

more or less polarized in comparison with the reactants (molecules, ions). The activated complex is solvated by the solvent molecules. Evidently, this solvation is accompanied by a volume effect. If the activated complex is more solvated (more polarized) than the reactants, its formation will bring to a contraction of the reacting system because the solvent molecules in the solvated complex are more densely packed than in the bulk of the solvent. On the other hand, if the solvated complex is less solvated than the reactants, there is a positive volume effect. This effect must not be analogous to the volume effect of the activated complex formation in absence of solvent.

Accordingly, the pressure effect on rates in different solvents enables one to evaluate Δv^\ddagger from equation (2) due to the solvation of the activated complex. We used this principle in a Menshutkin reaction -the reaction of pyridine with ethyl iodide. In general, the Menshutkin reaction (a tertiary amine - alkyl halogenide reaction) is a classical example for a large solvent effect on the reaction rate. The rate may vary sometimes by a factor of hundred. Similarly, the reaction rate is considerably higher at elevated pressures.

The above reaction was studied in six solvents at pressures up to 2000-3000 atmospheres. For the interpretation of the kinetic results it was necessary to measure the densities during the reaction and also the electrical conductivity of the product in the same solvents. It was found that the rate acceleration at elevated pressure in various solvents is different. This is a conclusive indication that the activated complex is considerably solvated. The volume effect due to the solvation of the activated complex is significantly smaller than that of the product ions. Hence, in some cases, the pressure effect may be applied to study the activated complex structure and properties.