

55-0076

GONIMG-55-0076

RETENTION COPY

M. 140

O. T. S.

59 18 750

U. S. DEPT. OF COMMERCE  
WASHINGTON 25, D. C.

Application of high pressures to the  
investigation of the mechanism of chemical reactions

M.G. Gonikberg

Uspekhi Khimii, 1955, 24, 14-31

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

20-7  
Microfilm \$2.40  
Photocopy \$3.30

SUMMARY

The theory of the effect of high pressure on the equilibria and rates of chemical reactions is briefly given. This theory is then applied to the results of certain experimental investigations of chemical reactions at high pressure, and is found to throw some light on their mechanisms. Reactions dealt with include thermal and catalytic cracking of paraffins, destructive hydrogenation of aromatic hydrocarbons, addition of alkyl halides to tertiary amines or pyridine in acetone, thermal polymerisation of styrene, and isotopic ion-exchange reactions. (Author)

"a"

Application of high pressures to the investigation of the  
mechanism of chemical reactions

M.G. Gonikberg

Uspekhi Khimii, 1955, 24, 14-34

Nature and basis of the method

Investigations of the mechanism of chemical reactions vary widely in their approach to the solution of a particular problem. Some of them aim at comparing the relations between certain atoms or groups of atoms before and after reaction. They include many investigations using labelled atoms. The aim of other investigations is the study of the effect of different variables in a chemical reaction on the course of the reaction; the observed changes can be compared with expectations on the basis of this or that scheme of reaction mechanism. Belonging to this group of investigations, in particular, are kinetic studies, which we will discuss in rather more detail.

Among the variables of a chemical process are the concentration of the components, the temperature, the pressure (or volume) and the duration of the process. The study of the effect of changes in concentration of the reactants on the velocity of the process is the standard kinetic method for investigating the mechanism of reactions. The change in the velocity of the process with temperature allows one to determine the value of the energy of activation (often called the "apparent" energy of activation) which in a series of cases indicates the character of the rate-determining step of the overall process.

Changes of pressure in gas-phase reactions are normally considered as equivalent to changes in concentration. This, however, is only true (and that approximately) for mixtures of gases at low pressures, and at temperatures considerably greater than the critical temperatures of the given gases; in other words, the concentration is proportional to the overall pressure only in the case of ideal gases. High pressure is an important parameter, whose change has a specific influence not only on the velocity, but also on the course of chemical processes. This is especially clearly seen in the case of liquid-phase reactions where the influence of pressure is only linked to an insignificant degree with changes in concentration.

If we know the laws of the effect of high pressure on the course of reactions of various types, we can apply them to a study of the mechanism of chemical processes.

The high-pressure approach to investigation of the mechanism of a chemical reaction consists essentially in studying the effect of high pressure on the velocity and the course of the reaction, and comparing the resulting data with results expected on the basis of possible schemes for the mechanism of reaction.

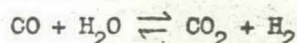
At present an overwhelming majority of investigations of chemical reactions at high pressure are carried out in the region of up to 1000 atm. Only in a few cases have pressures up to 10-12,000 atm. been applied. The results of these investigations indicate that at pressures of a few hundreds or thousands of atmospheres, as a rule, fundamental changes in reactivity do not occur. This is primarily due to the absence of any significant deformation of the molecules (atoms), radicals and ions at these pressures. In fact, from examination of compressibility data one may infer that significant deformation of molecules (atoms) of most substances occurs only at pressures of the order of tens of thousands of atmospheres.

The ability of substances to take part in chemical reactions is known to depend also on the reaction medium, and, in particular on its electrical and other physico-chemical properties. If we wish to use high pressures for the study of the mechanism of chemical processes, it is desirable in most cases that the influence of the medium on the course of the process which is to be studied should not depend substantially on the pressure. It is found that the variation of most physico-chemical properties of liquids in the range of pressure up to a few thousand atmospheres is not generally very significant. Transport phenomena are an exception to this rule; for example, the viscosity of liquids increases rapidly with an increase in pressure. This is one of the reasons why an increase in pressure can transfer a reaction from the field of kinetics to that of diffusion. On the basis of the above-mentioned considerations and the available experimental data, it is generally advisable to use pressures up to 2,000-3,000 atm. to investigate the mechanism of chemical reactions.<sup>1</sup>

In the first place we must examine the question of the effect of high pressure on the velocity and the course of various chemical processes. We commence our discussion by considering the problem of chemical equilibrium.

For a mixture of ideal gases, the shift in chemical equilibrium with a change in pressure is determined by the change in the number of moles during the reaction on the basis of the stoichiometric equation for the reaction. If the reaction proceeds with a diminution in the number of moles, the equilibrium concentration of reaction products will increase with an increase in pressure, or vice versa.

For a mixture of real gases, the relation between the chemical equilibrium and the pressure is more complicated and depends on the compressibility of the mixture at various pressures and compositions. Thus, for example, the water gas equilibrium



is shifted to the left by an increase in pressure, despite the fact that this reaction proceeds with no change in the number of molecules.

For reactions in the liquid phase, the influence of pressure on chemical equilibrium is less significant than for gaseous systems. However, in isolated cases it may prove to be quite marked. If, for example, the reaction  $\text{A} + \text{B} + \dots \rightleftharpoons \text{P} + \text{Q} + \dots$  is accompanied by a decrease in volume ( $-\Delta V$ ) of 25 cc/mole, the equilibrium constant

$$K_N = \frac{N_P \cdot N_Q \dots}{N_A \cdot N_B \dots}$$

at 100°C is increased 135 times when the pressure is increased from 1 to 6000 atm. Such large values of  $\Delta V$  are frequently found in liquid-phase reactions, proceeding with a diminution in the number of moles. Thus, for the dimerisation of cyclopentadiene at 40°C the value of  $\Delta V$  is -33.2 cc/mole at 1 atm., -31.1 cc/mole at 500 atm., and -27.6 cc/mole at 1000 atm.<sup>2)</sup>

In the solid phase, the change of volume during a reaction, which determines the pressure-dependence of chemical equilibrium, is usually even smaller than in liquids. Some exceptions to this rule are found in particular in decomposition reactions of solids, where not only solid but also gaseous products are formed, and are removed from the sphere of reaction.

We will not consider here the dependence of chemical equilibrium on pressure in gas - liquid, gas - solid and liquid - solid systems, nor in polyphasic systems (in this connection see <sup>3)</sup>).

<sup>1</sup> For the investigation of some problems concerning the mechanism of reactions (e.g., steric hindrance) very much greater pressures should be used (see 1)).

<sup>2</sup>  $N$  = mole fraction.

In parallel reactions the equilibrium is of course displaced towards the products whose formation is completed with the greatest decrease of volume.

The effect of pressure on chemical equilibrium may lead to a substantial change in the composition of the products, i.e. in the course of the reaction. We will give some examples. In multistage polymerisation, high pressure shifts the equilibrium towards products with a higher molecular weight 4). The reversible polymerisation of butyraldehyde and isobutyraldehyde under pressure is described in the literature. 5), 6) The polymers, obtained at pressures of up to 12,000 atm., slowly depolymerised at atmospheric pressure to give the original aldehydes. It appears that in this case polymerisation and depolymerisation are mainly associated with the effect of high pressures on the chemical equilibrium.

