

THE EFFECT OF PRESSURE ON THE RATE OF STERICALLY HINDERED REACTIONS

There are a few experimental data that indicate a considerable acceleration of sterically hindered reaction with increasing pressure. Thus, tetramethylethylene was completely polymerized within 3 hours under 23,000 atm. at 300°C., while only 20% (1) of it was polymerized in 50 hours at the same temperature and under a pressure of 200 atm. The pressure also accelerates strongly the thermal conversions of tetrachloroethylene at 300°, yielding hexachlorobutadiene and hexachloroethane (2). In both cases shown, the observed acceleration of the reaction by means of pressure is connected only to a small extent with the increase of the concentration of starting substances; the determining factor is the increase of the reaction rate constant with the increase of pressure.

According to the theory of transition state the variation of the reaction rate constant with pressure is determined by the value of the change in volume in the formation of an activated complex (Δv^\ddagger) (3):

$$\left(\frac{\partial \ln K}{\partial P} \right)_T = - \frac{-\Delta v^\ddagger}{RT} \quad (1)$$

It is evident that the change in volume of the reacting molecules in the formation of an activated complex ($\Delta v \text{ mol}$) is an important component of the value Δv^\ddagger ; together with this, an important rôle may be played by other volume effects, in particular, by the variation of the solvent volume (if the reaction is carried out in solution) as a result of the different solvation of reacting molecules and of the activated complex ($\Delta v^\ddagger \text{ sol.}$). In the following work, only $\Delta v^\ddagger \text{ mol.}$ will be considered. At the same time we shall limit ourselves to the consideration of Menshutkin reactions for which it is possible to use, with sufficient certainty, a fixed geometrical