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Abstract

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M. G. Gonikberg and A. I. Kitaigorodskii

On the Question of the Influence of Pressure on the Rate of Sterically Hindered Reactions

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The limited experimental data available indicate a considerable acceleration of sterically hindered reactions with increasing pressure. Thus, at 23,000 atm. and 300° tetramethylethylene was completely polymerized in 3 hours, whereas at the same temperature and a pressure of 200 atm. it was possible to polymerize only 20% of it in 50 hours (1). Pressure also strongly accelerates the thermal transformations of tetrachloroethylene at 300° with formation of hexachlorobutadiene and hexachloroethane (2). In both of the cases mentioned, the observed acceleration of the reaction by pressure is only to a small extent connected with an increase in the concentrations of the initial substances; the determining factor here is the increase in the reaction-rate constant with increasing pressure.

According to transition-state theory, the change of the reaction-rate constant with pressure is determined by the magnitude of the volume change upon formation of the activated complex ($\Delta v^{\neq}$) (3):

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta v^{\neq}}{RT}. \tag{1}$$

It is obvious that an important term in the quantity $\Delta v^{\neq}$ is the change in the volume of the reacting molecules themselves upon formation of the activated complex ($\Delta v^{\neq}_{\text{mol}}$); along with this, other volume effects may also play a noticeable role, in particular the change in the volume of the solvent (if the reaction is carried out in solution) as a result of the differing solvation of the reacting molecules and the activated complex ($\Delta v^{\neq}_{\text{solv}}$). In the present work only the quantities $\Delta v^{\neq}_{\text{mol}}$ will be considered. In doing so we shall restrict ourselves to consideration of Menshutkin reactions, for which one can with sufficient confidence make use of a definite geometrical model of the transition state. At the same time it should be noted that precisely the Menshutkin reactions have served as the object of a number of kinetic investigations at high pressures.

Leaving aside the possible participation of the solvent in Menshutkin reactions (4), we shall proceed from the conception of the structure of the activated complex shown in the scheme (Fig. 1) (5). According to this scheme, the bonds C

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$-R'$, $C-R''$, and $C-R'''$ lie in one plane. As for the N–C (or N–H) bonds in the amine, their arrangement relative to the plane passing through the nitrogen atom and parallel to the plane CR_3 depends on the structure of the amine molecule. Thus, if in the amine nitrogen is bonded to alkyl radicals or hydrogen atoms, these bonds are arranged pyramidally (with angles between them of 108°). If the radical is a phenyl nucleus, then the N–C bonds in the amine molecule lie in one plane, which, in our assumption, is parallel to the plane CR_3. Finally, for a complex with pyridine it is most probable that the pyridine ring is situated perpendicular to the plane CR_3.

We take the N···C distance in the activated complex to be equal to the length of the valence bond N–C (1.5 Å), although the possibility is not excluded (see (6)) that in reality it is somewhat larger. The approach of the N and C atoms to such a distance in itself causes a decrease in the volume of the activated complex, as compared with the volumes of the reacting molecules, by 8.4 Å^3, i.e., by 5 cm^3/mole for all Menshutkin reactions*. However, along with this volume effect, additional compressions arise upon formation of the activated complex, since the mutual approach of the two planes shown in Fig. 1 to a distance of 1.5 Å leads to the distances between some non-valently bonded atoms becoming smaller than the sums of their intermolecular radii (the new bond formed in the reaction, in our case N–C, is regarded as a valence bond).

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These additional compressions characterize (although, of course, not completely) the steric hindrance of the reaction. Under this treatment it turns out that Menshutkin reactions are sterically hindered to a greater or lesser degree.

Reactions with pyridine. In the pyridine molecule only the nitrogen atom lies in a plane parallel to the plane $CR'R''R'''$ and perpendicular to the nucleus (Fig. 2). The two "ortho"hydrogens do not reach this plane (by ~ 0.2 Å), and the two "ortho" carbons by 0.7 Å. In the reaction with methyl iodide, compression arises between the nitrogen atom and three hydrogen atoms (1.85 Å), between one H atom in CH_3J and an H atom in C_5H_5N (1.7 Å instead of 2.4 Å), and also between the C atoms in C_5H_5N and the H atoms in CH_3J. The sum of these compressions is 6.7 Å^3, i.e., 4 cm^3/mole; $\Delta v^{\neq}_{\text{mol}} = -9$ cm^3/mole**.

In the reaction with ethyl iodide, one compression $N ... H$ is replaced by $N ... CH_3$ (2.15 Å instead of 3.6 Å) and the interactions with the "ortho" carbons increase; $\Delta v^{\neq}_{\text{mol}} = -14$ cm^3/mole.

With further increase in the number of carbon atoms in the normal chain of the alkyl halide, the magnitude of $\Delta v^{\neq}_{\text{mol}}$ does not change.

In the reaction with isopropyl iodide, two compressions $N ... CH_3$ appear and the character of the interaction with the "ortho" carbons changes somewhat; $\Delta v^{\neq}_{\text{mol}} = -19$ cm^3/mole.

Reactions with trimethylamine. Let us consider the reaction of trimethylamine with isopropyl iodide. The most favorable mutual arrangement of the plane CR_3 and the pyramid $N(CH_3)_3$ is shown schematically in Fig. 3a (view along the C—J bond).

In the activated complex there will arise: compression $N ... H$ (1.85 Å), two compressions $N ... CH_3$ (2.15 Å), two compressions $CH_3 ... H$ (2.6 Å), and four compressions $CH_3 ... CH_3$ (2.7 Å). The calculated value of $\Delta v^{\neq}_{\text{mol}}$ is -24 cm^3/mol, i.e., larger than in the reaction of isopropyl iodide with pyridine. This value does not change when trimethylamine is replaced by triethylamine.