It is further known that many metal carbonyls are stable at their formation temperature only under conditions of high pressure (e.g.  $\text{Co}(\text{CO})_4$ ). Another example is the action of carbon monoxide on cobalt iodide at room temperature under pressure to give the unstable compound  $\text{CoI}_2 \cdot \text{CO}$ , which decomposes at atmospheric pressure. 7)

Because high pressure guarantees the stability of a series of unstable compounds, it has a marked effect on the course of certain catalytic reactions. For example, in the Oxo synthesis (the synthesis of alcohols from olefines, hydrogen and carbon monoxide over a cobalt-containing catalyst), the catalyst is probably not the cobalt itself, but a carbonyl or hydrocarbonyl of cobalt, which is only stable at high pressure. It is very characteristic that at atmospheric pressure the hydrocondensation of olefines with carbon monoxide and hydrogen produces not oxygen-containing compounds, but mainly hydrocarbons. 8), 9) A similar pressure-dependence of the composition of the products is found in syntheses starting from carbon monoxide and water. 10)

Many other examples of the effect of high pressure on the course of reactions by shifting the position of equilibrium could be given.

We will now examine the question of the influence of high pressure on the velocity of chemical reactions. It has already been mentioned above that in a mixture of ideal gases the concentrations of the components are proportional to the pressure; this also determines the pressure-dependence of the velocity of gaseous reactions when the pressure is small and the temperature is sufficiently high. In such cases the velocity constant itself does not depend on the pressure.

In real gaseous systems the dimensions of the molecules cannot be neglected in comparison with the lengths of their mean free paths. An approximate treatment of this case on the lines of the theory of active collisions for second order reactions leads to the conclusion that the velocity constant increases with the pressure.

It will be remembered that according to the theory of active collisions the number of two-component collisions leading to reaction is equal to  $z_0 e^{-E/RT}$ . Here,

$$z_0 = n_1 n_2 (r_1 + r_2)^2 \sqrt{\frac{8kT(M_1 + M_2)}{M_1 M_2}} \quad (I)$$

where  $n_1$  and  $n_2$  are the numbers of molecules of gases 1 and 2 in 1 cc;  $r_1$  and  $r_2$  are the radii of these molecules;  $M_1$  and  $M_2$  are their molecular weights; and  $E$  is the energy of activation. When  $n_1 = n_2 = 1$ , the number of active collisions is the velocity constant for the reaction,  $k$ .

When the pressure is increased, appropriate corrections must be introduced into equation (I). Thus, for example, according to the van der Waals correction, the number of binary collisions in the moderately compressed gas,  $z_0'$  is given by the equation:

$$z_0' = z_0 \cdot \frac{1}{1 - \sum n_i b_i} \quad (II)$$

where  $b_1$  is the constant of the van der Waals equation, which is equal to four times the volume of the molecule. It is easy to see that equation (II) leads to the conclusions that the velocity constant increases with an increase in the pressure. This is confirmed in particular by experimental data on the thermal decomposition of hydrogen iodide under pressure.<sup>11)</sup> The velocity constant for first-order gaseous reactions should, it appears, decrease slightly at high pressures (see 3)).

Nevertheless the effect of pressure on the velocity of most reactions in real gases is to a large extent governed by the change in concentration of the reactants. Thus, in the previously mentioned investigation of the decomposition of HI it was found that in the pressure range investigated (approximately up to 250 atm.) the velocity of the reaction increased 39.6 times (increase of the original concentration of HI by a factor of 21.9 and an increase of the velocity constant by a factor of 1.8).

For liquid-phase reactions, on the other hand, the change in the concentration of the reactants caused by the increase in pressure is comparatively small, owing to the much smaller compressibility of liquids in comparison with gases. Here the decisive factor is the pressure-dependence of the velocity constant for the reaction. In so-called normal reactions in the liquid phase, an increase in pressure up to 3000 atm. causes the velocity constant to increase by a factor of 1.5 to 2, and up to 5000 atm. by a factor of 2-3. The velocity constants of "slow" reactions increase considerably more rapidly with an increase in the pressure, often by a factor of 10-15 or more when the pressure is increased to 5000 atm. Decomposition reactions in the liquid phase are often retarded by an increase in the pressure (see 12)).

It may be noted that the pressure-dependence of the velocity constant of a reaction in the liquid phase is satisfactorily explained and also (in the simplest case of addition reactions) quantitatively interpreted by the transition state theory (see 13), 3)).

Application of the theory of transitional states leads to the equation:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (III)$$

where  $\Delta V^\ddagger$  is the change in volume associated with the formation of the activated complex (per mole).

In reactions between two or more substances the molar volume of the activated complex is, as a rule, smaller than the sum of the molar volumes of the reactants, since the separation distance between the molecules (atoms) composing the activated complex only slightly exceeds the normal length of chemical bonds. Therefore, according to equation (III), the velocity constant of such reactions should as a rule increase with the pressure.

For unimolecular decomposition reactions the bond undergoing rupture in the activated state is stretched; consequently, the molar volume of the substance in its activated state is rather larger than in its usual state. The velocity constant of such reactions, according to equation (III), should decrease slightly as the pressure is increased.

The effect of pressure on the velocity of a reaction can lead to considerable changes in the composition of the products of a complex process, i.e. on the course of the reaction. As an example may be cited the copolymerisation of ethylene and carbon monoxide in cyclohexane.<sup>14)</sup> On increasing the pressure from 1.6 to 306 atmosphere, not only was the molecular weight of the polymer increased (from 280 to 3400), but also the proportion of combined CO in the polymer became larger (from 12.6 to 41.8%), i.e. the chemical composition of the polymer was altered. The production of the highly polymerised polyethylene (polythene) in the presence of a very small amount of oxygen at pressures of more than 1000 atm.<sup>15)</sup> is apparently likewise dependent on such a marked acceleration of the chain-polymerisation of ethylene as a result of the application of high pressure.

It should be noted that in most cases which we came across, we are dealing with a simultaneous effect of high pressure on the equilibrium position and the velocity of chemical reactions. If, for example, during the atmospheric oxidation of propane the pressure is raised from 5 to 65 atm., the composition of the resulting mixture of alcohols is considerably changed; the percentage of methyl and ethyl alcohols falls from 95.4 to 59.9%, while the percentage of n-propyl and isopropyl alcohols rises from 4.6 to 40.1%, which is nearly a ten-fold increase.<sup>16)</sup> Such an effect of an increase in pressure may be explained by kinetic factors (higher reaction velocity, caused by the diminution of volume) together with thermodynamic factors (a shift of the equilibria of parallel reactions towards those products which are formed with a diminution of volume). Another example is furnished by the thermal decomposition of methyl alcohol at 350°C.<sup>17)</sup> Increasing the pressure from 600 to 6000 atm. led to the following changes in the composition of the gaseous reaction products:

Composition of gas (%)	(CH <sub>3</sub> ) <sub>2</sub> O	CH <sub>4</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>
at 600 atm.	8.05	39.8	31.2	10.95	7.3
at 6000 atm.	46.3	27.0	13.7	2.9	7.8

The marked increase in the percentage of dimethyl ether in the reaction products as the pressure is increased is similarly caused by the effect of pressure on the equilibrium and the velocity of the various reactions which take place during the thermal decomposition of methanol.

