



Destructive hydrogenation of ethylbenzene

Curve 1 - benzene fraction  
Curve 2 - toluene fraction

Деструктивное гидрирование этилбензола: 1 - бензольная фракция; 2 - толуольная фракция

A more detailed examination of this effect for several alkylbenzenes will doubtless make possible further clarification of the mechanism of destructive hydrogenation of aromatic hydrocarbons at high pressures of hydrogen.

It may be noted that the above-mentioned accelerating effect of the hydrogen pressure on the process is specific for aromatic hydrocarbons. Also discussed above was the effect of hydrogen on the thermal cracking of paraffins; it is noteworthy that the effect of the hydrogen pressure on the rate of thermal decomposition of naphthenic hydrocarbons also proved to be unusual. It was found <sup>35)</sup> that an increase in the hydrogen pressure retards the thermal transformations of methylcyclopentane, the proportion of cyclopentane in the reaction products increasing.

Thus, the difference between the mechanisms of the thermal decomposition of various kinds of hydrocarbons is reflected in the specific effect of high pressures of hydrogen on the velocity of these processes.

Investigation of the Mechanism of Liquid-Phase Reactions

Up to the present no work has been done with the specific aim of investigating the mechanism of liquid-phase reactions by the use of high pressure. Examination of the effect of high pressure on the rate of certain liquid-phase reactions nevertheless allows us to solve a number of important problems concerned with the mechanism of these reactions.

A) Addition of Ethyl Iodide to Pyridine

The velocity of reaction of alkyl halides with tertiary amines or pyridine is known to depend very strongly on the nature of the solvent. In this connection the view has been expressed in the literature <sup>36)</sup> that in these reactions the solvent takes part in the formation of the transitional structure, and enters into the activated complex. The correctness of such a statement may be tested by means of an investigation of the effect of high pressure on the rate of the investigated reaction in various solvents.

We will reconsider equation (III), which expresses the effect of pressure on the velocity constant of a reaction. We may expect the value of  $\Delta V^\ddagger$  to be the same for various solvents only if the solvent molecules themselves do not take part in the activated complex. Moreover, in this case the absolute value of  $\Delta V^\ddagger$  should be nearly equal to the volume change  $\Delta V$  for addition reactions (see 3)).

Now if  $\Delta V^\ddagger$  varies with the solvent and is widely different from  $\Delta V$ , this is an indication of the high probability that the solvent molecules take part in the formation of the activated complex.