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FRIEDEL-CRAFTS  
POLYMERIZATION

ON July 5-7, a symposium on Friedel-Crafts polymerization was held in the Chemical Laboratory, Trinity College, Dublin, under the chairmanship of Prof. M. G. Evans. Papers by Drs. F. S. Dainton, M. H. D. Milke, D. D. Eley, A. G. Evans, S. D. Hamann, G. W. Meadows, D. C. Pepper, F. T. Plesch, P. H. Plesch and A. W. Richards were presented. The discussion revealed the scarcity of quantitative information in this field, but resulted in appreciable clarification of a number of obscure points. A clear picture of the reaction mechanisms emerged, which should be of value as a guide to future work.

*Ionic character of the reactions.* This has always been inferred from the fact that olefines containing strongly electrophilic groups cannot be made to polymerize by Friedel-Crafts catalysts, and from the electrophilic character of the catalysts themselves. Also, the low overall activation-energies are characteristic of ionic rather than radical reactions. New evidence on this point has been provided by the observation (A. G. Evans and Hamann) that 1:1 diphenyl ethylene in the presence of several Friedel-Crafts catalysts shows the absorption spectrum of diphenyl methyl carbonium ion. The marked effect of the dielectric nature of the solvent on these polymerizations (Pepper) also indicates ionic processes in them. The electrical conductivities of monomer-catalyst solutions are very low or anomalous, so that it seems likely that the free carbonium ions are not present, but rather ion-pairs with the carbonium ion closely associated with a *gegen* anion derived from the catalyst. The large energy of charge separation, even in solutions of fairly high dielectric constant, would seem to rule out any appreciable concentration of free ions.

*Initiation process.* It has been shown conclusively (Evans and Meadows) that the polymerization of *isobutene* cannot be initiated by boron trifluoride alone, and most probably not by titanium chloride (Plesch) or by stannic chloride (Norris and Russell). Initiation of *isobutene* can be brought about only by complexes formed from the Friedel-Crafts compounds and certain hydroxylic co-catalysts, for example, water, *t*-butyl alcohol, acetic acid, etc. On the other hand, vinyl ethers (Eley and Richards) and styrene in solvents of high dielectric constant (Pepper) appear to need no co-catalyst. It is concluded that where co-catalysts are necessary, the initiation process must be the transfer of a proton from the catalyst-co-catalyst complex to the monomer, resulting in a carbonium ion-*gegen* anion pair. In such systems the simple polarization of the monomer double-bond by electron donation to the Friedel-Crafts catalyst itself appears to be inadequate for initiation. In systems which do not require an added co-catalyst the above conclusion is not so inevitable, but it seems likely that in these cases also initiation is due to proton (or carbonium ion) transfer from a catalyst-solvent, or even catalyst-monomer complex.

*Propagation step.* Preliminary kinetic information (Plesch) indicates that the activation energy for propagation of *isobutene* is low ( $\sim 4$  kcal./mol.), as might be expected for an ionic reaction. The propagation process is envisaged as the addition of a monomer or polymer carbonium ion, resulting in a

polymer carbonium ion which is one monomer unit longer but still associated with the *gegen* anion derived from the initiating complex.

*Termination step.* Kinetic investigations of the polymerization of vinyl ethers (Eley and Richards) and of styrene (Pepper) indicate that in both these systems the termination step is unimolecular. Full kinetic information for *isobutene* is not available, but here also a unimolecular termination reaction seems probable. In these systems, therefore, the termination process cannot be the combination of polymer carbonium ion with a free anion, but must be either the spontaneous expulsion of a positive charge, or some kind of 'internal neutralization'. In all systems studied there is evidence that each catalyst molecule (or catalyst-co-catalyst complex) gives rise to many polymer molecules, that is to say, the initiating complex must be regenerated in the termination process. There is also much evidence that the polymers contain a double bond, that is to say, a proton must be expelled from the carbonium ion. Such proton expulsion has been demonstrated spectroscopically (Dainton and Sutherland) in *isobutene* polymerized by boron trifluoride-deuterium oxide complex. The termination step is therefore envisaged as the loss of a proton from the carbonium ion to the *gegen* anion, thus regenerating the initiating complex and leaving a double bond at the end of the polymer molecule. For this combination of ions to be a unimolecular process, the polymer carbonium ion and the complex anion must be one kinetic unit, that is to say, the ions must always be in close association with one another.

*Transfer processes.* There is no evidence for transfer processes in the polymerization of *isobutene* or of styrene, but transfer to monomer appears to take place in vinyl ethers in that the molecular weight of the polymer is independent of the monomer concentration (Eley and Richards). The relative importance of transfer processes in terminating chains is dependent on the catalyst used, being negligible with stannic chloride but dominant with iodine and silver perchlorate. This observation provides further evidence that the catalyst-complex anion is always in close association with the growing polymer carbonium ion.

*Depropagation.* Reversal of the propagation process has been demonstrated (Dainton and Ivin) in the co-polymerization of butene and sulphur dioxide catalysed by silver ions and other catalysts. It is suggested (Dainton) that the low molecular weights usually obtained in Friedel-Crafts polymerizations at room temperature might be due largely to this cause. Especially in the polymerization of  $\alpha\alpha'$  disubstituted monomers, low 'ceiling temperatures' would be expected as a result of their lower heat of polymerization. Whether depropagation or transfer processes are the operative factors in limiting molecular weight can be decided from the form of the molecular weight-temperature relation. An interesting feature of these ionic polymerizations is that even at the end of the reaction the polymer has a terminal double bond, and catalyst is still present, that is, conditions are established for a mobile polymer  $\rightleftharpoons$  monomer equilibrium, so that if the temperature is raised depolymerization should ensue. There is some evidence that such mobile equilibrium may be established in *isobutene*-boron trifluoride hydrate systems, but further demonstrations are to be sought.