In the preceding section we have examined briefly the basic mechanisms of the effect of high pressure (up to a few thousand atmospheres) on the velocity and the course of chemical reactions. Higher pressures (of the order of tens of thousands of atmospheres) may lead to far-reaching qualitative changes in the reactivity of substances and therefore these pressures cannot generally be used to investigate the mechanism of chemical reactions.

From the data given here, it may be gathered that in a number of cases even the sign of the pressure effect (+ or -) allows us to determine the character of the rate-determining step in a complex process. Analysis of quantitative changes (reaction velocity or yield of products) caused by an increase in pressure makes it possible to choose between various schemes describing the mechanism of the reaction in question. Finally, qualitative data on the change in reaction products as a result of increased pressure also provide a very useful basis for choosing the most likely reaction mechanism.

We now pass on to an account of some results of the investigation of the mechanism of chemical reactions using high pressures.

#### Investigation of the Mechanism of Reactions in the Gaseous Phase

##### A) Thermal Cracking of Paraffinic Hydrocarbons

Previous investigations have established that at low pressures (of the order of a few atmospheres) the velocity of thermal cracking increases with an increase in the pressure in most cases which have been investigated (decomposition of ethane at 750 and 800°C.<sup>18)</sup>, decomposition of propane at 600°C.<sup>19)</sup>, decomposition of n-butane at 575°C.<sup>20)</sup> and 600°C.<sup>19)</sup>, decomposition of n-pentane at 580°C.<sup>21)</sup>); only in one investigation<sup>22)</sup> was high pressure observed to retard the cracking of ethane at 635°C.

In some recent work<sup>23)</sup>, the effect of high pressure on the velocity of the thermal cracking of n-hexane and n-heptane was investigated. Some results of this investigation are shown in Table 1.

Table 1

The thermal cracking of *n*-hexane and *n*-heptane (duration of experiment 3 hours).

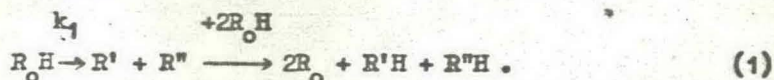
Temperature (°C)	Mean pressure of hydrocarbon (atm.)	Yield of liquid products	Unreacted hydrocarbon
		(% of initial hydrocarbon)	
		<i>n</i> -hexane	
430	300	40.0	11.3
430	560	54.3	20.0
430	910	71.8	32.4
430	1680	80.0	39.4
420	160	78.5	52.9
420	860	89.7	68.5
		<i>n</i> -heptane	
420	620	68.3	19.7
420	940	78.9	28.6
420	1150	88.5	39.8
420	1860	94.2	56.6
420	3100	96.7	59.3

From the data of Table 1 it may be seen that high pressure retards the thermal cracking of paraffinic hydrocarbons. This inhibition cannot be attributed to a change in the chemical equilibrium. This is especially borne out by comparison of the results of thermal and catalytic cracking carried out in the course of the same work (see below)\*; such a comparison shows that during catalytic cracking the decomposition of hydrocarbons and the production of gaseous and volatile liquid products proceed considerably faster than in thermal cracking under the same conditions of temperature and pressure. A similar retardation of the cracking of paraffins was also found in an investigation of the decomposition of propane at 600°C and 98 and 197 atm., and also of *n*-butane at 550°C and 104 and 172 atm.<sup>24)</sup>

It may be noted that as the pressure increases the yield of volatile products from the cracking decreases, and the proportion of higher-boiling hydrocarbons increases (in comparison with the original)<sup>25)</sup>.

From such investigations we gather that at low pressures (a few atmospheres) cracking is normally speeded up as the pressure is increased, and at high pressures (hundreds or thousands of atmospheres) it is retarded.

In one paper<sup>25)</sup> a chain-reaction scheme for the decomposition of paraffins has been put forward. It was assumed that the original hydrocarbon molecule  $R_0H$  first of all split to give smaller radicals which, reacting further with  $R_0H$  form the radical  $R_0$ :



The radical  $R_0$  may decompose to give a smaller radical  $R_1$  and an olefine:



It is also possible that  $R_0$  reacts with olefine molecules to produce longer radicals. Such reactions apparently play an important rôle in the cracking of paraffins mixed with olefines, but they cannot serve as the principal chain-breaking step in the absence of any addition, especially at high pressures (see<sup>26)</sup>); therefore they are not further considered.

\* Translator's note: while it may be true that the above-mentioned retardation is not caused by a change in equilibrium, this is not borne out by the facts adduced here.



The radicals produced by reaction (2) may in turn react with molecules of the original hydrocarbon, thereby continuing the chain reaction:



(see the right-hand part of equation 1).

Finally, the chain may be terminated, either on the wall of the reaction vessel ( $k_4$ )<sup>2</sup>, or by reaction (recombination or disproportionation) of the radicals  $R_0$  ( $k_5$ ),  $R_0$  and  $R_1$  ( $k_6$ ) and  $R_1$  ( $k_7$ ).

On the basis of this scheme we obtain the following equation for the rate  $w$  of the cracking process, referred to the concentration of the original hydrocarbon ( $R_0H$ ):

$$\frac{w}{(R_0H)} = \frac{2k_1k_2}{k_4 + \left[ k_5 + \frac{k_2k_6}{k_3} \cdot \frac{1}{(R_0H)} + \frac{k_2^2k_7}{k_3^2} \cdot \frac{1}{(R_0H)^2} \right] (R_0)} \quad (IV)$$

where round brackets denote concentrations.

Analysis of equation (IV) for various cases of selective reaction-chain-breaking leads to the following results:

a) When reaction chains normally terminate on the walls, the velocity of the reaction (in the units indicated) does not depend on the pressure (if we do not take into account the effect of pressure on the value of the rate constant). Consideration of the change in the velocity constant leads to the conclusion that the reaction is negligibly retarded by an increase in the pressure.

b) When reaction chains mainly end on radicals of the original hydrocarbon, the reaction is retarded by pressure:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1}{k_5} k_2 (R_0H)^{-\frac{1}{2}}} \quad (V)$$

c) when reaction chains mainly terminate on short radicals, the reaction is accelerated by pressure:

$$\frac{w}{(R_0H)} = \sqrt{\frac{2k_1}{k_7} k_3 (R_0H)^{\frac{1}{2}}} \quad (VI)$$

d) when reaction chains mainly finish by reaction of  $R_0$  with  $R_1$ , the rate of reaction is independent of pressure.

