

however, increases with increasing pressure due to the contraction in the formation of the transition state.

Sometimes even an approximate estimation of Δv^\ddagger enables one to assign a probable reaction mechanism. For instance, it was shown in the Institute of Organic Chemistry that the rate of isomerization of methylcyclopentane into cyclohexane in the presence of aluminum chloride is considerably slower under hydrostatic or nitrogen pressure. An approximate estimate of the pressure effect on the rate constant k from equation (2) excluded the possibility that the rate retardation is due to pressure alone. This explanation would be plausible if the transition state volume of the methylcyclopentane molecule is increased tens of percents ($\Delta v \approx 30 \text{ cm}^3/\text{mole}$). However, this is not possible. It is concluded that the isomerization includes a stage in which the volume is increased considerably and that the rate of attaining the equilibrium of this stage is rate determining for the overall process. This stage may be the dehydrogenation: $\text{C}_5\text{H}_9\text{CH} \rightleftharpoons \text{C}_5\text{H}_7\text{CH}_3 + \text{H}_2$ (N. D. Zelinskii and M. B. Turovoi-Polyak, 1932).

To confirm this hypothesis, the effect of hydrogen pressure on the rate of methylcyclopentane isomerization was studied. If the dehydrogenation is accompanied by hydrogen gas liberation and if the equilibrium of this reaction determines the rate of isomerization, hydrogen should be more effective than nitrogen or hydrostatic pressure in retarding the rate of isomerization. This was confirmed by experiment. For instance, at 80° and a nitrogen pressure of 600 atm the yield of cyclohexane from methylcyclopentane in 3 hours was about 40%, whereas at the same pressure of hydrogen the yield was only 10%. Subsequent studies have shown that this mechanism prevails also in the isomerization of five- and six-membered rings