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DEHYDROGENATION OF ALKANES AND ALKENES AT LOW PRESSURES

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I. INTRODUCTION

The catalytic dehydrogenation to alkenes and alkadienes of alkanes containing 2 to 5 carbon atoms is a promising method for the preparation of unsaturated hydrocarbons. In recent years there has been greatly increased interest in the preparation of alkenes and alkadienes by the catalytic dehydrogenation of low-molecular-weight alkanes at low pressures of the starting materials, because thermodynamic calculations have shown that under these conditions considerable yields of useful products should be obtained. Notwithstanding a certain complexity in the technological design of dehydrogenation processes at low hydrocarbon pressures (that is, under vacuum or with the use of solvents), the application of such processes results in substantial economic gains. It is for this reason that, in the United States and Western Europe, the production of bivinyl by Houdry's method has been developed as the most economic method of dehydrogenation[2]; in this method n-butane is dehydrogenated under vacuum in a single stage[1]. In the USSR the problem of using this method is under consideration[3,4].

A large amount of experimental information on the catalytic dehydrogenation of hydrocarbons at low pressures is now available, and this merits a special review; in our opinion such a review provides an essential supplement to modern informative reviews[5-7] on the dehydrogenation of hydrocarbons. The present review considers problems of the thermodynamics of the dehydrogenation of C_2–C_6 hydrocarbons at low pressures, as well as catalysts and the operating conditions for industrial applications of the process.

II. THERMODYNAMIC CALCULATIONS OF HYDROCARBON DEHYDROGENATIONS

Thermodynamic calculations permit us to select the optimal conditions for carrying out a reaction. Using such calculations, we can calculate whether a given reaction could proceed in such a way as to give a useful product in sufficiently high yield to warrant its practical application, and also the most favourable temperatures and pressures for carrying out the reaction. An increase in the temperature of a process and reduction in pressure result in an increase in the degree of equilibrium dehydrogenation, and therefore favour an increased yield of alkenes or alkadienes[5,8].

Using experimental data on the dehydrogenation of alkanes in the presence of chromium catalysts, Frey and Huppke[9] determined the equilibrium constants for the dehydrogenation of n-butane to each of the isomeric butenes, and of propane to propene, and ethane to ethylene. Using the data of these workers, Zharkova[10] determined the dependence of $\lg k_{equil}$ on temperature. Dement'eva and coworkers[11,12] calculated the dependence of the degree of dehydrogenation of n-butane, isobutane, and propane on

temperature and pressure. Moreover, using experimental results on the dehydrogenation of n-butenes to buta-1,3-diene on chromium(III) oxide at 404–534°C, these workers also calculated the equilibrium constants of this reaction for the temperature range mentioned. Kassel[13] and Pitzer[14] calculated the equilibrium constants for the dehydrogenation of butane and the equilibrium composition at various temperatures. Aston and coworkers[15] calculated equilibrium constants for the dehydrogenation of n-butane to n-butene and buta-1,3-diene at 25–1227°C, and of individual n-butenes and their mixture to buta-1,3-diene over the same temperature range. The difference between the values of k_{equil} found experimentally[9] and the calculated values[15] is due to experimental errors in the investigation of a mixture with components present in low concentrations.

Balandin and coworkers[16] made a thermodynamic calculation of equilibria in the butene–butadiene system, and found that the yields of butadiene increase with decreasing pressure, the most favourable results being obtained at a temperature of 550–600°C and a pressure below atmospheric.

Using published data[6,17], Bogdanov[18] derived an equation for determining the equilibrium composition in the dehydrogenation of n-butane to n-butenes and buta-1,3-diene in the presence of an inert gas or water vapour as diluent. The author regards the dehydrogenation of n-butane as consisting of two successive reactions: n-butane is first dehydrogenated to n-butene (a mixture of isomers of but-1-ene, *cis*-but-2-ene, and *trans*-but-2-ene), and the butenes are then dehydrogenated to buta-1,3-diene. For this reason, the equilibrium constants for these reaction were calculated for each isomer separately, and the values found were then used to calculate the overall equilibrium constant (Table 1).

The values of the constants obtained are in satisfactory agreement with the corresponding values obtained by other workers. Dilution of n-butane with an inert gas greatly improves conversion into n-butenes and buta-1,3-diene. At 527°C and with a 1 : 5 molar dilution of butane with inert gas, the conversion of butane into butenes and butadiene reaches 62.5%, compared with 36.7% without dilution. At 527°C and a 1 : 10 dilution with inert gas the conversion of n-butenes to buta-1,3-diene is 28.7%, compared with 10% without dilution[18]. Dilution of a butane–butene mixture (30% of n-butenes and 70% butane) with an inert gas also increases the degree of conversion into butadiene. Thus, at 600°C and a 1 : 5 dilution, conversion increases from 13.8% without dilution to 34.3%, that is, by a factor of two and a half. The authors point out that dilution with hydrogen leads to a sharp fall in conversion.

TABLE 1. Temperature dependence of the equilibrium constants for the dehydrogenation of n-butane to n-butenes (total isomers) and of n-butenes to buta-1,3-diene[18].

Temperature, °C	k_{equil} (dehydrogenation of n-butane to n-butenes)	k_{equil} (dehydrogenation of n-butenes to buta-1,3-diene)
427	0.0111	0.000680
527	0.154	0.0102
627	1.21	0.0851
727	6.35	0.462

In a thesis, Khodakov[19] derived an equation for calculating the equilibrium conversion of n-butane into butenes (mixture of isomers) and an equation for the calculation of the equilibrium conversion of n-butane with allowance for side-reactions, that is, when the process is not selective.