The results given here lead to the conclusion that at low pressures the breaking of reaction chains in the thermal cracking takes place mainly by reaction of "short" radicals ( $R_1$ ), while at high pressures it is mainly due to reactions of "long" radicals ( $R_0$ ). This assumption is confirmed by inspection of the ratio of the probabilities ( $\delta$ ) of these two ways of chain-breaking:

$$\frac{\delta(R_0)}{\delta(R_1)} = \frac{k_3^2 \cdot k_5}{k_2^2 \cdot k_7} (R_0H)^2 \quad (VII)$$

It follows from equation (VII) that the ratio of the probabilities of chains terminating on  $R_0$  and on  $R_1$  is proportional to the square of the concentration of the original hydrocarbon, i.e. it increases very rapidly with an increase in pressure, which is a qualitative confirmation of the hypothesis given above. An approximate quantitative treatment of this question<sup>25)</sup> also led to the conclusion that an increase in pressure, say from 5 to 500 atm., can cause the indicated change in the chain-breaking process.<sup>26)</sup>

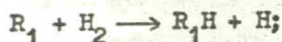
\*  $k$  = velocity constant.

25) Analysis of the effect of pressure on the value of the velocity constant itself does not alter this conclusion.

It may be noted that in one of the investigations mentioned above<sup>23)</sup> interesting data were obtained on the effect of hydrogen pressure on the velocity of thermal cracking of paraffins. It was found that at low pressures of hydrogen the cracking was retarded, but a marked increase in the pressure of hydrogen led to some speeding-up of the process. Thus, for examples, the following results were obtained from the experiments with n-heptane:

Partial pressure of hydrogen (atm.)	—*	250	640	1100
Yield (wt.-% of original heptane)				
(a) unreacted n-heptane		33.3	71.8	65.1
(b) gaseous and liquid products boiling below 48°C		37.7	20.5	27.5
				38.5

Carrying out the cracking under a pressure of hydrogen prevents not only polymerisation reactions, but also destructive alkylation. It appears that this also provides an explanation for the increased proportion of unreacted n-heptane found on carrying out the process under 250 atm. of hydrogen, in comparison with thermal cracking in the absence of hydrogen. It may be supposed that the reason for the increased cracking on further increasing the pressure of hydrogen is that part of the hydrogen enters the reaction chain according to the equations:



A similar acceleration of the thermal decomposition of hydrocarbons as the partial pressure of hydrogen is increased (from 200 to 400 mm. Hg.) has recently been observed in the case of propane<sup>27)</sup>.

Thus, the use of high pressures for investigating the mechanism of the thermal cracking of paraffins has proved fruitful, and has allowed an explanation of some new features of this process.

#### B) Homogeneous Destructive Hydrogenation of Aromatic Hydrocarbons.

When the kinetics of the homogeneous destructive hydrogenation of toluene under a high pressure of hydrogen was first investigated,<sup>28)</sup> it was found that the velocity of this reaction is independent of the metal packing and in the first approximation may be expressed by the equation for a bimolecular reaction between toluene and hydrogen. The experimentally determined value of the energy of activation was 66,000 cal/mole; the pre-exponential term of the Arrhenius equation was found to be 60 times larger than that calculated from the theory of active collisions.

A recent investigation of the homogeneous destructive hydrogenation of toluene at 455-490°C. with pressures of hydrogen up to 1350 atm. led to the following results<sup>29)</sup>:

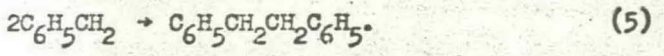
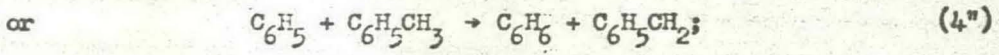
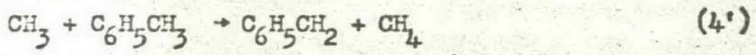
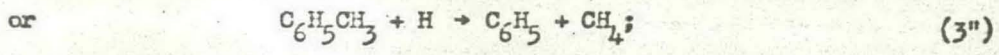
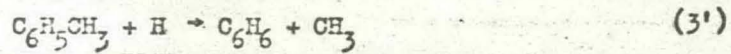
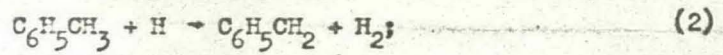
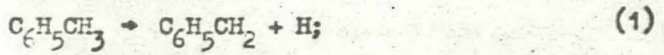
- The velocity of the reaction (as followed by the yield of benzene) increases with increasing hydrogen concentration, but somewhat less than proportionally. Thus, when the concentration of hydrogen was increased 3.8 times, the velocity of the reaction increased about 2.5 times.
- The reaction velocity is approximately proportional to the square root of the toluene concentration.
- The surface area of the wall of the reaction vessel and the surface area/volume ratio have no significant effect on the reaction velocity.

\* In the absence of hydrogen under a total pressure of 130 atm.

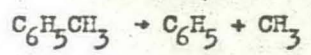
d) Diphenyl and ditolyl were found among the reaction products.

e) It was established that under the conditions of reaction dibenzyl underwent very considerable destructive hydrogenations.

It may be noted that earlier, in experiments on the thermal decomposition of toluene at 470°C under pressure (30), ditolyl was also found in the reaction products. Ref. 31) describes an investigation of the initial period of thermal decomposition of toluene (up to 1%) on passing toluene vapour through a quartz tube at 738-864°C followed by rapid cooling of the reaction products. The gaseous reaction products consisted of 59-62% hydrogen and 38-41% methane. The liquid products were benzene and dibenzyl (1 mole of dibenzyl per mole of gas liberated). On the basis of these facts it was decided that the reaction proceeds by the following stages:

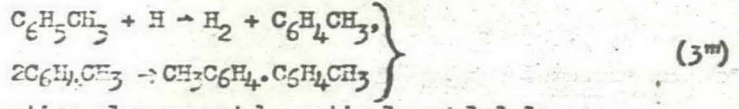


The assumption that the breaking of the carbon-carbon bond



is the first step in the reaction could not explain the high concentration of hydrogen in the reaction products, while the above-mentioned scheme satisfactorily explains the production of hydrogen and the amount of dibenzyl produced.

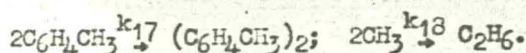
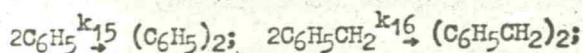
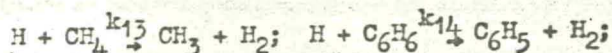
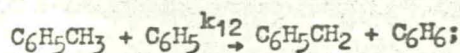
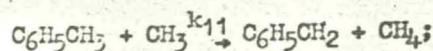
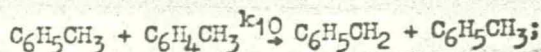
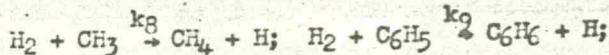
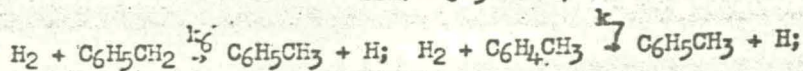
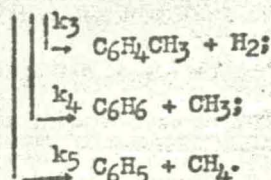
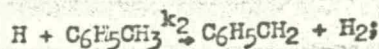
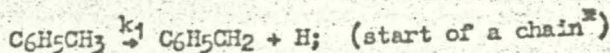
Reactions (3') and (5'') represent an interesting type of radical reactions. Data obtained in recent years indicate the likelihood of such reactions taking place (see 32-34)). It is evident that the scheme for the thermal decomposition of toluene could be supplemented with an equation for the production of ditolyl:



Although the following reaction also cannot be entirely excluded:



If we accept the above-mentioned reaction scheme for the thermal decomposition of toluene, it follows that in the presence of hydrogen under pressure radicals formed by the thermal decomposition will react with molecular hydrogen (and also with molecules of toluene and of reaction products). Reaction with hydrogen molecules leads to the production of atomic hydrogen and also to the initiation of a reaction chain. Thus a probable scheme for the mechanism of the destructive hydrogenation of toluene may be written as follows:



Certain "cross-reactions" might also be added, leading to the formation of ethylbenzene, xylene, methyldiphenyl, diphenylmethane and other products. Among the reaction products are ethane 29, 30). As for dibenzyl, obtained by some workers 31), it was shown 29) that under the experimental conditions it underwent destructive hydrogenation.

If it is assumed that most reaction chains end on tolyl radicals, analysis of the above scheme of reaction leads to the following formula for the rate of production of benzene, w:

$$w = \sqrt{\frac{k_1}{k_{17}}} \frac{(k_4 + k_5)}{k_3} (\text{H}_2) \sqrt{(\text{C}_6\text{H}_5\text{CH}_3)} \left[ k_7 + k_{10} \frac{(\text{C}_6\text{H}_5\text{CH}_3)}{(\text{H}_2)} \right]. \quad \text{(VIII)}$$

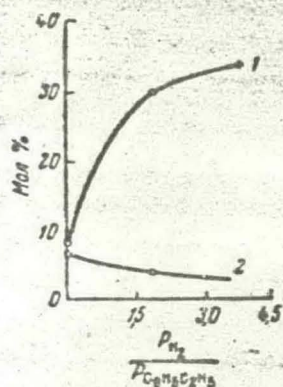
Similar formulae may also be obtained by assuming that most reaction chains end on methyl or phenyl (but not benzyl) radicals.

Comparison of equation (VIII) with the experimental results given in ref. 29) (see above) shows that this equation is in qualitative agreement with the experimental data.

Investigation of the destructive hydrogenation of toluene under high pressure thus enables us to put forward a scheme for a chain mechanism for this process, which can be used to derive an expression for the reaction velocity in qualitative agreement with the experimental results.

A very interesting investigation has also been made of the homogeneous destructive hydrogenation of ethylbenzene 28). The ratio of benzene to toluene increases rapidly with the partial pressure of hydrogen (see figure on next page).

\* Reaction (1') (see above) can also initiate a reaction chain.



Destructive hydrogenation of ethylbenzene

Curve 1 - benzene fraction  
Curve 2 - toluene fraction

Деструктивное гидрирование этилбензола: 1 - бензольная фракция; 2 - толуольная фракция

A more detailed examination of this effect for several alkylbenzenes will doubtless make possible further clarification of the mechanism of destructive hydrogenation of aromatic hydrocarbons at high pressures of hydrogen.

It may be noted that the above-mentioned accelerating effect of the hydrogen pressure on the process is specific for aromatic hydrocarbons. Also discussed above was the effect of hydrogen on the thermal cracking of paraffins; it is noteworthy that the effect of the hydrogen pressure on the rate of thermal decomposition of naphthenic hydrocarbons also proved to be unusual. It was found<sup>35)</sup> that an increase in the hydrogen pressure retards the thermal transformations of methylcyclopentane, the proportion of cyclopentane in the reaction products increasing.

Thus, the difference between the mechanisms of the thermal decomposition of various kinds of hydrocarbons is reflected in the specific effect of high pressures of hydrogen on the velocity of these processes.

Investigation of the Mechanism of Liquid-Phase Reactions

Up to the present no work has been done with the specific aim of investigating the mechanism of liquid-phase reactions by the use of high pressure. Examination of the effect of high pressure on the rate of certain liquid-phase reactions nevertheless allows us to solve a number of important problems concerned with the mechanism of these reactions.

A) Addition of Ethyl Iodide to Pyridine

The velocity of reaction of alkyl halides with tertiary amines or pyridine is known to depend very strongly on the nature of the solvent. In this connection the view has been expressed in the literature<sup>36)</sup> that in these reactions the solvent takes part in the formation of the transitional structure, and enters into the activated complex. The correctness of such a statement may be tested by means of an investigation of the effect of high pressure on the rate of the investigated reaction in various solvents.

We will reconsider equation (III), which expresses the effect of pressure on the velocity constant of a reaction. We may expect the value of  $\Delta V^\ddagger$  to be the same for various solvents only if the solvent molecules themselves do not take part in the activated complex. Moreover, in this case the absolute value of  $\Delta V^\ddagger$  should be nearly equal to the volume change  $\Delta V$  for addition reactions (see 3)).

Now if  $\Delta V^\ddagger$  varies with the solvent and is widely different from  $\Delta V$ , this is an indication of the high probability that the solvent molecules take part in the formation of the activated complex.

Some results of investigations of the effect of pressure on the rate of addition of alkyl halides to tertiary amines and pyridine in acetone are given in Table 2<sup>12)</sup>.

Table 2

Reaction velocity in acetone at high pressures<sup>12)</sup>

Reaction	Temperature (°C)	Pressure p (kg/cm <sup>2</sup> )	$k_p/k_0$	$A_0$
$(CH_3)_3N + i-C_3H_7I$	60	3000	16.4	$1.87 \times 10^7$
$(C_2H_5)_3N + i-C_3H_7I$	60	3000	16.0	$3.76 \times 10^7$
$C_5H_5N + CH_3I$	60	3000	6.78	$1.96 \times 10^7$
$C_5H_5N + C_2H_5I$	40	2980	6.85	$2.13 \times 10^7$
		5000	14.7	
		8500	48.0	
$C_5H_5N + n-C_4H_9Br$	60	3000	8.14	$1.33 \times 10^7$
$C_5H_5N + n-C_4H_9I$	60	3000	6.16	$2.66 \times 10^8$
$C_5H_5N + i-C_3H_7I$	60	3000	9.60	$7.91 \times 10^8$
$C_6H_5N(CH_3)_2 + i-C_3H_7I$	60	3000	25.5	
		5000	80	
		8500	200	
		12000	493	

From the data of Table 2 it may be seen that the investigated reactions are "slow" (exponential term  $A_0 \sim 10^7-10^8$ ) and strongly accelerated by pressure. In one of the papers quoted<sup>12)</sup>, data are given for the value of  $\Delta V$  (i.e. the volume change) for the reaction of pyridine with ethyl iodide in acetone. Comparison of the values of  $\Delta V$  given here with values of  $\Delta V^\ddagger$  calculated from experimental data by use of equation (III) showed that at 30°C and 1 atm.,  $\Delta V^\ddagger$  (-20.0 cm<sup>3</sup>/mole) was 2.7 times less than  $\Delta V$  (-54.3 cm<sup>3</sup>/mole). This fact, it would seem, bears witness to the value of the hypothesis that the solvent takes part in the activated complex. However, it was subsequently discovered<sup>37)</sup> that the indicated difference between the values of  $\Delta V^\ddagger$  and  $\Delta V$  is caused by the solvation of the product (N-ethylpyridine iodide) by acetone, which leads to the large negative value of  $\Delta V$ . Now if we compare the value of  $\Delta V^\ddagger$  with the change in volume during the reaction, calculated from the molar volumes of the original pure liquid components and of the reaction product (see 37)), we find a very close agreement (-20.0 and -20.5 cm<sup>3</sup>/mole respectively at 30°C and 1 atm.) It has also been shown<sup>38)</sup> that solvation by acetone does not have a noticeable effect on the value of  $\Delta V^\ddagger$ . This is seen from the data cited below on the change of the rate of the investigated reaction with increasing pressure in different solvents.

