

model of the transition state. It should be mentioned in connection with this that, Menshutkin's reactions have served as the object of a series of kinetical investigations under high pressures.

Digressing from a possible participation of the solvent in Menshutkin's reactions (4), we shall start with a presentation of the structure of the activated complex shown schematically in Fig. 1 (5). According to this scheme, the C-R', C-R'' and C-R''' bonds are in the same plane. As for the N-C (or N-H) bonds in the amino group, their position, with regard to the plane passing through the nitrogen atom and parallel to the CR₃ plane, depends upon the structure of the amine molecule. Thus, if nitrogen in the amine is linked to alkyl radicals or hydrogen atoms, these bonds are arranged pyramidally (with the angles between them - 108°). If the radical is a phenyl group, then the N-C bonds in the amine molecule are in the same plane, which, according to our hypothesis, is parallel to the CR₃ plane. Finally, in the case of a complex with pyridine it is most probable that the pyridine ring is perpendicular to the CR₃ plane.

The N...C distance in the activated complex was assumed to be equal to the length of the valence bond N-C (1.5Å), although the possibility, [see (6)] that in reality it is somewhat longer, is not excluded. The approach of N and C atoms at such a distance itself explains for all Menshutkin* reactions, a decrease of the volume of the activated complex in comparison with the volumes of reacting molecules. This volume decrease amounts to 8.4³, i.e. 5 cc/mol. Nevertheless, additional compressions arise in the formation of

* The following values of intermolecular radii (7) are used, here and in what follows, for the calculation of the compression in the formation of the activated complex: R_H=1.2Å; R_N=1.6Å; R_C=1.8Å; R_{CH₃}=2.0Å. The lengths of C-H and C-C bonds are considered as equal, respectively, to 1.1 and 1.55Å.