manchester. This Conference was convened by Prof. M. Polanyi, and some hundred and seventy academic and industrial research workers were present. In welcoming the guests, Prof. Polanyi said that similar meetings on a smaller scale had been held previously at the Universities of Manchester and Leeds, but that this was the first large-scale meeting of its kind, in which the subject under discussion was of such general interest to both academic and industrial research workers. He hoped that further conferences of a similar nature would be held.

The first part of the discussion was concerned with the physical chemistry of the Friedel-Crafts catalysts. Dr. F. Fairbrother, in a paper on "The Catalytic Halides", discussed the reasons for the catalytic activity of these halides, and the way in which their catalytic power is exercised. One of the outstanding features of these Friedel-Crafts catalysts is that they are all electrophilic in character, and Dr. Fairbrother described two kinds of experimental investigation by which a comparison of the electrophilic character of inorganic halides may be made. The first was the study of the exchange of radioactive bromine between an organic bromide and an inorganic bromide. From these experiments it was found that the ease of halogen exchange could be correlated with the catalytic activity of the inorganic bromide on one hand, and with the ionizability of the organic bromide on the other hand. This exchange of radio-bromine must mean that the interaction of the inorganic bromide with the organic bromide causes the original C-Br bond to break. This was discussed in terms of the reaction:

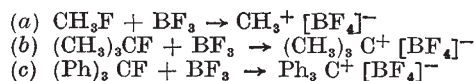


That is, the exchange may take place through the formation of an ion pair, the partners of which are able to rotate relative to one another, so that on disengagement and reformation of neutral molecules an exchange of halogen atoms may have taken place. If a polar but un-ionized addition compound is formed, the actual exchange of bromine atoms, it was suggested, could only occur by the rupture of such an addition compound. In the second experimental investigation which Dr. Fairbrother described, dielectric polarization measurements were carried out on solutions containing a metallic bromide and an organic bromide to determine the equilibrium concentration of ion pairs. This equilibrium concentration was found to be very small in general, as had been predicted from a consideration of the endothermicity of the process. These findings were also confirmed by measurements of the dielectric polarization and colour of metal halide - triphenylmethyl halide double compounds.

Dr. H. A. Skinner spoke on "The Molecular Structures of the Catalytic Halides". He summarized the results of electron diffraction studies of the halides of Groups II, III, IV and V of the Periodic Table. These results showed that, in general, the metal-halogen bond distances are shorter than those which would be expected if the bonds were of the normal covalent type. For those metal halides known to

show catalytic activity in Friedel-Crafts reactions, the most active catalysts show a greater percentage bond-contraction than do the weaker catalysts. The fact that the silicon halides are not catalytically active although they show a marked bond contraction was considered in relation to the low dipole moment of the Si-Cl bond, and the suggestion was made that one of the factors upon which the catalytic activity of the halide $M-X$ depends is the ionic nature of the bond in the sense $M^+ X^-$.

Thermochemical calculations were given for the interaction of the catalyst and the organic halide for the case of boron trifluoride and organic fluoride. The three reactions



were examined, and the conclusion was reached that reaction (a) is endothermic and unlikely to occur, whereas reactions (b) and (c) are exothermic, and probably will occur. These results were compared with the experimental observations of Burwell and Archer that the tertiary alkyl fluorides more readily undergo Friedel-Crafts reactions in the presence of boron trifluoride than do the primary alkyl fluorides, and with the fact observed by Wiberg, that triphenylmethyl fluoride readily forms a complex with boron trifluoride.

Dr. P. H. Sykes, in a paper on "Friedel-Crafts Catalysts in Carbon-Monoxide Reactions", discussed the addition of carbon monoxide to ethers, alkyl halides, alcohols and aromatic hydrocarbons using aluminium chloride, boron trifluoride, hydrogen fluoride and sulphuric acid as catalysts. Dr. Sykes discussed the formation of complexes between the catalyst and the reactants and between the catalyst and the products, and suggested that in many cases the effectiveness of the catalyst is due to the fact that the decrease in free energy from catalyst-reactant complex to catalyst-product complex is more marked than the decrease in free energy of the reaction in the absence of catalyst. It was suggested that this is the reason why aluminium chloride catalyses the production of benzaldehyde from benzene and carbon monoxide, a reaction for which, in the absence of catalyst, there is an increase of free energy of 5 kcal./mole. Evidence was brought forward to show that the aluminium chloride-product complexes are more stable than the corresponding boron trifluoride complexes, so that if, in the absence of catalyst, a reaction is thermodynamically unfavourable, aluminium chloride has a very great advantage over boron trifluoride as a catalyst for that reaction.

As regards the mechanism of these reactions, Dr. Sykes gave evidence for the presence of HCOCl as an intermediate in the reactions catalysed by aluminium chloride. The activation of the other reactant molecule was considered for the case of the formation of *iso*-butyric acid from carbon monoxide and propanol. The fact that both normal propanol and *iso*-propanol react with carbon monoxide to form *iso*-butyric acid suggests that the reaction proceeds through the formation of an intermediate carbonium ion, since carbonium ions are known to be easily rearranged.