\*  $k_0$  and  $A_0$  are the velocity constant and the pre-exponential term of the Arrhenius equation at atmospheric pressure;  $k_p$  is the velocity constant at pressure p.

Table 3

Velocity constant for the reaction of pyridine with ethyl iodide at 60°

solvent	$k_1$ atm.	$k_{3000}$ atm.	$k_{3000} : k_1$ atm.
Hexane	$4,75 \cdot 10^{-5}$	$3,71 \cdot 10^{-4}$	7.8
Acetone	$7,61 \cdot 10^{-3}$	$5,99 \cdot 10^{-2}$	7.9

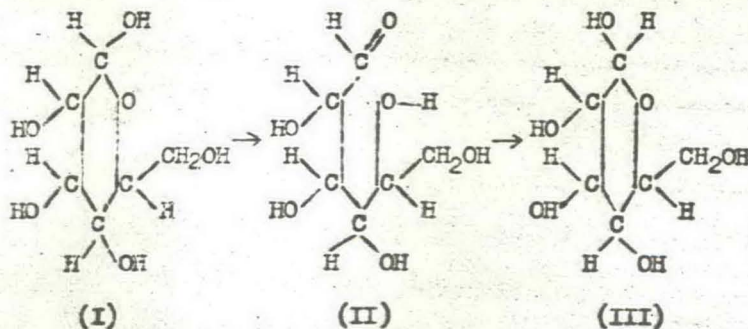
It may be mentioned that the reaction product is insoluble in hexane. Nevertheless, the change in velocity constant with pressure is exactly the same in hexane as in acetone, where the reaction product is solvated.

The data given here confirm the hypothesis that acetone molecules do not enter into the composition of the activated complex for the reaction between pyridine and ethyl iodide.

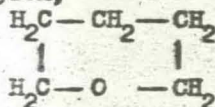
b) The Mutarotation of Glucose

The mutarotation of glucose in aqueous solution has been studied over a wide range of pressure - up to 10,000 atmospheres<sup>39)</sup> (see also<sup>40)</sup>). The investigation has shown that this reaction, which is found to be unimolecular, is accelerated by pressure. Values of  $\Delta V^\ddagger$ , calculated by equation (III), were  $-9 \text{ cm}^3/\text{mole}$  in the pressure range 1-2500 atm.,  $-8 \text{ cm}^3/\text{mole}$  from 2500 to 5000 atm., and  $5 \text{ cm}^3/\text{mole}$  from 5000 to 10,000 atm. Such a decrease in the average negative value of  $\Delta V^\ddagger$  is quite natural if the compressibility of the substances at such high pressures is taken into account. In this connection it is known that in the reaction between pyridine and ethyl iodide, the value of  $-\Delta V^\ddagger$  also falls from  $16.4 \text{ cm}^3/\text{mole}$  in the pressure range 1-3000 atm. to  $8.0 \text{ cm}^3/\text{mole}$  in the range 5000-8500 atm.<sup>41)</sup>

At present it may be assumed, on the basis of many investigations, that the conversion of  $\alpha$ -glucose to  $\beta$ -glucose (I and III, below) proceeds via an open aldehyde chain (II), i.e.



The question arises, which stage of this process is responsible for the increased reaction rate as the pressure rises. It has been suggested in the literature<sup>40)</sup> that the stage in question is the formation of the aldehydic compound. On the basis of the results obtained from the investigation of the reaction under pressure, such a suggestion would lead to the result that under the experimental conditions the ring-opening would entail a diminution of the volume. In all similar cases, a decrease in volume does not occur when a ring is opened, but, on the contrary, during the cyclisation of an open chain. Thus, for example, tetrahydropyran,



is denser than n-valeraldehyde,  $\text{CH}_3(\text{CH}_2)_3\text{CHO}$ . In this case the difference in molar volumes is more than  $7 \text{ cm}^3/\text{mole}$ , i.e. not far from the  $\Delta V^\ddagger$  for the mutarotation of glucose.

\*  $k$  is expressed in litres/mole minute<sup>-1</sup>.

From the data given above we may conclude that the rate-determining stage of the mutarotation of glucose is not the formation of an aldehydic compound but the ring closure. The part played by the solvent (water) in forming the activated complex from  $\alpha$ -glucose is also not excluded. However, the question of the role of the solvent in the activated complex can only be decided, as we saw above, by investigation of the rate of reaction under pressure in various solvents.\*

### c) Thermal Polymerisation of Styrene

The use of high pressure for the investigation of polymerisation reactions is complicated by the fact that in most investigated cases an increase in pressure produces not only an increase in polymerisation, but also an increase in the molecular weight of polymer produced. Nevertheless, it is also possible to obtain interesting information about reactions of this type by analysing the effect of pressure on the rate of the process. Some data on the polymerisation of styrene under pressure will be analysed below with this object.

If we investigate a thermal chain polymerisation of an organic compound in the absence of special catalysts, and with as much atmospheric oxygen removed as possible, it may be supposed that the basic stages of the process - initiation, growth and breaking of reaction chains - occur mainly through collision and chemical reaction either of molecules of monomer, or of a molecule and a radical, or of two radicals. If these stages of the polymerisation process occur through the formation of an activated complex, then (if there is additivity of molar volumes for the monomeric links of the polymer chain) the volume change  $\Delta V^\ddagger$  for all of these stages should be the same. Thus it follows that pressure should increase to equal extents the velocity constants for the chain initiation process in thermal polymerisation, for the growth of the chains (i.e. the rapid addition of a sequence of monomer molecules), and for their breaking.

Starting from the fact that the rate of polymerisation usually settles down to a constant period (up to polymer yields of a few dozen per cent.), we may consider the polymerisation in this stage as approximately a zero - order reaction with the velocity constant.

$$k_0 = \frac{k_1 \cdot k_2}{k_3} \quad (IX)$$

where  $k_1$ ,  $k_2$  and  $k_3$  are the velocity constants for the chain initiation, growth, and termination reactions. This entails the assumption that the molecular weight of the polymer remains constant. Consequently, the value of  $k_0$  should determine the rate of polymerisation, as long as the molecular weight does remain constant. When the molecular weight of the polymer increases with the pressure at which the polymerisation reaction takes place, an appropriate correction must be introduced into equation (IX), with replacement of  $k_0$  by  $k'_0$ , which is equal to

$$k'_0 = \frac{\bar{M}_0}{\bar{M}_p}$$

where  $\bar{M}_0$  and  $\bar{M}_p$  are the molecular weights of polymer at 1 atm. and at  $p$  atm. respectively.

