

opalescence until exposed to the atmosphere. With a ratio of chloride to acid less than about 4, the curves showing the progress of reaction with time are slightly sigmoid, but for higher values of this ratio their slopes decrease monotonically from the start. For starting temperatures near -80°C ., the maximum rate of the polymerization under adiabatic conditions is found to be a function of the concentrations of isobutene, titanium chloride and trichloroacetic acid, and of the initial temperature. The detailed relationships are being investigated.

Picric acid, the dissociation constant of which is of the same order as that of trichloroacetic acid, was found to be inactive as co-catalyst, but did not affect the polymerization afterwards induced in the same reaction mixture by the addition of trichloroacetic acid. Monochloroacetic and dichloroacetic acids were found to possess practically no co-catalytic activity at -75°C ., but slowed down considerably the polymerization afterwards induced by the addition of trichloroacetic acid.

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¹ Evans, A. G., *et al.*, *Nature*, **157**, 102 (1946).

² Plesch, Polanyi and Skinner, Discussion on "Some Aspects of the Chemistry of Macromolecules", *J. Chem. Soc.*, 257 (1947).

³ Evans, A. G., and Polanyi, *J. Chem. Soc.*, 252 (1947).

⁴ Evans, A. G., Meadows and Polanyi, *Nature*, **158**, 94 (1946).

⁵ Evans, Meadows and Polanyi (see following letter).

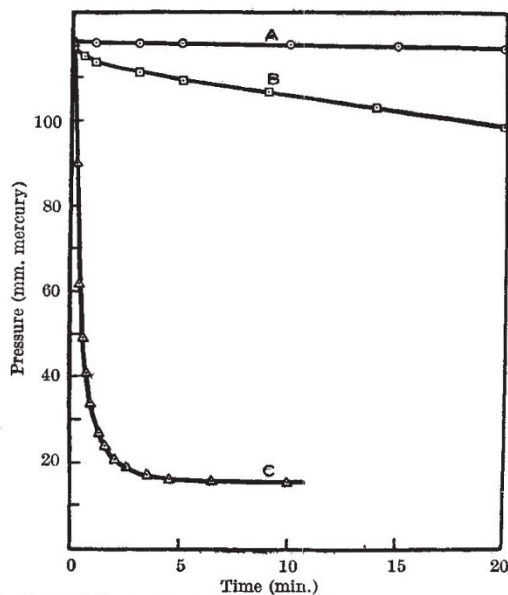
Polymerization of Olefins by Friedel-Crafts Catalysts

EARLIER work has shown that pure isobutene gas and pure di-isobutene vapour do not undergo reaction when mixed with gaseous boron trifluoride¹. In the presence of a trace of some third component, or co-catalyst as we shall call it, these monomers undergo very rapid polymerization when mixed with boron trifluoride. Water¹ and *t*-butyl alcohol² act as co-catalysts in this way.

We now find that acetic acid also is an effective co-catalyst in these reactions. Isobutene gas containing as little as 0.06 per cent acetic acid vapour polymerizes very rapidly when boron trifluoride is mixed with it (Curve C). The introduction of boron trifluoride into this isobutene-acetic acid mixture is accompanied by a dense fog and by the formation of liquid polymer throughout the whole system. The slow reaction which occurs when purified isobutene gas is mixed with boron-trifluoride is shown for comparison (Curve A).

The action of the co-catalyst has been attributed to the fact that it forms an addition complex with the boron trifluoride, which complex then loses a proton to the olefin, thus forming a carbonium ion which can initiate a polymerization chain³.

We have prepared a crystalline boron trifluoride acetic acid complex by mixing acetic acid vapour with excess boron trifluoride gas*. The introduction of purified isobutene gas into a system containing crystals of this complex resulted in the rapid polymerization of the isobutene. This polymerization took place entirely on the surface of the complex. Since the complex covered only a very small portion of the reaction vessel surface, the major part of this surface was completely free from liquid polymer.



A: Boron trifluoride + purified isobutene + 0.01 mm. acetic acid
B: " " " " + 0.01 " " "
C: " " " " + 0.06 " " "

This experiment shows that in this case the polymerization of isobutene is a heterogeneous process occurring on the surface of particles of complex.

Further evidence for this conclusion was obtained by the following method. Isobutene gas, containing sufficient water as co-catalyst to give a slow reaction, was mixed with boron trifluoride in a reaction vessel (vessel 1). After 1-2 hours, this reaction mixture was expanded into a second reaction vessel (vessel 2), and the connexion between these vessels was then closed. It was found that the polymerization continued in vessel 1, but that there was no reaction in vessel 2.

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* A crystalline complex between boron trifluoride and acetic acid has been isolated by Meerwein and Pannwitz, *J. pr. Chem.*, **141**, 123 (1934).

¹ Evans, A. G., Meadows and Polanyi, *Nature*, **158**, 94 (1946). Evans, A. G., and Weinberger, *Nature*, **159**, 437 (1947).

² Evans, A. G., and Polanyi, *J. Chem. Soc.*, 252 (1947).

Use of a Palladium Tube Technique in the Study of the Role of Hydrogen in Combustion Systems

FROM the experiments of H. B. Dixon¹ and later workers, the importance of the presence of hydrogen-containing species in the combustion of carbon monoxide is generally recognized. The wet oxidation is a chain reaction in which these bodies provide the chain carriers. Recent experiments^{2,3} which prove the dominant role of the wet carbon monoxide-oxygen reaction during the high-temperature oxidation of carbon leads to a similar conclusion, namely, that small amounts of hydrogen or its compounds are necessary for the production of fully burnt gases during the combustion of solid fuels.

We have found that the stationary hydrogen concentration obtaining during the combustion of carbon