

Investigation of the Mechanism of Catalytic Reactions

Some high pressure investigations of the mechanism of catalytic reactions have been carried out, including the isomerisation of paraffinic and naphthenic hydrocarbons in the presence of aluminium chloride under pressure.

The effect of hydrostatic pressure and of pressure of hydrogen on the rate of isomerisation of methylcyclopentane to cyclohexane has been investigated in the presence of aluminium chloride at 80°C⁴⁸⁾. Zelinskii and Turova-Polyak⁴⁹⁾ have previously found that cyclohexane is reversibly isomerised to give methylcyclopentane in the presence of anhydrous aluminium chloride. At 80°C. the isomerisation is substantially free from side reactions. At low temperatures the equilibrium is shifted towards cyclohexane.* In this paper⁴⁹⁾ it was suggested that the isomerisation proceeds via the dehydrogenation of the hydrocarbon with the production of hydrogen. This assumption, however, was not confirmed by experiment.

Let us assume that dehydrogenation leading to the production of hydrogen is one of the first stages in the isomerisation of methylcyclopentane in the presence of aluminium chloride. An increase in pressure should naturally shift the equilibrium for this stage of the reaction towards the parent substance, since this stage is accompanied by a considerable increase in pressure. This shift in the equilibrium leads to a diminished concentration of dehydrogenation products, and thus considerably retards the further stages of the isomerisation.

A considerable retardation of the isomerisation on increasing the pressure might accordingly have been considered as one of the reasons in support of the above hypothesis. However, this reason is insufficient, as the retardation may also be caused by some other intermediate stage of the reaction, accompanied by a change in volume, for example a dissociation of the original hydrocarbon across a C-C bond. To obtain additional support for the hypothesis in question, we should also investigate the effect of the hydrogen pressure on the rate of isomerisation. In this case we should observe a greater retardation of the polymerisation than under an ordinary hydrostatic pressure, since hydrogen is not only a gas exerting pressure, but also one of the products of the dehydrogenation reaction; consequently, an increase in its partial pressure should further reduce the equilibrium concentration of dehydrogenated hydrocarbon.

But if the isomerisation of hydrocarbons is a process of intramolecular rearrangement, it will not be accompanied by the formation of hydrogen, and as is usual for unimolecular reactions it should be only slightly retarded by pressure no matter what gas is exerting this pressure.

Investigation has shown⁴⁸⁾ that the isomerisation of methylcyclopentane to cyclohexane in the presence of aluminium chloride is retarded appreciably more strongly by pressure than it would be in the case of intramolecular rearrangement, proceeding as is usual for unimolecular reactions. It was also found that a pressure of hydrogen retards the reaction to a considerably greater degree than a pressure of nitrogen (see Table 5).

Table 5

Isomerisation of methylcyclopentane in the presence of aluminium chloride at 80°C.

Pressure of nitrogen (atm.)	Yield of cyclohexane (%)	Pressure of hydrogen (atm.)	Yield of cyclohexane (%)
1	60.5	25	61
140	60	130	48.5
460	48.5	460	17
660	38.5	615	8

* An increase in pressure should shift the equilibrium very slightly further towards cyclohexane.