We now consider the change in the velocity constants for chain initiation, growth and termination as the pressure is increased; this should fix the value of  $\Delta V^\ddagger$ . It is easily shown (see 43)) that  $\Delta V^\ddagger$  is approximately equal to  $\Delta V$  (the change in volume when one mole of dimer dissociates to give two moles of monomer). Then, by combination of equations (III) and (IX) and substitution of  $k'_0$ , we obtain

$$\left( \frac{\partial \ln k'_0}{\partial p} \right)_T \approx - \frac{V}{RT} \quad (X)$$

\* It has recently been shown (42) that the ionisation of alkyl halides in aqueous alcohol solution increases with pressure, which throws light on the role of



compound,  
the  
stion  
us ve  
ous  
  
actions  
case  
  
n  
his  
  
und  
moved  
  
lecule  
c is  
the  
nts  
of the  
or  
  
es  
wo  
ler  
  
IX)  
owth,  
uld  
remain  
ssure  
  
is  
  
ion,  
  
d  
  
)  
  
ous

If the experimental data satisfy equation (X), this indicates the usefulness of the above simplified scheme for the mechanism of polymerisation. In calculations according to this scheme, the effect of the walls and of impurities in the reaction mixture, and also of other factors (e.g. the change in the viscosity of the medium at high pressures), is eliminated by reducing the value of the velocity at a given pressure to that which it would have during the formation of a polymer of constant molecular weight at atmospheric pressure.

Equation (X) was tested on kinetic data for the thermal polymerisation of styrene under pressure (44) and on dilatometric data for the decrease in volume occurring during the polymerisation of styrene at various pressures (45). The results of the calculations are shown in Table 4.

Table 4

Block polymerisation of styrene at 100°C.

$$[k'_p] = k'_{o(p)} : k'_{o(1 \text{ atm.})}$$

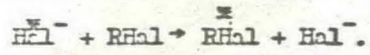
P (atm.)	k <sub>o</sub> % change/hr.	k <sub>p</sub> × 10 <sup>-5</sup>	[k <sub>p</sub> ]	
			Experimental	Calculated
1	3.40	4.40	1	1
1000	5.06	6.69	1.0	1.93
2000	15.09	7.10	2.93	3.25
3000	34.3	8.28	5.42	5.22
4000	50.0	9.18	7.13	8.16

As we can see from Table 4, the calculated and experimental values of [k<sub>p</sub>] agree adequately at pressures of 2000, 3000 and 4000 atm.; only at a pressure of 1000 atm. is a significant divergence found. The assumptions on which the calculation is based therefore appear to be valid.

d) Isotopic Ion-Exchange Reactions

The investigation of the effect of pressure on the rate of isotopic exchange reactions is of interest, since these reactions are distinguished by complete equality of the molar volumes and the compressibilities of the reactants and the products. Hence, pressure has here no effect on the chemical equilibrium.

The exchange reaction between alkyl halides and alkali metal halides in alcoholic solution is an ion-molecule reaction, as shown by recent work: (46)



In this case it is to be expected that increased pressure will speed up the reaction, since in chemical reactions between two or more molecules the formation of an intermediate compound is usually associated with an increase in volume (see 3)).

Experiment confirms this hypothesis. A study (47) has been made of the effect of pressure on the rates of the isotopic exchange reactions between propyl iodide and I<sup>131</sup> ions, and between propyl bromide and Br<sup>82</sup> ions. It was shown that these reactions are accelerated by pressure like "normal" bimolecular reactions; thus, for example, the velocity constant of the former reaction increases more than 2½ times as the pressure is increased from 1 to 2400 atm. Results of high pressure investigations of reactions have therefore so far confirmed facts obtained with the aid of other methods.

### Investigation of the Mechanism of Catalytic Reactions

Some high pressure investigations of the mechanism of catalytic reactions have been carried out, including the isomerisation of paraffinic and naphthenic hydrocarbons in the presence of aluminium chloride under pressure.

The effect of hydrostatic pressure and of pressure of hydrogen on the rate of isomerisation of methylcyclopentane to cyclohexane has been investigated in the presence of aluminium chloride at 80°C<sup>48)</sup>. Zelinskii and Turova-Folyak<sup>49)</sup> have previously found that cyclohexane is reversibly isomerised to give methylcyclopentane in the presence of anhydrous aluminium chloride. At 80°C. the isomerisation is substantially free from side reactions. At low temperatures the equilibrium is shifted towards cyclohexane.\* In this paper<sup>49)</sup> it was suggested that the isomerisation proceeds via the dehydrogenation of the hydrocarbon with the production of hydrogen. This assumption, however, was not confirmed by experiment.

Let us assume that dehydrogenation leading to the production of hydrogen is one of the first stages in the isomerisation of methylcyclopentane in the presence of aluminium chloride. An increase in pressure should naturally shift the equilibrium for this stage of the reaction towards the parent substance, since this stage is accompanied by a considerable increase in pressure. This shift in the equilibrium leads to a diminished concentration of dehydrogenation products, and thus considerably retards the further stages of the isomerisation.

A considerable retardation of the isomerisation on increasing the pressure might accordingly have been considered as one of the reasons in support of the above hypothesis. However, this reason is insufficient, as the retardation may also be caused by some other intermediate stage of the reaction, accompanied by a change in volume, for example a dissociation of the original hydrocarbon across a C-C bond. To obtain additional support for the hypothesis in question, we should also investigate the effect of the hydrogen pressure on the rate of isomerisation. In this case we should observe a greater retardation of the polymerisation than under an ordinary hydrostatic pressure, since hydrogen is not only a gas exerting pressure, but also one of the products of the dehydrogenation reaction; consequently, an increase in its partial pressure should further reduce the equilibrium concentration of dehydrogenated hydrocarbon.

But if the isomerisation of hydrocarbons is a process of intramolecular rearrangement, it will not be accompanied by the formation of hydrogen, and as is usual for unimolecular reactions it should be only slightly retarded by pressure no matter what gas is exerting this pressure.

Investigation has shown<sup>48)</sup> that the isomerisation of methylcyclopentane to cyclohexane in the presence of aluminium chloride is retarded appreciably more strongly by pressure than it would be in the case of intramolecular rearrangement, proceeding as is usual for unimolecular reactions. It was also found that a pressure of hydrogen retards the reaction to a considerably greater degree than a pressure of nitrogen (see Table 5).

Table 5

Isomerisation of methylcyclopentane in the presence of aluminium chloride at 80°C.

Pressure of nitrogen (atm.)	Yield of cyclohexane (%)	Pressure of hydrogen (atm.)	Yield of cyclohexane (%)
1	60.5	25	61
140	60	130	48.5
460	48.5	460	17
660	38.5	615	8

\* An increase in pressure should shift the equilibrium very slightly further towards cyclohexane.

ions  
re.  
gated  
m  
tions.  
his  
ena-

This investigation thus allowed us to extend our knowledge of the mechanism of the isomerisation of saturated hydrocarbons in the presence of aluminium chloride; the experimental results confirm the hypothesis that this process includes as one of its first stages dehydrogenation with the production of hydrogen.