As with C_4 hydrocarbons, in the dehydrogenation of isopentane, a reduction in pressure and an increase in temperature also increases the yield of isoprene.

Ghosh and Roy[20] studied the reaction equilibrium in the dehydrogenation of 3-methylbut-1-ene at 330–450°C and a pressure of 10–35 mmHg on an aluminochromium catalyst with the addition of oxides of vanadium and molybdenum. These workers determined the equilibrium constants at the temperatures mentioned and calculated the dependence of free energy change on temperature for the dehydrogenation of isopentane to methylbutene, and of methylbutenes to isoprene. Shuikin and coworkers[21,22] calculated the equilibrium constants and the degree of dehydrogenation for the conversion of isopentane into methylbutenes at 327–627°C and atmospheric pressure. Bogdanov and Bol'shakov[23,24] made a detailed thermodynmaic calculation for the dehydrogenation of isopentane, methylbutenes, and isopentane–methylbutene mixtures at 427–727°C. The equilibrium constants and compositions of the equilibrium mixtures were calculated over the given temperature range at atmospheric pressure and at inert gas dilutions of 1 : 1 to 1 : 10 (molar). Calculations analogous to those used for the dehydrogenation of butane, butenes, and their mixtures were used to determine the overall equilibrium constant k' for the dehydrogenation of isopentane to methylbutenes (mixture of isomers); this constant was taken as the sum of the equilibrium constants of the dehydrogenation of isopentane to 2-methylbut-1-ene (k_1'), 3-methylbut-1-ene (k_2'), and 2-methylbut-2-ene (k_3'):

$$k' = k_1' + k_2' + k_3'.$$

The overall equilibrium constant for the dehydrogenation of methylbutenes to isoprene, k'', is calculated from the equation:

$$\frac{1}{k''} = \frac{1}{k_1''} + \frac{1}{k_2''} + \frac{1}{k_3''},$$

where k_1'', k_2'', and k_3'' are the equilibrium constants for the dehydrogenation to isoprene of 2-methylbut-1-ene, 3-methylbut-1-ene, and 2-methylbut-2-ene respectively. The calculated equilibrium constants were used to determine the composition of the equilibrium mixtures formed in the dehydrogenation of isopentane to methylbutenes and isoprene. The degree of conversion of isopentane into methylbutenes and isoprene was calculated from the composition of the equilibrium mixtures (Table 2).

The figures in Table 2 clearly show that dilution of isopentane with an inert diluent at atmospheric pressure, or a corresponding reduction of total pressure in the system, greatly increases the conversion of isopentane into methylbutenes and isoprene. Thus, at 527°C and a molar dilution of 1 : 5 the conversion into methylbutenes and isoprene reaches 80.8%, compared with 57.8% without dilution. Temperature change greatly influences the nature of the isopentane conversion. At temperatures below 600°C isopentane is converted mainly into methylbutenes, but at higher temperatures the conversion of isopentane into isoprene increases sharply, and smaller amounts of the methylbutenes are formed. At very high temperatures, particularly at very low pressures, isoprene is the main dehydrogenation product.

TABLE 2. Effect of an inert diluent on the conversion of isopentane into methylbutenes and isoprene at various temperatures.

Temperature, °C	Dilution of isopentane, molar ratio	Conversion of isopentane, % into methylbutenes	into isoprene	into methylbutenes + isoprene	Temperature, °C	Dilution of isopentane, molar ratio	Conversion of isopentane, % into methylbutenes	into isoprene	into methylbutenes + isoprene
427	1:0	19.1	0.1	19.2	627	1:0	74.8	15.0	89.8
	1:5	37.9	0.7	38.6		1:5	61.9	35.3	97.2
	1:10	47.1	1.0	48.1		1:10	52.5	46.3	98.8
527	1:0	55.9	1.9	57.8	727	1:0	50.9	47.4	98.3
	1:5	73.3	7.5	80.8		1:5	28.4	71.3	99.7
	1:10	75.0	11.9	86.9		1:10	20.1	79.6	99.7

Fridshtein and Chechik[25] made a thermodynamic calculation for the isopentane–methylbutenes–isoprene–hydrogen system over the temperature range 450–650°C for pressures of 1, 0.3, and 0.2 ata. These workers determined the equilibrium constants for the dehydrogenation of isopentane and isopentane–methylbutene mixtures to isoprene, and also the equilibrium composition of the dehydrogenation products (Fig. 1). These calculations showed that a significant yield of isoprene and methylbutenes can only be obtained at a temperature higher than 550°C and a pressure lower that 0.3 ata.

It follows from calculations of the equilibrium composition of mixtures in the dehydrogenation of methylbutenes (mixture of isomers) and isopentane–methylbutene mixtures to isoprene[23] that a reduction of pressure in the system, or dilution of the starting material, significantly increases the degree of conversion into isoprene (Fig. 2).

The work of Chang and coworkers[26] is also of interest; they established the relationship between the individual methylpentenes formed when isopentane is dehydrogenated under vacuum, and they give the equilibrium constants and equilibrium composition of the reaction products at 427–627°C at a residual pressure of 100 mmHg and also at atmospheric pressure (Fig. 3). Reduction of the pressure increases the yield of isoprene; thus at 602°C and 100 mmHg it is thermodynamically possible almost completely to decompose isopentane to yield 51.7% of methylpentenes and 46.5% of isoprene. These results are in good agreement with calculations made by other workers[23–25].

