

Translated From: Vestnik AN SSSR, Vol. 31, No. 5, 1961, pp. 39-45

MECHANISM OF CHEMICAL REACTIONS

AT HIGH PRESSURES

by

Dr. Chem. Sci. M. G. Gonikberg

Pages 10

Photocopy 1/10

Microfilm 0.80

62-16064

One of the important fields of chemistry at high and ultra-high pressures is the study of reaction rates and courses in order to elucidate the mechanism. Recently this field has been developed considerably, especially in its application to the study of liquid phase organic reaction mechanism.

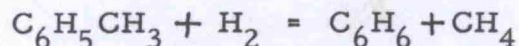
A simple case is the study of pressure effect on the rate and course of chemical processes in the gaseous phase at temperatures much above the critical. Under such conditions the partial pressures of the components are approximately proportional to their concentrations. Furthermore, the amount of any component in the gas mixture can be varied by adding this component (or any other component) to the mixture with corresponding pressure increase. In such a fashion the pressure effect is equivalent to changing the concentration ratio of reactants and products, i. e. the usual methods of reaction mechanism study may be applied. In these methods it is customary to compare the empirical reaction rate and product composition with theoretical values derived from an assumed reaction mechanism.

As an example for applying high pressure to reaction mechanism study in the gaseous phase at high temperatures we may bring the homogeneous destructive hydrogenation of alkylbenzenes, a reaction of practical significance. In this reaction an alkyl radical is cleaved from the alkylbenzene at 500-800 ° under hydrogen pressure in the absence of catalysts.

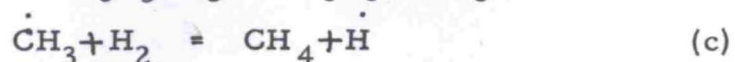
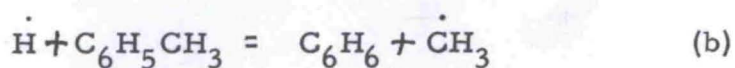
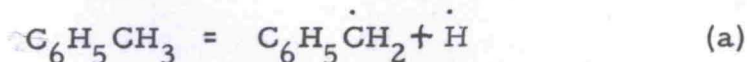
THIS TRANSLATION IS BEING FURNISHED FOR
PRIVATE USE AND RESEARCH ONLY. IT MAY
NOT BE SOLD OR PUBLISHED IN ANY FORM
WITHOUT THE PERMISSION OF THE AUTHOR.
PROPERTY OF SLA TRANSLATION CENTER

C15

For instance, benzene is obtained from toluene at a 90% yield. Previously it was thought that this is a bimolecular process:



However, studies at the Organic Chemistry Institute of the USSR Academy of Sciences have shown that for a wide range of pressures (up to 1350 atm) this is actually a complex radical-chain mechanism including the following steps:



Reaction (a) -the rupture of the weakest bond in toluene- is the source of atomic hydrogen which interacts with a second toluene molecule in reaction (b) forming a new radical which sustains the chain mechanism in reaction (c). Most interesting is reaction (b) in which a hydrogen atom extracts the CH_3 radical from toluene.

A mechanism including an analogous step was proposed for the homogeneous destructive hydrogenation of other alkylbenzenes. In accordance with this mechanism one may expect that increased hydrogen pressure will bring to an accelerated cleaving of the alkyl group from the benzene nucleus. This was confirmed in isopropylbenzene: increasing the pressure from 200 to 600 atm (at 475°), the propane content of the hydrocarbon products increased from 21 to 59%.

As the pressure increases the rate of the gas phase reaction gradually deviates from calculated rates obtained from kinetic expressions derived for normal pressures. The classical theory of activated collisions explains this deviation on the basis of the decreasing free mean path between colliding molecules with increasing pressure until it becomes proportional

to the molecular diameter itself. Various corrections for this effect yield positive results only for moderately dense gaseous mixtures. With further increase in pressure (in particular at temperatures not much above the critical), the corrections become unsatisfactory due to the absence of a correct equation of state.

