

LETTERS TO THE EDITORS

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Friedel - Crafts Catalysts and Polymerization

DURING the past four years we have been investigating the mechanism of two closely allied reactions—the polymerization of isobutene and the dimerization of di-isobutene. Both these reactions are catalysed by Friedel - Crafts catalysts. Although we have not yet brought these investigations to the point where the mechanism can be definitely established, we have accumulated sufficient data to draw the following conclusions. In order that the reaction may take place at an appreciable rate, it is not sufficient that only the Friedel - Crafts catalyst and the monomer should be present together in the same system; the presence of a third component, probably water, is necessary for rapid reaction to occur.

1. Hexane was shaken in an atmosphere of boron trifluoride in a high-vacuum apparatus and then introduced directly into di-isobutene contained in a closed Dewar vessel in an atmosphere of dry nitrogen. In some of these experiments it was observed that on the addition of the boron trifluoride - hexane solution only a very slow reaction occurred (as measured by the temperature rise). After about 30 min., the reaction had practically stopped, although only about 25 per cent of the monomer had reacted. When, at this point, the Dewar vessel was opened up to the air and the contents stirred gently, the temperature rose rapidly and the reaction proceeded to completion within 2-3 min. This sudden occurrence of the reaction could not be due to the action of stirring, since the solution had been vigorously stirred before opening it to the air.

2. We have also made up the catalyst solution by bubbling boron trifluoride through hexane contained in a burette. Various quantities of this boron trifluoride - hexane solution were added to di-isobutene contained in a closed Dewar vessel. It was found that when a small quantity of the catalyst solution was used, the extent of the reaction depended on the amount of catalyst solution added. Experiments were carried out in which the quantity of catalyst solution added was such as to cause only about 70-80 per cent of the monomer to react. When this limited reaction had stopped, a boron trifluoride - nitrogen stream was bubbled through the solution still contained in the closed Dewar vessel. The partial pressure of boron trifluoride in this gas stream was made the same as that which the catalyst-monomer solution would possess at the initial moment of mixing. It was found in some experiments that this boron trifluoride - nitrogen stream could be bubbled through the solution in the Dewar vessel without further reaction occurring, although as much as 20-30 per cent of the original monomer had not reacted. The boron trifluoride was then blown out of the system by a stream of nitrogen, the Dewar vessel opened to air and two samples of the liquid removed. One of these was distilled and the presence of about 20-30 per cent of unreacted monomer confirmed. The other sample was placed in another Dewar vessel and the same boron trifluoride - nitrogen stream as previously used was bubbled through it. This time the remaining monomer reacted quite rapidly.

3. The reaction of di-isobutene was also studied by bubbling boron trifluoride through cyclo-hexane in a Dewar vessel and adding di-isobutene to the saturated solution. The bubbling of boron trifluoride was maintained throughout the experiment. The reaction followed a first-order law, the asymptote of which, however, often corresponded to only 80 per cent of the monomer having reacted. Further experiments were made in which successive samples of di-isobutene were added to the boron trifluoride - cyclohexane solution, the Dewar vessel remaining closed throughout this sequence of additions, and the bubbling of boron trifluoride being steadily continued. It was found that the first-order rate constant of the di-isobutene reaction varied from one sample to another by as much as a factor of 2.

4. A solution of titanium tetrachloride in hexane was added to a solution of isobutene in hexane in a closed system at a temperature of -90°C . It was found that a very slow reaction occurred, the rate of which rapidly decreased with time. If laboratory air was blown through the solution even 150 min. after the initial mixing of catalyst and monomer, a rapid reaction took place. This, however, did not necessarily lead to the complete reaction of the monomer (compare section 3), but reaction could be made complete by repeating the blowing through of air. Laboratory air, nitrogen and oxygen, each dried by passage through two liquid-air traps, were not effective in causing the fast reaction. Dried nitrogen re-humidified to contain water vapour at a partial pressure of less than 4 mm. was effective.

These results, which have accumulated over a long period of investigation, lead us to the following conclusions: (a) In the dimerization of di-isobutene and the polymerization of isobutene, it is essential that a trace of some third component, X (probably water) shall be present in order that the reaction shall proceed at an appreciable rate. The velocity constant of these reactions is not solely determined by the concentration of catalyst and monomer. (b) The effect of this third component in accelerating the reaction-rate may cease before all the monomer has reacted. This suggests that the third body X is involved in the initiation of a reaction chain which may be terminated in some way before all the monomer has reacted, and that more X is then required to cause the further reaction of the monomer. Having participated in the initiation of a reaction chain, the third component X is no longer able to initiate further chains. This would be the case if the reaction chain were an energy chain in which the energy of initiation came from the heat of combination of a molecule of catalyst with a molecule of X. It would also be the case if the reaction chain were a proton chain in which the initiating proton was liberated from the third component X when this molecule combines with a molecule of catalyst.

We have not yet mastered the technique of reliably excluding the factor X in the way described in experiments 1 and 2, but this has been achieved by the process described in experiment 4.

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