

From the data given above we may conclude that the rate-determining stage of the mutarotation of glucose is not the formation of an aldehydic compound but the ring closure. The part played by the solvent (water) in forming the activated complex from α -glucose is also not excluded. However, the question of the role of the solvent in the activated complex can only be decided, as we saw above, by investigation of the rate of reaction under pressure in various solvents.*

c) Thermal Polymerisation of Styrene

The use of high pressure for the investigation of polymerisation reactions is complicated by the fact that in most investigated cases an increase in pressure produces not only an increase in polymerisation, but also an increase in the molecular weight of polymer produced. Nevertheless, it is also possible to obtain interesting information about reactions of this type by analysing the effect of pressure on the rate of the process. Some data on the polymerisation of styrene under pressure will be analysed below with this object.

If we investigate a thermal chain polymerisation of an organic compound in the absence of special catalysts, and with as much atmospheric oxygen removed as possible, it may be supposed that the basic stages of the process - initiation, growth and breaking of reaction chains - occur mainly through collision and chemical reaction either of molecules of monomer, or of a molecule and a radical, or of two radicals. If these stages of the polymerisation process occur through the formation of an activated complex, then (if there is additivity of molar volumes for the monomeric links of the polymer chain) the volume change ΔV^\ddagger for all of these stages should be the same. Thus it follows that pressure should increase to equal extents the velocity constants for the chain initiation process in thermal polymerisation, for the growth of the chains (i.e. the rapid addition of a sequence of monomer molecules), and for their breaking.

Starting from the fact that the rate of polymerisation usually settles down to a constant period (up to polymer yields of a few dozen per cent.), we may consider the polymerisation in this stage as approximately a zero - order reaction with the velocity constant.

$$k_0 = \frac{k_1 \cdot k_2}{k_3} \quad (IX)$$

where k_1 , k_2 and k_3 are the velocity constants for the chain initiation, growth, and termination reactions. This entails the assumption that the molecular weight of the polymer remains constant. Consequently, the value of k_0 should determine the rate of polymerisation, as long as the molecular weight does remain constant. When the molecular weight of the polymer increases with the pressure at which the polymerisation reaction takes place, an appropriate correction must be introduced into equation (IX), with replacement of k_0 by k'_0 , which is equal to

$$k'_0 = \frac{\bar{M}_0}{\bar{M}_p} k_0$$

where \bar{M}_0 and \bar{M}_p are the molecular weights of polymer at 1 atm. and at p atm. respectively.

We now consider the change in the velocity constants for chain initiation, growth and termination as the pressure is increased; this should fix the value of ΔV^\ddagger . It is easily shown (see 43)) that ΔV^\ddagger is approximately equal to ΔV (the change in volume when one mole of dimer dissociates to give two moles of monomer). Then, by combination of equations (III) and (IX) and substitution of k'_0 , we obtain

$$\left(\frac{\partial \ln k'_0}{\partial p} \right)_T \approx - \frac{V}{RT} \quad (X)$$

* It has recently been shown (42) that the ionisation of alkyl halides in aqueous alcohol solution increases with pressure, which throws light on the role of