With C_6 hydrocarbons, a thermodynamic calculation for the dehydrogenation reaction has only been made for one isomer—neohexane[27].

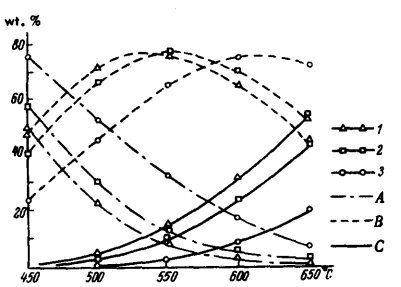


Fig. 1. Equilibrium composition of products of dehydrogenation of isopentane at different pressures: 1) 0.2 ata, 2) 0.3 ata, 3) 1.0 ata; *A*) isopentane; *B*) methylbutenes; *C*) isoprene.

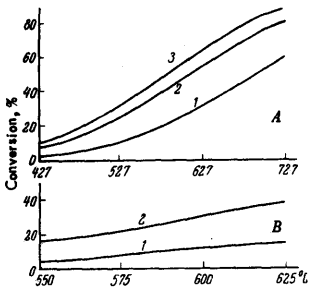


Fig. 2. Effect of an inert diluent on the conversion of methylbutenes into isoprene (*A*) and isopentane–methylbutene mixtures (70 : 30) into isoprene (*B*) as a function of temperature: 1) without dilution; 2) dilution 1 : 5; 3) dilution 1 : 10.

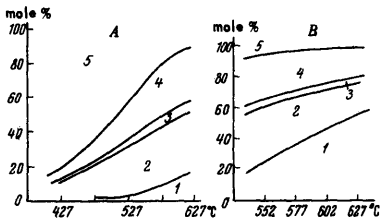


Fig. 3. Equilibrium composition of dehydrogenation products of isopentane at atmospheric pressure (*A*) and at a residual pressure of 100 mmHg (*B*): 1) isoprene; 2) 2-methylbut-2-ene; 3) 3-methylbut-1-ene; 4) 2-methylbut-1-ene; 5) isopentane.

Thus the thermodynamic data show convincingly that the most suitable conditions for the dehydrogenation of alkanes and alkenes to give alkadienes are high temperatures (~600–700°C) and low pressures (~100 mmHg).

Thermodynamic calculations do not, of course, give any indications of reaction rates, but only indicate the most suitable conditions for the reaction. It is therefore necessary to find catalysts which increase the rate of a given reaction and suppress side-reactions which reduce the yield of required products.

It is also useful to examine the behaviour of petroleum hydrocarbon fractions at high temperatures and low pressures in the absence of catalysts. It has been shown in a number of papers on the thermal cracking and pyrolysis of alkanes under reduced pressure that at 400–800°C the hydrocarbons are cleaved at the C–C bonds[28–48]. Dehydrogenation takes place to only a slight extent.

At high temperatures, ethane[28–35] and ethylene[36] give a number of saturated and unsaturated C_1–C_4 products.

When propane is subjected to a cracking process at 590°C and a pressure of 20 mmHg, it is decomposed to a slight extent (up to 10%) and the sum of the $H_2 + C_3H_6$ products formed is equal to the sum of the $CH_4 + C_2H_4$ products[37]. When the degree of decomposition increases, the predominating reaction is demethanisation, that is, the amount of $CH_4 + C_2H_4$ formed is greater than the amount of $H_2 + C_3H_6$ produced.

TABLE 3. Composition of issuing gas in the thermal cracking of isopentane (820°C, 109 mmHg, $\tau_{contact}$ = 0.015 s).

Composition of gas	Content, %	Composition of gas	Content, %
iso-C_5H_{12}	19.0	C_3H_6	12.4
α-C_4H_8	0.7	C_3H_8	0.4
β-C_4H_8	6.0	C_2H_2	0.2
iso-C_4H_8	5.6	$C_2H_4+C_2H_6$	16.0
C_4H_6	0.4	CH_4	23.1
n-C_4H_{10}	0.4	H_2	17.0
iso-C_4H_{10}	0.1	coke(CO_2)	0.2

The main reaction that occurs in the cracking of butane[40] is decomposition into methane and propene, and to a lesser degree into ethane and ethylene. Dehydrogenation proceeds to only a slight extent[40-42]. Reports on the kinetics and mechanism of thermal decomposition of butane have been published[43,44]. Isobutane[40] decomposes preferentially into 2-methylpropene and hydrogen (580°C, 20 mmHg), smaller proportions decomposing into methane and propene, and into ethane and ethylene.

When the cracking of propane is initiated by the addition of 1–3% of azomethane, dehydrogenation predominates over demethanisation[45]. The reverse is true for isobutane[45]. In the sensitised cracking of butane, the direction of the reaction and the ratio of the products are the same as in ordinary cracking.

Isopentane is cracked[46-48] preferentially into C_2 and C_3 hydrocarbons; butenes are formed to a lesser extent (Table 3).

The thermal decomposition of hydrocarbons is a free-radical chain reaction. The predominant decomposition of the hydrocarbon molecules at the C–C bond in contrast to decomposition at the C–H bond (dehydrogenation) under thermal-cracking conditions is due to the lower energy of the C–C bond compared with the C–H bond[49]. Catalysts can change the direction of the thermal decomposition reaction so that dehydrogenation of alkanes and alkenes to alkadienes becomes the predominant reaction.