A clear picture of the main steps in an ionic polymerization has thus emerged. The initiating agent is not the simple Friedel-Crafts compound, but an ionic complex of it with a co-catalyst, solvent or perhaps monomer. Initiation consists in transfer from the complex to the monomer of a proton (or positively charged fragment) forming a carbonium ion which remains in close association with the anionic residue of the complex. The carbonium ion grows by adding monomer to form larger carbonium ions which at each stage maintain this close association. The *gegen* anion must, therefore, be regarded as 'travelling along' the propagating chain as it grows. Termination consists of the spontaneous loss of a proton to the *gegen* anion, leaving a double bond in the polymer and a regenerated initiating complex.

The above theory of the reaction mechanism is in accordance with the available experimental evidence, but is almost certainly over-simplified. There are still many obscurities which await clarification. For example, the initiating complexes of boron trifluoride with water or acetic acid are ionic crystals insoluble in *isobutene*, and in these systems the polymerization reactions are probably heterogeneous. It may be unsafe, therefore, to include these systems and the homogeneous polymerizations of vinyl ethers and styrene in one generalization about reaction mechanisms. In the homogeneous systems, the possible existence of solvent-catalyst complexes, and the details of the effect of dielectric constant, are still unsettled. A serious deficiency in the experimental evidence is that in systems where there is spectroscopic information about end-groups and catalyst fragments in the molecule there are few kinetic data, and vice versa. The relative importance of transfer or depropagation processes as the factors limiting molecular weight still remain to be explored.

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## THE HEALTH OF ENGLAND AND WALES

THE report of the Ministry of Health for the year ending March 31, 1948, and the report of the Chief Medical Officer for the year ending December 31, 1947, which are again published together to form a comprehensive survey of the health and health services of England and Wales\*, once more record excellent health statistics.

During the period covered by the Ministry of Health's report, the birth-rate (20.5 per thousand of the population) was the highest since 1921; the infant mortality-rate (41.37 per thousand related live births) was the lowest recorded, and may be compared with the rates of 50.57 in 1939 and 153.1 during the years 1871-75; the still-birth-rate was 24.1 per thousand of all births, compared with 38.3 per thousand in 1938; and the maternal mortality-rate was 1.17, which may be compared with the rate of 3.94 for 1938. In 1921 there was also a high birth-rate and a very hot, dry summer, yet the infant mortality-rate was 83. It is evident, therefore, that many children and mothers owe their existence to-day to the careful, painstaking work of all those who

\* Report of the Ministry of Health for the Year ended March 31, 1948, including the Report of the Chief Medical Officer on the State of the Public Health for the year ended December 31, 1947. (Cmd. 7734.) Pp. 282. (London: H.M. Stationery Office, 1949.) 5s. net.

administer the maternal and child-care services described in this report.

Deaths from diphtheria were half those recorded in 1946. A table shows the remarkable decline in the number of deaths due to this disease since 1941, and other figures quoted show how much is owed to the policy of immunization followed in Great Britain. The experience of other countries has been very different. During the period reviewed by the report, scarlet fever caused only forty-two deaths, a new low record; deaths from measles reached a new low level; diabetes killed fewer people than it has ever done; and the notifications of dysentery were further reduced. Another low record was the combined death-rate for children under fifteen afflicted with rheumatic fever and heart disease (39 per million). These results were achieved during a period which included an exceptionally severe winter, an exceptional scarcity of fuel, rationing of bread and potatoes, and reductions of the rations of meat and bacon. Probably the hard winter caused the rise reported in the number of deaths of old people and the slight increase in the deaths from tuberculosis. The sections of the report which describe the extensive work on the control of tuberculosis show what excellent work is being done to fight this scourge, and include details of the valuable work of the mass miniature-radiography units, the number of which is being increased.

The other details given by the report provide, on every page, evidence of the devoted work of health workers of every kind. The epidemiology of infectious diseases during 1947 was, on the whole, satisfactory, but the unexpected epidemic of poliomyelitis ('infantile paralysis') reached a figure (18 per hundred thousand) four and a half times higher than that of the heaviest epidemic previously recorded; and 707 deaths occurred. This was the first large-scale epidemic of this disease, which is again causing trouble this year. Possibly many people suffer mild, unrecognized attacks of it, and many carriers exist. Knowledge of it is increasing slowly, but at present we know little of its methods of spreading. The report states that most people seem to have considerable immunity to it and that children, especially those less than five years of age, seem to be becoming less susceptible. Nearly two-thirds of the people who died of this disease during the period covered by this report were more than fifteen years old, so that the term 'poliomyelitis' is preferable to the term 'infantile paralysis'.

The report records a marked fall of new cases of syphilis and gonorrhoea, and suggests that a decline of war-time infections, together with increased public knowledge of the seriousness of these diseases and earlier and more effective treatment of them, may lead to a progressive reduction of their incidence. The crude civilian death-rate from cancer did not change during the period under review.

The work done upon other aspects of national health cannot be adequately described in a short review. The report includes descriptions of the work of the Public Health Laboratory Service upon the Vi-phaging of typhoid and paratyphoid bacilli, the testing and regulation of ice-cream manufacture and investigation of outbreaks of food-poisoning; the national blood-transfusion service, the increased and very valuable work of which has, since the War, received less public notice than it deserves; and the extremely valuable work, always in progress, on diets and nutrition, the efficiency of which is probably the basis of the excellent health of the people. Other