Reactions with dimethylaniline. In the free dimethylaniline molecule the plane of the phenyl nucleus is taken out of the plane

$$\begin{array}{c} C \\ N \\ | \\ C \end{array}$$

as a result of steric interactions of the two "ortho" hydrogens with the methyl groups. Upon entering into the activated complex, the phenyl nucleus

Fig. 3. Scheme of the structure of the activated complex (view along the C—J bond) in reactions: a –trimethylamine + isopropyl iodide, b –dimethylaniline + isopropyl iodide; 1 –centers of amine atoms, 2 –centers of haloalkyl atoms

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* Here and below, for calculating the compression upon formation of the activated complex, we use the following values of intermolecular radii (7): $R_H = 1.2$ Å; $R_N = 1.6$ Å; $R_C = 1.8$ Å; $R_{CH_3} = 2.0$ Å. The lengths of the C–H and C–C bonds are taken to be, respectively, 1.1 and 1.55 Å.

** Taking into account the compression upon formation of the C–N bond (see above).

Fig. 3. Scheme of the structure of the activated complex (view along the C—J bond) in reactions: a —trimethylamine + isopropyl iodide, b —dimethylaniline + isopropyl iodide; 1 —centers of amine atoms, 2 —centers of haloalkyl atoms

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will rotate in such a way that all carbon atoms lie in one plane. During this rotation two shortened distances (within the molecule) $CH_3 \ldots H$, equal to 2.5 Å, will arise, which will lead to a slight decrease in volume.

The mutual arrangement of the approaching planes in the reaction of dimethylaniline with isopropyl iodide is shown in Fig. 3b (view from the side of the atom J). In the activated complex the following compressions arise: one $N \ldots H$ (1.85 Å), two $N \ldots CH_3$ (2.15 Å), one $H \ldots H$ (2.1 Å), two $H \ldots C$ (1.9 and 2.1 Å), two $CH_3 \ldots H$ (1.8 and 2.0 Å), two $CH_3 \ldots C$ (2.0 and 2.1 Å), three $CH_3 \ldots CH_3$ (2.1 Å). The value of $\Delta v^{\neq}_{\mathrm{mol}}$ for this reaction is -44 cm^3/mol.

In the reaction of dimethylaniline with methyl iodide and ethyl iodide, the values of $\Delta v^{\neq}_{\mathrm{mol}}$ are respectively -19 and -29 cm^3/mol.

Replacement of an "ortho" hydrogen in the dimethylaniline molecule by a methyl group leads to some increase in $(-\Delta v^{\neq}_{\mathrm{mol}})$ for the reaction with methyl iodide (to 22 cm^3/mol).

Thus, the values of $(-\Delta v^{\neq}_{\mathrm{mol}})$ calculated according to the scheme set forth above reach, for some Menshutkin reactions, magnitudes of several tens of cubic centimeters per mole, which should lead to a very considerable acceleration of these reactions with increasing pressure according to equation (1). Such acceleration does indeed take place, as is evident from the data given in Table 1. The ratios of the rate constants

in each of the Menschutkin reactions investigated at a pressure of 3000 kg/cm^2 and at atmospheric pressure (K_{3000}/K_1), which characterize the acceleration of the reaction with increasing pressure, change quite in parallel with the quantities $(-\Delta v^{\neq}_{\mathrm{mol}})$ calculated by us for the reactions considered.

Thus, taking into account the steric hindrance of the process of formation of the activated complex (defined by us as the mutual approach of valence-unbound atoms to distances smaller than the sum of their intermolecular radii) makes it possible to explain qualitatively the different acceleration by pressure of Menschutkin reactions that differ in the structure of the amines and alkyl halides participating in them. In particular, the increase in the acceleration of these reactions by pressure becomes understandable on passing from CH_3J to C_2H_5J and iso-C_3H_7J, from C_5H_5N to $(CH_3)_3N$ and $C_6H_5N(CH_3)_2$, and also the identical pressure effect in the reactions of trimethylamine and triethylamine. Naturally, for a complete analysis of the influence of pressure on the rate of Menschutkin reactions it is necessary to take account of all components of $\Delta v^{\neq}$.

Table 1

Values of $\Delta v^{\neq}_{\text{mol}}$ and the influence of pressure on the rate constants of Menschutkin reactions (in acetone at 60°)

Reactions	$\Delta v^{\neq}_{\text{mol}}$, cm^3/mole	K_{3000}/K_1
$C_5H_5N + CH_3J$	−9	6.8 ([8])
$C_5H_5N + C_2H_5J$	−14	7.9 ([9])
C_5H_5N + n. C_4H_9J	−14	6.5 ([8])
C_5H_5N + iso-C_3H_7J	−19	9.6 ([8])
o-$CH_3C_6H_4N(CH_3)_2 + CH_3J$	−22	11.5 ([10])
$(CH_3)_3N$ + iso-C_3H_7J	−24	16.4 ([8])
$(C_2H_5)_3N$ + iso-C_3H_7J	−24	16.0 ([8])
$C_6H_5N(CH_3)_2$ + iso-C_3H_7J	−44	25.5 ([8])

We believe that the concepts developed in this work and the simple calculations carried out, despite their approximate character, make it possible to explain the very considerable acceleration of sterically hindered reactions with increasing pressure. It may also be assumed that the study of the kinetics of reactions at high pressures will prove useful for testing various ideas about the structure of the activated complex in these reactions.

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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* In addition to the data of Table 1, we note that in the reactions of dimethylaniline with CH_3J and C_2H_5J in methanol at 25° the values of K_{3000}/K_1 are, respectively, 10 and 12 ([11]).

Note: Figure translations are in progress. See original paper for figures.

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