The following is an example for such a deviation. In 1956, the English workers R. Lard, A. Morrel and L. Sid published a paper in the issue of the Discussions of the Faraday Society devoted to the physico-chemical processes at high pressures on the kinetics of thermal polymerization of ethylene at 200-360° at 1200-2000 atm. According to the proposed reaction mechanism the polymerization rate should have been proportional to the squared concentration of ethylene. The empirical kinetic equation gave completely unexpected results: the exponent of the ethylene concentration was ten times greater (about 20). This discrepancy was attributed to the varying rate constant with increasing pressure.

The effect of pressure on rate constants is of special interest in this field. To analyze this effect the structure and properties of the activated complex must be known. In distinction to the activated collision theory, the theory of transition state considers the interaction of two or more particles, not as an instantaneous act, but as a lasting process with accompanying energy change in the system. The state of the system in which the potential energy equals the peak of the reaction energy barrier is called transition state or activated complex. A better knowledge of the transition state is of enormous importance for chemistry, since the structure and properties of the activated complex determines the mechanism of the elementary act in a chemical process.

Pressure has a considerable effect on liquid phase rate constants.

This is explained completely by the transition state theory. The rate constant k is proportional to the equilibrium constant K^\ddagger of the reaction in which the activated complex is formed from the initial reactants

$$K = \kappa \frac{KT}{h} K^\ddagger, \quad (1)$$

where K and h are the Boltzmann and Planck constants, respectively, and κ is the transmission coefficient which indicates the probability that the activated complex, upon reaching the reaction barrier peak, will pass toward the reaction products. Taking the logarithm of equation (1) and differentiating with regard to the pressure at constant temperature (assuming that κ is independent of pressure), we obtain

$$\frac{\partial \ln k}{\partial P} = \frac{\Delta v^\ddagger}{RT}, \quad (2)$$

where Δv^\ddagger is the volume change during the formation of the activated complex from the reactants, R is the gas constant, T is the absolute temperature.

From equation (2) it is possible to determine the volume change during the formation of the activated complex by experimental measurement of the rate constant dependence on pressure, and, consequently, also the volume of the activated complex itself (provided the volume of the reactants is known). On the other hand, Δv^\ddagger can be estimated in some cases by means of reasonable models for the transition state. Comparison of the measured and calculated value of Δv^\ddagger enables one to verify the model and the implied structure of the activated complex.

From equation (2) the following deductions are made. The rate of unimolecular reactions (in which the volume of the activated complex is larger than the reactant because of the stretching bond) decreases with increasing pressure. The rate of a bi- or multi-molecular reaction,

however, increases with increasing pressure due to the contraction in the formation of the transition state.

Sometimes even an approximate estimation of Δv^\ddagger enables one to assign a probable reaction mechanism. For instance, it was shown in the Institute of Organic Chemistry that the rate of isomerization of methylcyclopentane into cyclohexane in the presence of aluminum chloride is considerably slower under hydrostatic or nitrogen pressure. An approximate estimate of the pressure effect on the rate constant k from equation (2) excluded the possibility that the rate retardation is due to pressure alone. This explanation would be plausible if the transition state volume of the methylcyclopentane molecule is increased tens of percents ($\Delta v \approx 30 \text{ cm}^3/\text{mole}$). However, this is not possible. It is concluded that the isomerization includes a stage in which the volume is increased considerably and that the rate of attaining the equilibrium of this stage is rate determining for the overall process. This stage may be the dehydrogenation: $\text{C}_5\text{H}_9\text{CH} \rightleftharpoons \text{C}_5\text{H}_7\text{CH}_3 + \text{H}_2$ (N. D. Zelinskii and M. B. Turovoi-Polyak, 1932).