III. CATALYSTS FOR THE DEHYDROGENATION OF ALKANES AND ALKENES AT LOW PRESSURES

The extensive patent literature that has appeared over the past 25 to 30 years is evidence of the great amount of work that has been done in the selection and study of catalysts for the dehydrogenation of alkanes and alkenes to alkadienes at low pressures. More than 100 patents giving proposed catalysts for these processes have been published during this period, mainly in the United States, but also in England, France, the Federal German Republic, and other countries. Most of the catalysts refer to the preparation of butadiene and isoprene from the corresponding alkenes; the minority have been proposed for producing these diene hydrocarbons from the alkanes n-butane and isopentane. Reduction of pressure is achieved either by dilution with water vapour or an inert gas or by evacuation. The composition of the catalysts varies with the method used to reduce the pressure.

Several types of catalysts have been developed for the dehydrogenation of mono-alkenes diluted by water vapour. The ones that have been used most extensively are those proposed by the firm Standard Oil Development, based on oxides of metals of Group II of the Periodic System: Mg [50-60], Zn [61,62], Be [61-64]; their composition includes iron(III) oxide, and also copper(II) oxide as a stabiliser and potassium oxide as a promoter. The general composition of catalysts of this type may be expressed as follows (parts by weight): $MO:Fe_2O_3:CuO:K_2O = 80:20:5:5$, where M = Mg, Zn, or Be. Of such catalysts, Catalyst 1707 has been used industrially; it has the following composition (wt.%): 72.4 MgO; 18.4 Fe_2O_3; 4.6 CuO; 4.6 K_2O.[51-57] Various modifications of these catalysts were examined in the course of their development[50,51,55,61,65-67]. CaO and SrO [50,51,56] have been proposed as promoters, and oxides of Ag, Zn, Cd, Th, Co, and Mn [51] as stabilisers. Iron(III) oxide has been replaced by MnO_2.[61]

The Shell Development Company and others have done work on the selection of catalysts based on iron(III) oxide with potassium compounds as promoters[68-77] and also with the inclusion of oxides of Cr, Bi, Ti, Al, and compounds of Cu, Pb, and Li. The catalysts of this type that have been most widely used are Contact Shell 105 (9 Fe_2O_3, 4 Cr_2O_3, 6 K_2CO_3) and Contact Shell 205 (Contact Shell 105, but with a higher content of K_2CO_3).[1]

For the dehydrogenation of butenes to butadiene, the firm I. G. Farbenindustrie used a catalyst consisting of more than 50% of ZnO and oxides or salts of Cr, V, Mo, U, W, etc.[78-81]; zinc oxide has also been used with other additives[82].

Schulze and coworkers (Phillips Petroleum Company)[83-85] patented a bauxite catalyst for this process; this consists of bauxite and the oxide or hydroxide of Ba, Mg, Sr, or Cr; they also patented catalysts containing combinations of Al_2O_3 with oxides or hydroxides of Ba, Mg, and K [86]. Bauxite catalysts have also been tried in processes in which the starting material is diluted with inert gases[87-89].

Britton and Dietzler (Dow Chemical Company) and other workers (Esso Research Company) have made a new type of catalyst (nickel phosphate catalyst) for the dehydrogenation of alkenes in the presence of water vapour[90-95]. A similar catalyst has been developed in Czechoslovakia[96,97]. Its composition may be represented by the formula $Ca_8Ni(PO_4)_6$. The addition of small amounts of Cr_2O_3 and graphite improves the properties of this catalyst[90,92-95].

There are references[98] to the use of graphite and carbon as catalysts; these have been tried for n-butenes diluted with water vapour, N_2, and CO_2. Silver vanadate[99] and metals of Group VIII (Ni) [100] have been used as catalysts in this process with CO_2 as the diluent, and CaO has been used with N_2 as the diluent[101], but these catalysts have not found extensive use.

All the catalysts described have been tried in the dehydrogenation of n-butenes to butadiene under various conditions (550–800°C, space velocity 100–800 h^{-1}), the alkenes being diluted with water vapour in the ratio 1 : 7 to 1 : 15. The use of a CaNi–phosphate catalyst requires the introduction of large quantities of water vapour (the ratio of n-butenes to water vapour is 1 : 20). The operating life without regeneration of Type 1707 and CaNi–phosphate catalysts is 0.5–1 h; catalysts based on Fe_2O_3 can be

used without regeneration for 8–12 h, and bauxite catalysts for 6 h. Regeneration is effected by means of superheated steam, alone or mixed with air. On Catalyst 1707 the yield of butadiene calculated on the butenes passed through is 28 to 30%, and the selectivity is 68 to 85%; the catalyst is stable and does not lose its activity or selectivity over a period of several months. Iron and bauxite catalysts give a lower conversion of n-butenes into butadiene (20–26% and 20% respectively).

On a CaNi–phosphate catalyst butenes are converted into butadiene in 30–35% yield; under production conditions this catalyst gives a butene conversion of 35% with a selectivity of 86–88%. Thus, the use of a CaNi–phosphate catalyst ensures high yields of butadiene, based on butenes passed through and decomposed, although it requires regeneration more frequently and is more expensive than catalysts based on iron oxide. The useful life of a CaNi–phosphate catalyst is 6–7 months, and that of an iron catalyst 2–3 months.

