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THE EFFECT OF PRESSURE ON THE RATE OF STERICALLY HINDERED REACTIONS

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THE EFFECT OF PRESSURE ON THE RATE OF STERICALLY HINDERED REACTIONS

There are a few experimental data that indicate a considerable acceleration of sterically hindered reaction with increasing pressure. Thus, tetramethylethylene was completely polymerized within 3 hours under 23,000 atm. at 300°C., while only 20% (1) of it was polymerized in 50 hours at the same temperature and under a pressure of 200 atm. The pressure also accelerates strongly the thermal conversions of tetrachloroethylene at 300°, yielding hexachlorobutadiene and hexachloroethane (2). In both cases shown, the observed acceleration of the reaction by means of pressure is connected only to a small extent with the increase of the concentration of starting substances; the determining factor is the increase of the reaction rate constant with the increase of pressure.

According to the theory of transition state the variation of the reaction rate constant with pressure is determined by the value of the change in volume in the formation of an activated complex (Δv^\ddagger) (3):

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

It is evident that the change in volume of the reacting molecules in the formation of an activated complex ($\Delta v \text{ mol}$) is an important component of the value Δv^\ddagger ; together with this, an important rôle may be played by other volume effects, in particular, by the variation of the solvent volume (if the reaction is carried out in solution) as a result of the different solvation of reacting molecules and of the activated complex ($\Delta v^\ddagger \text{ sol.}$). In the following work, only $\Delta v^\ddagger \text{ mol.}$ will be considered. At the same time we shall limit ourselves to the consideration of Menshutkin reactions for which it is possible to use, with sufficient certainty, a fixed geometrical

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.

the activated complex together with this volume effect, since the mutual approach to a distance of 1.5\AA of the two planes shown in Fig. 1 leads to the fact that the distances between some atoms that are not linked by valence bonds become smaller than the sum of their intermolecular radii (the new bond formed in the reactor, in our case N-C, will be considered as a valence bond).

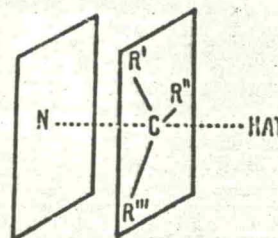


Fig. 1. Scheme of the structure of the activated complex in Menshutkin reactions.

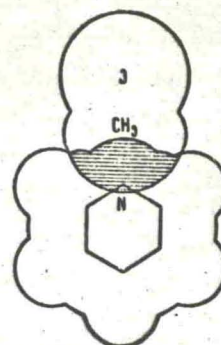


Fig. 2. Activated complex in the reaction of pyridine with methyl iodide. The compression is cross-hatched.

These additional compressions characterize (although, of course, incompletely) the steric hindrance of the reaction. It appears, from this consideration, that Menshutkin reactions are sterically hindered, to a greater or smaller extent.

Reactions with pyridine. In the pyridine molecule there is only one nitrogen atom situated in the plane parallel to the $CR'R''R'''$ plane and perpendicular to the ring (Fig. 2). Two "ortho"-hydrogens do not reach this plane (by $\sim 0.2\text{\AA}$), and two "ortho"-carbons - by 0.7\AA . A compression originates, in the reaction with methyl iodide, between nitrogen atom and three hydrogen atoms (1.85\AA), between one H in CH_3I and an H atom in C_5H_5N (1.7\AA instead of 2.4\AA) and also between C atoms in C_5H_5N and H atoms in CH_3I . The sum of these compressions is equal to 6.7\AA^3 , i.e. 4 cc/mol.;

$$\Delta v_{\text{mol.}}^{\neq} = -9 \text{ cc/mol.}$$

In the reaction with ethyl iodide, one compression $N\dots H$ is changed into $N\dots CH_3$ (2.15\AA instead of 3.6\AA) and there arise interactions with "ortho"-carbons; $\Delta v_{\text{mol.}}^{\neq} = -14 \text{ cc/mol.}$

The value $\Delta v_{\text{mol.}}^{\neq}$ does not change with further increase of the number of carbon atoms in the normal little chain of alkyl halide.

In the reaction with isopropyl iodide, there are two $N\dots CH_3$ compressions and the character of the interaction with "ortho"-carbons is somewhat changed,


$$\Delta v_{\text{mol.}}^{\neq} = -19 \text{ cc/mol.}$$

Reactions with trimethylamine. Consider the reaction of trimethylamine with isopropyl iodide. The most preferable mutual disposition of the CR_3 plane and $N(CH_3)_3$ pyramide is represented by the scheme in Fig. 3a (along the C-I bond).

In the activated complex originate the following compressions: compression $N\dots H$ (1.85\AA), two $N\dots CH_3$ compressions (2.6\AA) and four $CH_3\dots CH_3$ compressions (2.7\AA). The calculated value of $\Delta v_{\text{mol.}}^{\neq}$ is equal to -24 cc/mol. , i.e. larger than in the reaction of isopropyl iodide with pyridine. This value does not

** Including the compression in the formation of a C-N bond (see above).

change upon substitution of trimethylamine by triethylamine.

Reactions with dimethylaniline. In a free dimethylaniline molecule, the plane of benzene ring is drawn out from the  plane as a consequence of steric interactions of two "ortho"-hydrogens with methyl groups.