The mechanism established by the above-mentioned experiments<sup>48)</sup> has also been confirmed by an investigation of the isomerisation of n-hexane in presence of aluminium chloride<sup>50)</sup>. Also in this case the isomerisation reaction is abruptly inhibited by a pressure of hydrogen.

Thus it appears that high pressure methods could find wide application in the investigation of heterogeneous catalytic reactions. In a paper mentioned above<sup>25)</sup> an account is given of the effect of high pressure on the presence of an aluminosilicate catalyst. In this paper the following data were given:

gen  
e  
m  
as

Temperature (°C)	410	410	420	420
Average pressure of n-heptane (atm.)	350	820	450	1100
Yield in wt.-% of charge:				
(a) Of unchanged n-heptane,	54.5	37.4	35.0	20.9
(b) Of gaseous and liquid products boiling below 48°C.	31.8	45.3	51.1	64.5

ssure  
hc  
l  
esis  
on

As seen from the above data, the catalytic cracking of n-heptane is accelerated by high pressure. At the same time the thermal cracking of n-heptane is retarded by high pressure (see above). Thus the results obtained reflect the essential difference between thermal and catalytic processes; they confirm the fact that the rate-determining step in catalytic cracking is adsorption or some sort of reaction of the hydrocarbon with the catalyst, whence an acceleration of the process in question by increased pressure is to be expected.

a-  
c  
f  
ed

We may mention in closing that high pressure can also be useful in studying the catalysts themselves. This is borne out by the results of investigations of catalysed chemical reactions at various pressures (a survey of such investigations is given in ref. 3).

Literature

is  
so  
30°C.

1. M.G. Gonikberg et al, Doklady Acad. Sci. U.S.S.R., 1954, 97, 1023.
2. M.G. Gonikberg and L.F. Vereshchagin, J. Phys. Chem. U.S.S.R., 1949, 23, 447.
3. M.G. Gonikberg, "Chemical equilibrium and reaction velocity at high pressures," Acad. Sci. U.S.S.R., 1953.
4. M.G. Gonikberg, Doklady Acad. Sci. U.S.S.R., 1952, 86, 297.
5. P.W. Bridgman & I.B. Conant, Proc. Nat. Acad. Sci., 1929, 15, 680.
6. I.B. Conant & W.R. Peterson, J. A.C.S., 1932, 54, 628.
7. H. Schulten, Z. anorg. allg. Chem., 1939, 243, 145.
8. Ya.T. Eidus and K.V. Puzitsky, Doklady Acad. Sci. U.S.S.R., 1946, 65, 35.
9. N.D. Zelinsky, *ibid*, 1948, 60, 235.
10. H. K6lbel & F. Engelhardt, Brennstoff-Chem., 1952, 33, 13.
11. G.B. Kistiakowsky, J.A.C.S., 1928, 50, 2315.
12. M.W. Perrin, Trans. Faraday Soc., 1938, 34, 144.
13. L. Evans & M. Polanyi, *ibid*, 1935, 21, 875.
14. L.M. Brubaker et al, J.A.C.S., 1952, 74, 1509.
15. A.I. Dintses et al., Bull. Mendel'ev All-Union Chem. Soc., 1940, No. 6-7, 43.
16. D.M. Nowitt, Chem. Rev., 1937, 21, 399.
17. A. Apin et al, J. Gen. Chem. U.S.S.R., 1940, 863.
18. G. Egloff et al, Ind. Eng. Chem., 1936, 28, 1283.
19. G. Egloff, The reactions of pure hydrocarbons, N.Y., 1937.
20. A.I. Dintses, Uspekhi Khim., 1938, 7, 405.

ards

21. W.G. Appleby et al, J.A.C.S., 1947, 69, 2274.
22. A.I. Dintses et al, J. Gen. Chem. U.S.S.R., 1937, 7, 1063.
23. M.G. Gonikberg et al, Doklady Acad. Sci. U.S.S.R., 1953, 89, 483.
24. H.J. Hopp and F.E. Frey, Ind. Eng. Chem., 1953, 45, 410.
25. M.G. Gonikberg and V.V. Voevodsky, Bull. Acad. Sci. U.S.S.R. (Chem. Section), 1954, 370.
26. A.D. Stepukhovich, Doklady Acad. Sci. U.S.S.R., 1953, 79, 455.
27. K.U. Ingold et al, Proc. Roy. Soc., 1951, A203, 486.
28. M.S. Nemtsor, Uspekhi Khim., 1938, 7, 1617.
29. M.G. Gonikberg and V.E. Nikitenkov, Bull. Acad. Sci. U.S.S.R. (Chem. Section), 1954, 936.
30. F. Hoffmann & K. Laig, Brennstoff-Chem., 1929, 10, 20.
31. M. Szwarc, J. Chem. Phys., 1948, 16, 128.
32. Gomer, Hoyer, J.A.C.S., 1949, 71, 3390.
33. F.E. Blacket and W.E. Bell, Disc. Faraday Soc., 1953, No. 14, 70.
34. B. de B. Darwent, Disc. Faraday Soc., 1953, No. 14, 129.
35. A.E. Gavrilova et al, Doklady Acad. Sci. U.S.S.R., 1954, 96, 987.
36. V.A. Goldschmitt, Acta Phys. Chim. U.S.S.R., 1940, 12, 25.
37. M.G. Gonikberg and G.S. Fevich, J. Phys. Chem. U.S.S.R., 1949, 23, 383.
38. R.O. Gibson et al, Proc. Roy. Soc., 1935, 150, 223.
39. V.K. Bobolev and O.I. Leipunsky, J. Phys. Chem. U.S.S.R., 1941, 15, 1104.
40. F.V. Sander, J. Biol. Chem., 1943, 148, 311.
41. A.E. Stearn and H. Eyring, Chem. Rev., 1941, 29, 509.
42. J. Buchanan and S.D. Haman, Trans. Faraday Soc., 1953, 49, 1425.
43. M.G. Gonikberg and L.F. Vereshchagin, J. Phys. Chem. U.S.S.R., 1952, 26, 407.
44. R.C. Gillham, Trans. Faraday Soc., 1950, 46, 497.
45. P.P. Kobeko et al, J. Phys. Chem. U.S.S.R., 1950, 24, 345, 415.
46. M.B. Neiman et al, Doklady Acad. Sci. U.S.S.R., 1952, 82, 1289.
47. M.B. Neiman et al, Doklady Acad. Sci. U.S.S.R., 1953, 92, 365.
48. N.D. Gonikberg et al, Doklady Acad. Sci. U.S.S.R., 1952, 83, 81.
49. N.D. Zelinskii and M.B. Turova-Polyak, J. Gen. Chem. U.S.S.R., 1932, 2, 666.
50. M.G. Gonikberg et al, Bull. Acad. Sci. U.S.S.R. (Chem. Section), 1952, 157.