All the types of catalysts encountered in patents for use in the dehydrogenation of n-butenes in the presence of water vapour have also been used for the dehydrogenation of methylbutenes to isoprene: this includes Type 1707 catalyst[59], iron[77], zinc[82], bauxite[83], and CaNi–phosphate catalysts[90,94,97]. The best yields of isoprene (over 40%) were obtained with a CaNi–phosphate catalyst over the temperature range 640–650°C, with a space velocity of 0.9–1.0 h^{-1}, a 1 : 17 dilution with water vapour, and a contact time of 5–10 min[97]. 2,3-Dimethylbutane was dehydrogenated to 2,8-dimethylbutadiene on the same catalyst[94].

The catalytic dehydrogenation of alkanes to unsaturated hydrocarbons in the presence of water vapour has not been widely used: the available information consists of isolated references[102,103] indicating that n-butane is converted into a mixture of butenes and butadiene in 20% yield on an aluminochromium catalyst containing V_2O_5 or MoO_3.

In the dehydrogenation of alkanes, alkenes, and their C_4–C_5 mixtures under reduced pressure, aluminochromium catalysts[104–118] containing about 20% of Cr_2O_3, sometimes with the addition of 1–5% of BeO, SiO_2, and K_2O, are mainly used[96,119–121]. These catalysts are notable for their high activity, long-term stability, and the simplicity with which they are prepared. Thus, in the dehydrogenation on an aluminochromium catalyst (80% Al_2O_3, 20% Cr_2O_3)[113] of a butane–butene mixture containing 62% of butenes, the yield of butadiene is 18–21% (590–600°C, 50 mmHg, contact time 0.2 s). A chromium–vanadium oxide catalyst[122] has also been used for the dehydrogenation of butane–butene mixtures. In the dehydrogenation of monoalkanes under reduced pressure, apart from aluminochromium catalysts, catalysts consisting of Al_2O_3 in a mixture with V_2O_5 and Ag[123], or oxides of Ti, Zr, Ce, Hf, Th[124] and V, Ce, Ta[125], have been used. When the first of these catalysts[123] is used, butenes are converted into butadiene in 35% yield (660°C, 97 mmHg, 482 h^{-1}).

In some instances, the partial pressure of the starting hydrocarbon was reduced by dilution with hydrogen[126,127].

Several papers on the dehydrogenation of hydrocarbons under the conditions mentioned above deal with catalysts of practical interest, but do not propose any fundamentally new catalysts.

Thus, the search for active and selective catalysts for use in the dehydrogenation of alkanes and alkenes at low pressures, which has long been in progress, is still being intensively pursued at the present time.

IV. DEHYDROGENATION OF BUTANE AND BUTENES TO BUTADIENE

The dehydrogenation of butane, butenes, and their mixtures to buta-1,3-diene at low pressures of the initial hydrocarbons has been studied at fairly high temperatures. In addition to the main dehydrogenations, in which butane is converted into a mixture of butene isomers, and the butenes to butadiene, the process is accompanied by a number of side-reactions, such as isomerisation, formation of saturated and unsaturated C_1–C_3 hydrocarbons, as well as coke formation on the catalyst, which necessitates its regeneration. These reactions are undesirable since they lower the yield of the required product, buta-1,3-diene. The extent to which they occur depends on many factors, including the composition of the catalyst, the degree of hydrocarbon conversion, and the conditions under which the process is carried out.

Fedorov and coworkers[128] studied the dehydrogenation of but-2-ene diluted with nitrogen on different catalysts. On the best of these, magnesium oxide, the yield of butadiene was 25–29%.

Balandin and coworkers[16,129–131] studied the dehydrogenation of butenes to butadiene on chromium catalysts at low pressure, the starting material being diluted with nitrogen and carbon dioxide. When a 1 : 7.5 dilution with carbon monoxide was used at 600°C the yield of butadiene was 34.2 with a selectivity of 75%. It was found that the following side-reactions occurred, in which carbon dioxide reacted with butene and with hydrogen:

$$C_4H_8 + 4\,CO_2 = 8\,CO + 4\,H_2,$$
$$H_2 + CO_2 = H_2O + CO.$$

The side-reactions play only a small part here, since the yield of butadiene increases with increasing dilution. Experiments in which butenes were dehydrogenated on a chromium catalyst at a residual pressure of 180 mmHg showed that, when the temperature is increased from 550° to 600°C, the yield of butadiene increases from 14 to 28–29%, that is, by a factor of two[16]. In addition to the dehydrogenation of butene[131], reactions occur in which the initial butene and the butadiene formed are decomposed and hydrogenated. But-1-ene and but-2-ene are dehydrogenated at about the same rate[130]. Experiments with a mixture of butene and butadiene show that the decomposition of butadiene increases with temperature and also with its concentration in the initial mixture.

Grosse and coworkers[132] dehydrogenated n-butenes on an aluminochromium catalyst at 600°C and 190 mmHg. Under these conditions a lower yield of butadiene per pass was obtained (18–23%).

Balandin and coworkers[131] studied the kinetics of dehydrogenation of butene on a chromium catalyst at low pressure. The kinetic equation has the following form:

$$V = k\,\frac{[C_4H_8]}{[C_4H_8] + \Sigma Z_n [A_n]},$$

where k is the dehydrogenation rate constant; Z_n is the relative adsorption coefficient of a compound; and A_n is its partial pressure.

The apparent activation energy of butenes and bivinyl at a residual pressure of 180 mmHg with a contact time of 0.3 s was 26.3–27.9 kcal $mole^{-1}$ at 551–660°C, and 34.3–34.7 kcal $mole^{-1}$ at 535–559°C.