To confirm this hypothesis, the effect of hydrogen pressure on the rate of methylcyclopentane isomerization was studied. If the dehydrogenation is accompanied by hydrogen gas liberation and if the equilibrium of this reaction determines the rate of isomerization, hydrogen should be more effective than nitrogen or hydrostatic pressure in retarding the rate of isomerization. This was confirmed by experiment. For instance, at 80° and a nitrogen pressure of 600 atm the yield of cyclohexane from methylcyclopentane in 3 hours was about 40%, whereas at the same pressure of hydrogen the yield was only 10%. Subsequent studies have shown that this mechanism prevails also in the isomerization of five- and six-membered rings

even in the presence of a heterogeneous catalyst.

In this example the estimation of Δv^\ddagger was very crude, so to speak only qualitative. Frequently, this factor can be calculated with sufficient accuracy. Thus, the comparison between experimental and theoretical results (as obtained from equation (2)) enables one to decide on the validity of a certain activated complex model. Let us apply this principle for two diene syntheses -the isomerization of isoprene and the dimerization of cyclopentadiene. As is well known for diene syntheses, two reaction mechanisms are possible. A biradical mechanism in which the activated complex resembles an unsaturated hydrocarbon with an open bond, or a mechanism with a cyclic intermediate resembling the dimer.

The reactions were studied between the pressure range of 1 to several thousand atmospheres (whereby the reaction rate increases enormously with increasing pressure) and the following interesting results were obtained. In the dimerization of isoprene the volume of the activated complex is equal to the volume of the corresponding unsaturated hydrocarbon with an open bond, attesting to the biradical mechanism (Ch. Wholling and J. Peisakh). In the second reaction -the dimerization of cyclopentadiene- the volume of the activated complex is close to the volume of the reaction product -dicyclopentadiene. It was concluded that the latter reaction has a cyclic activated complex intermediate (B. Raistrick, R. Sapiro and D. Newitt, M.G. Gonikberg and L. V. Vereshchagin). Here the application of elevated pressures was extremely convenient for the study of activated complex structure.

In solution chemistry the reaction mechanism is usually solvent dependent. The medium effect on rate and reaction course is a cardinal problem of chemistry. Essentially, this involves the participation of the solvent in the transition state, or its effect on the properties of the activated complex. For instance, in all heterolytic reactions the activated complex is

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.

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

Menshutkin reaction is a convenient example since the activated complex model is known usually with sufficient accuracy to estimate Δv^\ddagger for the overlapping sphere of the van der Waals radii. This work and the subsequent experimental investigations, performed by the author and B. S. Elyanov in the Institute of Organic Chemistry, have confirmed in full the above hypotheses and allowed the introduction of the supposition that in some reactions the volume contraction during activated complex formation is a measure of steric hindrance.

An interesting application of high pressure is in the field of collective interactions such as polymerization. Let us assume that the activated complex contains a large number of molecules, n . In that case Δv^\ddagger is roughly $(n-1)$ times larger than in a bimolecular reaction. A polymorphic transition may serve as an example. R. Ventorf reported in the XVII International Congress on Pure and Applied Chemistry on the effect of pressure on the reaction rate of the polymorphic transition of diamond into graphite at 1700-2200°. Pressure retards the reaction significantly (the experiments were performed in a vacuum and at 20,000 atm). Ventorf estimated $\Delta v^\ddagger \approx 168 \text{ cm}^3/\text{gr atom}$, which is 50 times more than the volume occupied by 1 gr atom of carbon in crystalline form. It was concluded that the polymorphic transition of diamond to graphite is a collective act in which a large number of carbon atoms participate.

The mentioned polymorphic transition is characterized by volume expansion during transition state formation (Δv^\ddagger positive). For Δv^\ddagger negative the reaction rate is expected to increase with increasing pressure, such as in polymerizations. Pressure effect studies may indicate the fact of collective interaction and also give some information on the number of participants in this interaction.

There is an increasing number of publications in many countries on the pressure effect on reaction rate and course. It is desired that this new approach for reaction mechanism investigation be applied on a wider basis in the chemical laboratories of the scientific institutions and universities of our country.

W. J. T. Lincoln Laboratory

APR 8 1951

Reaction - Kinetics