The volume contraction during transition state formation in a bi- or multi-molecular non-solvated process is explained on account of a shorter distance between the reacting substances than the sum of the van der Waals radii of the participating atoms. By participating atoms one means not only the bond forming atoms but also those which may cause a "steric hindrance". The greater the sphere described by the sum of the van der Waals radii overlapping the transition state, the more pronounced is the volume contraction and, consequently, the more acceleration is observed at elevated pressures. Therefore it is expected that sterically hindered reactions will have an especially large pressure effect.

These conclusions have been reached from ultra-high pressure studies performed simultaneously by V. M. Zhulin and V. P. Butuzov in which pressures up to 30,000 atmospheres at temperatures up to 350° were applied during hours in the thermal polymerization of tetramethylethylene (2.3 - dimethylbutene -2) and the thermal conversion of tetrachlorethylene (with formation of hexachlorobutadiene). Both reactions do not occur at atmospheric pressure, probably due to steric hindrance. However, they will proceed at high and ultra-high pressures. The accelerating effect of pressure on these reactions was experimentally established. As mentioned, this effect finds a rational explanation in the transition state theory.

In these examples the model of the activated complex was quite uncertain, preventing an accurate interpretation of the results. It was desired to confirm rigorously the steric hindrance hypothesis and the volume contraction during transition state formation. For this purpose M. G. Gonikberg and A. I. Kitaogorodski have examined the experimental results of several authors on the pressure effect on rates of Menshutkin reactions with various steric hindrances in a single solvent - acetone. Here again the