This reaction has also been studied by Shcheglova and Pshezhetskii[133] at 450–500°C and butene partial pressures of 0.05–0.3 atm, nitrogen being used as a diluent; they found that the kinetics of dehydrogenation of n-butenes on an aluminochromium catalyst correspond to the equation:

$$W = kC_2^{0.5}$$

where C_2 is the concentration of butene.

The value found for the activation energy was 27 ± 1 kcal mole^{-1}. They showed that the addition of 10% of hydrogen has no effect on the rate of dehydrogenation of butene, but 20% of hydrogen slightly reduces the rate. The addition of butadiene did not significantly reduce the rate of dehydrogenation. However, the relative adsorption coefficients of butene, butadiene, and hydrogen on an aluminochromium catalyst indicate that butadiene has a high adsorption coefficient, that is, on a catalytically active surface butadiene is more strongly adsorbed than butene, but hydrogen is adsorbed to about the same degree as butene; the adsorption coefficients of butene, butadiene, and hydrogen at 560°C are in the ratios 1 : 9.5 : 0.82.[131] Thus the presence of butadiene must have an appreciable effect on the rate of dehydrogenation.

When butadiene is dehydrogenated on a mixed oxide catalyst[134] in the presence of water vapour the ratio of the relative adsorption coefficients for butene, butadiene, and hydrogen is found to be 1 : 4.9 : 0.8 at 580°C, and 1 : 3.7 : 0.8 at 600°C.

Beakberger and Watson[135] found that, with Catalyst 1707, and water vapour as a diluent, the rate of the reaction may be expressed by the following equation:

$$W = \frac{k\left(P_{C_4H_8} - \frac{P_{C_4H_6} \cdot P_{H_2}}{k_{equil}}\right)}{(1 + k_{C_4H_8} \cdot P_{C_4H_8} + k_{C_4H_6} \cdot P_{C_4H_6} + k_{H_2} \cdot P_{H_2} + k_A P_A)^2}$$

where k is the rate constant; k_{equil} is the equilibrium constant of the dehydrogenation reaction; $k_{C_4H_8}$, $k_{C_4H_6}$, k_{H_2}, k_A are the equilibrium adsorption constants for C_4H_8, C_4H_6, H_2, and aromatic compounds respectively; and P is the partial pressure. The activation energy of this process, with water vapour as the diluent, was 17 kcal mole^{-1}.

For the same n-butene dehydrogenation on an oxide-type industrial catalyst with water vapour as diluent, Tyuryaev and Kolobikhin[136] give another kinetic reaction of the form: $r = kP^n_{C_4H_8}$, where $P_{C_4H_8}$ is the partial pressure of the butenes, and $n = 0.35$ (found by a graphical procedure).

The mechanism of dehydrogenation of butane and butene has also been studied by means of radioactive carbon, ^{14}C.[137,138] A mixture (1 : 1) of butane and butene, diluted with water vapour (1 : 9) was dehydrogenated on a chromium catalyst at 635°C. The results of the experiment show that the formation of butadiene is mainly due to the dehydrogenation of butene:

$$C_4H_{10} \rightarrow C_4H_8 \rightarrow C_4H_6.$$

It was then shown[137] that, in addition to dehydrogenation, a reaction occurs in which hydrogen is exchanged between butane and butene, that is, hydrogenation of butene and dehydrogenation of butane occur at the same time. The rates of dehydrogenation of butane to butene (W_1), to butadiene (W_2), and of butene to batadiene (W_3) on a chromium catalyst are related by the following ratios: $W_1 : W_2 : W_3 = 20 : 1 : 1000$.

$$C_4H_{10} \xrightarrow{W_1} C_4H_8 \quad C_4H_8 \xrightarrow{W_2} C_4H_6 \quad C_4H_8 \xrightarrow{W_3}$$

Thus butadiene is formed from butene, and there is virtually no conversion of butane into butadiene.

When the reaction is carried out on an aluminochromium catalyst at a pressure of 250 mmHg and a temperature of 600°C, that is, under conditions favouring the dehydrogenation of butane[138], more than 96% of the butadiene formed is derived from butene. The ratio of the reaction rates then is: $W_1 : W_2 : W_3 = 18 : 1 : 25$.

The ratio $W_1 : W_2$ is therefore the same for dehydrogenation on a chromium as on an aluminochromium catalyst. Carbon and resinous products are formed by the decomposition of butene and, to a greater extent, of butadiene[138,139]. If the process is carried out in the presence of water vapour, a large amount of carbon dioxide is formed, and no coke is deposited since the greater part of the carbon deposited on the catalyst is oxidised to CO and CO_2 by the water-gas reaction. The reaction rates for the formation of CO_2 from C_4H_6, C_4H_8, and C_4H_{10} are in the ratio 60 : 4 : 1 [137]; this shows that the formation of CO_2 is the result of a secondary bivinyl-conversion reaction. Kolobikhin and Tyuryaev[140] studied the reaction for the conversion of butadiene in the presence of water vapour on a catalyst used for the dehydrogenation of n-butenes. They showed that the main reactions are the hydrogenation of butadiene and its decomposition to give coke. The greater part of the coke reacts with water vapour to form CO and CO_2. Coke deposition appears to be the main cause of the reduction of catalyst activity.