Dr. A. G. Evans read a paper on "Low Temperature Polymerization" by A. G. Evans and M. Polanyi. The polymerization of *iso*-butene catalysed by boron trifluoride is of great interest because it occurs with

explosive violence at low temperatures. Owing to the difficulties of studying the kinetics of the *isobutene* polymerization, these authors decided to study the boron trifluoride catalysed reaction of di-*isobutene*, C_8H_{16} . Under the catalytic influence of boron trifluoride, di-*isobutene* reacts quite readily, but yields nothing of higher molecular weight than $C_{16}H_{32}$. The fact that di-*isobutene* does not polymerize under these conditions, whereas *isobutene* does, was discussed in terms of steric hindrance. It was shown that steric hindrance in the polymer molecule, which is appreciable even when the monomer is *isobutene*, would be prohibitively large for the case of di-*isobutene*. Thus it was assumed that the mechanism of the di-*isobutene* reaction is the same as that of *isobutene*; the absence of a polymerization reaction in the case of di-*isobutene* was attributed solely to steric reasons.

To account for the kinetic results obtained, the possibility of an energy chain-mechanism was discussed. It was suggested that the initiation of the energy chain is due to the reaction of boron trifluoride with some component X , of which only a trace is present, to give BF_3X^* , a hot molecule, the energy of formation of which has not been dissipated into thermal energy. In this way, one molecule of the component X may be effective in causing the reaction of many di-*isobutene* molecules. This mechanism would lead to products having a structure similar to that found for the actual products by infrared examination. It is found that $C_{16}H_{32}$ is not the only product of the reaction; appreciable quantities of $C_{12}H_{24}$ are also produced. This suggests that the $C_{16}H_{32}$ molecules may be capable of disruption and thus supports the idea of an energy chain-mechanism.

Polymerization in the gas phase was discussed by Prof. H. W. Melville in a paper on "The Mechanism of Polymerization of Vinyl Compounds". Prof. Melville discussed two ways of inducing polymerization reactions in the vapour phase: (a) by methyl radicals or hydrogen atoms, and (b) by photoactivation. In the case of methyl methacrylate, these two methods of initiating polymerization chains give rise to reactions which have entirely different kinetics. The most striking difference is that the photoactivated polymerization proceeds in the dark long after the light is switched off, whereas in the case of the polymerization initiated by free radicals the life-time is of the order of a few milliseconds.

Prof. Melville gave an account of very interesting experiments on the photopolymerization of vinyl acetate. In the vapour phase the reaction-rate is pressure-dependent, but there is a critical pressure below which no polymerization occurs. To explain these results it must be assumed that the photoactivated vinyl acetate molecule may lose its energy spontaneously, that is, in a collision-free process. Confirmation of this hypothesis comes from the fact that inert gases inhibit the reaction, not by reacting with the growing polymer, but by interaction with the initially excited vinyl acetate molecules before polymerization starts. This direct photo-polymerization is found to be quite a different reaction from that which occurs when the polymerization of vinyl acetate is induced by free radicals.

Prof. Melville described the method by which he has evaluated the individual velocity constants, k_p and k_t , for the propagation and the termination reactions in the vinyl acetate polymerization. By obtaining values of the propagation constant at

various temperatures, it was found that the activation energy for the propagation reaction is 4,400 cal. and the temperature independent factor is 1.48×10^5 l. mol.⁻¹ sec.⁻¹ (which means a steric factor of 10^{-6}). For the termination reaction it was found that the activation energy is zero and the temperature independent factor is 2.47×10^9 l. mol.⁻¹ sec.⁻¹ (which corresponds to a steric factor of 10^{-2}). These experiments have been repeated at double the chain-length, and the results obtained show that the propagation constant k_p decreases only slightly as the molecular size is doubled, and that the ratio $k_p/k_t^{1/2}$ is, to a good approximation, independent of molecular size.

Prof. M. G. Evans concluded the second half of the discussion by reading a paper on "Energy Transfer in Chemical Reactions". Prof. Evans considered the theoretical calculation of steric factors for the propagation and termination reactions of polymerization, and compared the values obtained in this way with those found experimentally by Prof. Melville. He showed that the steric factor for propagation given by the transition state theory is of the same order as that which is found experimentally. In the case of termination reactions, however, the theory is unable to interpret the experimental results. He suggested that the possibility of an energy chain (in which the growing polymer molecule is always energetically active at the terminal double-bond) might be understood if it be assumed that an active double-bond is one that is in the triplet state. In this case the resonance requirements in the transition state for the addition of a molecule of monomer to the end of an active polymer may result in the double-bond of the added monomer being converted into the triplet state, and thereby activated.

A. G. EVANS.

IMPEDANCE BRIDGE WITH A 10^9 TO 1 RANGE

FOR measuring the impedances of a wide variety of coils used in electronic and communication apparatus the Bell Laboratories have designed a wide-range audio-frequency bridge, and a carrier-frequency bridge, about twenty-five of which have been constructed for the various manufacturing plants of the Western Electric Company. The bridges have been described in an article by H. T. Wilhelm (*Bell Lab. Rec.*, **23**, No. 3; March 1945).

The audio-frequency bridge can measure inductance from one microhenry to 1,000 henrys, and resistance from 0.001 ohm to 1 megohm. This extremely wide range is secured by providing six component ranges, any one of which may be selected by operating a single range dial. Depending on the position of this dial, the normal reading of the bridge is multiplied by 0.01, 0.1, 1.0, 10, 100, or 1,000. The frequency range of the bridge is from 20 to 10,000 cycles. One arm (AB) includes a conductance and a capacitance standard in parallel, each controlled by four dials. A six-position range dial selects resistors for the two resistance arms (BC and AD) that will result in the desired multiplying constant. Six resistors in the AD arm and three in the BC arm are used for this purpose. The inductance component of the impedance under test is determined by the capacitance standard, and four dials which control this standard are marked directly in terms of inductance, ranging from steps of 0.1 henry at the left to 0.0001 henry