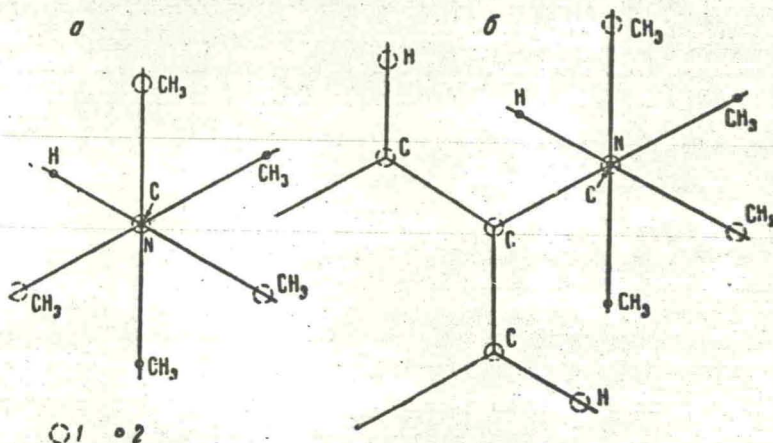


Fig. 3. Scheme of the structure of the activated complex (view along the C-I bond) in the following reactions: (a) -trimethylamine + isopropyl iodide; (b) dimethylaniline + isopropyl iodide; iodide; (1) -centers of the amine atoms; (2) -centers of the atoms of the alkyl halide.

The benzene ring is turned up, upon entering into an activated complex, in such a way that all carbon atoms are found in one plane. In this turning originate two contracted distances (inside the molecule) $\text{CH}_3 \dots \text{H}$, equal to 2.5\AA , which leads to a insignificant volume contraction.

The mutual disposition of the approaching planes in the reaction of dimethylaniline with isopropyl iodide is shown in Fig. 3b (from the side of the I atom). The following compressions originate in the activated complex: one $\text{N} \dots \text{H}$ (1.85\AA), two $\text{N} \dots \text{CH}_3$ (2.15\AA), one $\text{H} \dots \text{H}$ (2.1\AA), two $\text{H} \dots \text{C}$ (1.9 and 2.1\AA), two $\text{CH}_3 \dots \text{H}$ (1.8 and 2.0\AA), two $\text{CH}_3 \dots \text{C}$ (2.0 and 2.1\AA), three $\text{CH}_3 \dots \text{CH}_3$ (2.1\AA). The value of $\Delta V_{\text{mol.}}$ for this reaction is equal to -44 cc/mol.

The value of $\Delta^{\ddagger}v_{\text{mol.}}$ in the reaction of dimethylaniline with methyl iodide and ethyl iodide are equal, respectively, to -19 and -29 cc/mol.

The substitution of "ortho"-hydrogen in dimethylaniline molecule with a methyl group leads to some increase ($-\Delta^{\ddagger}v_{\text{mol.}}$) for the reaction with methyl iodide (up to 22 cc/mol.).

In this way, the values ($-\Delta^{\ddagger}v_{\text{mol.}}$), calculated according to the above scheme, attain for some Menshutkin reactions, the values of several tens cubic centimeters per mol. This should lead according to equation (1) to an extremely significant acceleration of these reactions with increase of pressure. This acceleration actually takes place, as seen from the data shown in Table 1. The relations of the rate constants for each of the investigated Menshutkin reactions under a pressure of 3000 kg/sq. cm. and at atmospheric pressure (K_{3000}/K_1), characterizing the acceleration of the reaction with the pressure increase, vary perfectly "symbatically" with the values ($-\Delta^{\ddagger}v_{\text{mol.}}$) calculated for the reactions under consideration.

Table 1

The value $\Delta^{\ddagger}v_{\text{mol.}}$ and the effect of pressure on the rate constants of Menshutkin reactions (in acetone at 60°C.).

Reactions	$\Delta^{\ddagger}v_{\text{mol.}}$ cc/mol.	K_{3000}/K_1
$\text{C}_5\text{H}_5\text{N} + \text{CH}_3\text{I}$	-9	6.8(8)
$\text{C}_5\text{H}_5\text{N} + \text{C}_2\text{H}_5\text{I}$	-14	7.9(9)
$\text{C}_5\text{H}_5\text{N} + \textit{n}\text{-C}_4\text{H}_9\text{I}$	-14	6.5(8)
$\text{C}_5\text{H}_5\text{N} + \textit{iso}\text{-C}_3\text{H}_7\text{I}$	-19	9.6(8)
$\text{o-CH}_3\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{CH}_3\text{I}$	-22	11.5(10)
$(\text{CH}_3)_3\text{N} + \textit{iso}\text{-C}_3\text{H}_7\text{I}$	-24	16.4(8)
$(\text{C}_2\text{H}_5)_3\text{N} + \textit{iso}\text{-C}_3\text{H}_7\text{I}$	-24	16.0(8)
$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 + \textit{iso}\text{-C}_3\text{H}_7\text{I}$	-44	25.5(8)

In this way, the calculation of the steric hindrance of the process of formation of the activated complex (determined by us as a mutual approaching of valence-bond-free atoms to distances smaller than the sum of their molecular radii) permits a quantitative explanation of the different accelerations by means of pressure of Menshutkin reactions that differ in the structure of participating amines and alkyl halides. The increase of acceleration of these reactions under pressure in the transition from CH_3I to $\text{C}_2\text{H}_5\text{I}$ and iso - $\text{C}_3\text{H}_7\text{I}$ *, from $\text{C}_5\text{H}_5\text{N}$ to $(\text{CH}_3)_3\text{N}$ and $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, and also the unique effect of pressure in the reactions of trimethylamine and triethylamine, becomes particularly clear. It is essential for a complete analysis of the effect of pressure on the rate of Menshutkin reactions to calculate all ΔV components.

We think that the notions developed in this work as well as the simple calculations shown, in spite of their approximate character, permit an explanation of the extremely important acceleration of sterically hindered reactions with increase of pressure. It may be assumed, together with this, that an investigation of the reaction kinetics under high pressures is helpful also for the verification of these or other presentations of the structure of the activated complex in these reactions.

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