Beakberger and Watson[135] and Kearby[141] carried out experiments on the dehydrogenation of n-butenes on Catalyst 1707 and its modifications, water vapour being used as diluent. In addition to butadiene and hydrogen, the dehydrogenation products also contained low-molecular alkenes and alkanes (propene, ethylene, propane, ethane, methane) and carbon dioxide. At 665°C, with butenes at a space velocity of 500 h^{-1} and a water-vapour dilution of 1 : 14, the yield of butadiene is 28%, based on the amount of butene passed through, and 74% based on the amount decomposed. Results of the industrial use of Catalyst 1707 and of catalysts based on iron oxide (Shell-105 and Shell-205) are also given in articles by Reidel[142], Reilly[143], and Kearby[5]. Britton and Dietzler[144] obtained better yields of butadiene on a catalyst of composition $Ca_8Ni(PO_4)_6$ containing 1–2% of chromium(III) oxide. When a high water-vapour dilution was used (molar ratio of water vapour to butene 20 : 1) on a laboratory apparatus, the yield of butadiene was 93–97% based on n-butenes consumed, the conversion being 20–45% (525–650°C, space velocity 100–200 h^{-1}). Increasing the duration of the cycle from 1 to 2 h reduces the conversion of n-butene by 2–3%. The conversion increases as the space velocity decreases.

Thus, on this catalyst the dehydrogenation is characterised by high yields and selectivity. However, a disadvantage is the high yield of carbonyl compounds (4% of the butene obtained) and acetylene hydrocarbons (1%) [143].

Data on the industrial use of calcium–nickel–phosphate, termed Dow B, are given in papers by several authors[143,145,146]. At 620–680°C, a butene space velocity of 125–175 h^{-1}, and a molar ratio of water vapour to n-butene of 20 : 1, butadiene was obtained in 90–94% yield with a conversion per pass of 45–55%.[146]

Diaconescu and coworkers[147] dehydrogenated butenes on a catalyst consisting of a mixture of oxides of magnesium, iron, copper, and potassium (73.5; 18.0; 4.3; 4.2% respectively) and a catalyst based on calcium and nickel

phosphates (PO_4 58.0; Ca 33.3; Ni 6.6; Cr_2O_3 2.17). The best yields of butadiene were obtained on a calcium–nickel–phosphate catalyst.

Recently great attention has been paid in the Soviet Union to the single-stage dehydrogenation of n-butane to butadiene. Single stage dehydrogenation greatly simplifies the technological arrangement as compared with the two-stage process, since it is no longer necessary to separate the butenes from the products of the first dehydrogenation stage. Moreover, the large amount of water vapour used in the dehydrogenation of the butenes to butadiene is saved. The single-stage method is advantageously carried out by dehydrogenatiny butane–butene mixtures, since fresh butane is sent for dehydrogenation with the recirculating butane–butene mixture that remains after separation of the butadiene from the reaction products. A large number of patents, but only a small number of papers, have been published on the direct preparation of butadiene from n-butene. A method for the preparation of bivinyl in one stage was first studied by Pshezhetskii and coworkers[148]. A butane–butene mixture containing 32–38% of butenes was dehydrogenated on an aluminochromium catalyst. At a temperature of 600°C and a pressure of 100–150 mmHg, the yield of butadiene was 14–15%, based on the amount of mixture passed through, and 60–68% based on the amount consumed. Dehydrogenation of pure n-butane under the same conditions gave 10.9 to 12.4% of butadiene based on the amount of butane passed through.

Balandin and coworkers[149] obtained 31% of butadiene, based on the amount of butenes passed through, or 15.7% based on the amount of butane–butene mixture (57 : 43) passed through at 600°C, 180 mmHg, and a contact time of 0.82 s.

Komarewsky[150] dehydrogenated butane on a selective dehydrogenation catalyst at 540–650°C and pressures of from 35 to 753 mmHg. The conversion to butadiene was 12.2% of butane per pass, with only slight carbon deposition (0.2%). By recirculation, 74% of butadiene can be obtained with only 2.3% of coke being deposited on the catalyst. Dehydrogenation of a technical butane–butene fraction of cracking gas (containing 35.7% of butenes) on a chromium catalyst at 180 mmHg and 600°C gave a butadiene yield of 31–35.5% based on the amount of butene passed through, or 9–10% based on the total flow[151].

Bogdanova and coworkers dehydrogenated butane–butene mixtures on an oxide catalyst in the presence of water vapour[152]. When the butene content of the initial mixture is increased from 41.4 to 65%, the yield of butadiene based on the total flow increases from 16.9 to 24.1%, but the yield based on the amount of butene passed through decreases from 40.8 to 38.4%. The yield of butadiene based on butene passed through increases in comparison with the yields obtained in experiments with pure butene because butane acts as a diluent, lowering the partial pressure of the butenes. On this catalyst butane is dehydrogenated only to a slight extent.

The catalysts K-3 and K-5 were found to be insufficiently active and selective in the dehydrogenation of a butane–butene mixture (60 : 40) at 600°C [18] (molar dilution with nitrogen 1 : 4 to 1 : 5). Under these conditions the yield of butadiene was 15–17% based on mixture passed through, and 70–75% based on mixture consumed. In the presence of hydrogen, a significantly lower amount of butadiene was obtained per pass. At the same time the yield of butadiene based on the amount of raw material decomposed increases because the thermal decomposition of butadiene, which is accompanied by the elimination of hydrogen, is inhibited. Worse results were obtained when methane, ethylene, or propene was used as a diluent. In experiments on the dehydrogenation of butane–butene mixtures containing 33% of butene at 600°C and 140 mmHg, 19% of butadiene was obtained[153]. Blowing the catalyst with hydrogen at high temperature improves the characteristics of the process (the yield of butadiene increases, the catalyst becomes more selective, and less coke is deposited). This is due to desorption at high temperature of the water formed when the catalyst is reduced by hydrogen.

Lyubarskii and coworkers[154] studied the kinetics of dehydrogenation of n-butane on an aluminochromium catalyst containing 6% of chromium(III) oxide at 460–500°C and partial butane pressures of from 0.1 to 1 atm, with nitrogen as diluent[154]. It was found that the reaction is inhibited by butene; a small amount of butene in the starting gas greatly reduces the degree of conversion of butane. Admixture of hydrogen has little effect on the rate of dehydrogenation. The kinetics of dehydrogenation are represented by the equation:

$$W = k_1 \frac{C_1}{C_2^{0.5}}$$

where C_1 is the concentration of butane, and C_2 is the concentration of butenes.

The effective rate of dehydrogenation of butane with allowance for reversibility of the reaction is expressed by the following equation[7]:

$$W_{\text{eff}} = k_1 \frac{C_1}{C_2^{0.5}} - k_2 C_2^{0.5} C_{H_2},$$

where C_{H_2} is the concentration of hydrogen.

The activation energy for the dehydrogenation of n-butane to butenes with nitrogen as diluent was 40 ± 1 kcal mole^{-1} at 460–500°C.

The conditions have been established[153] for the single-stage dehydrogenation of butane on Catalyst K-117; these are: a temperature of 590°C, a pressure of 150 mmHg, an operating cycle of 7 min, a space velocity of 400–600 h^{-1}, and a 67 : 33 butane–butene mixture.

On the industrial scale, the single-stage dehydrogenation of butane to butadiene has been effected by Houdry's method. The results of operations on the first semi-industrial and industrial plants for the dehydrogenation of butane and butane–butene mixtures have been described[155,156]. Butane was dehydrogenated on chromium(III) oxide–aluminium oxide catalysts at 580–590°C, at a residual pressure of 130 mmHg and a space velocity of 1–1.5 h^{-1}. The total duration of the cycle is 20 to 25 min, with a contact time of 7–10 min. The yield of butadiene is 32.7% based on the butane passed through. Later, the single-stage process was perfected and adopted industrially in the United States[157,158], the German Federal Republic[159], and France[160]. Dehydrogenation is carried out under vacuum on an aluminochromium catalyst. The duration of the dehydrogenation and regeneration cycles is 7–10 min. The amount of heat adsorbed in the endothermic dehydrogenation is balanced by the heat evolved in the burning of the coke deposited on the catalyst during regeneration. To ensure thermal balancing in the process, the catalyst is mixed with an inert material with a high heat

capacity, such as alundum, kaolin, refractory brick, etc. Fresh butane being fed into the dehydrogenation process is first mixed with the recirculating butane–butene mixture obtained after the butadiene has been removed from the dehydrogenation products of the initial mixture. The following are the optimal parameters for the process and the yield of butadiene reported in the literature[158]: temperature 600–607°C, pressure 100–150 mmHg, space velocity 2 h^{-1}, yield of butadiene 50–55%.

Bol'shakov has reviewed the literature on the single-stage dehydrogenation of butane to butadiene in reactors with an adiabatic regenerative cycle[161].

V. DEHYDROGENATION OF ISOPENTANE AND PENTENES

In the catalytic dehydrogenation of isopentane, three alkene isomers with the iso-structure are formed: 3-methylbut-1-ene, 2-methylbut-1-ene, and 2-methylbut-2-ene, and these are converted into isoprene. Table 4 gives data on the dehydrogenation of individual pentenes, with both the normal and iso-structure, and their mixtures.

Both Grosse and coworkers[132], and Mamedaliev and coworkers[162], concluded that the degree of dehydrogenation of methylbutenes is independent of the position of the double bond. On cannot agree with Grosse's conclusion, since the dehydrogenation of individual methylbutenes was studied with different contact times. Gorin and coworkers[163] established that 3-methylbut-1-ene is dehydrogenated to a lesser degree than two other methylbutenes under the same conditions. This conclusion has been confirmed by the work of Bogdanova and coworkers[164], in which higher yields of isoprene were obtained in the dehydrogenation of 2-methylbut-2-ene. Having studied the isomerisation of methylbutenes under dehydrogenation conditions, these workers suggested[164] that isoprene is mainly formed from 2-methylbut-2-ene, and to a lesser extent from 2-methylbut-1-ene, but 3-methylbut-1-ene isomerises to the two other methylbutenes. They studied the dehydrogenation of individual methylbutenes to isoprene with water vapour as a diluent and showed that the activation energies for the dehydrogenation of all three isomers are similar (20.9–22.1 kcal $mole^{-1}$).

TABLE 4. Data on the dehydrogenation of individual pentenes and their mixtures.

Starting alkene	Catalyst	Pressure (mmHg) or water-vapour dilution	Temperature, °C	Space velocity (h^{-1}) or contact time, s	Yield of alkadiene, wt. % of raw material	Reference
3-Methylbut-1-ene	Cr—Al c with 4% Cr_2O_3	190	600	0.05 s	21.4	132
2-Methylbut-2-ene + + 2-methylbut-1-ene	ditto	190	600	0.39 s	22.3	
Pent-2-ene	»	190	600	0.40 s	30.3	
3-Methylbut-1-ene	K-16	180	600	2.0 h^{-1}	28.5	162
2-Methylbut-1-ene	»	180	600	2.0 »	26.0	
3-Methylbut-1-ene	K-16	1:10	540	2.0 »	22.7	163
2-Methylbut-1-ene	»	»	540	2.0 »	27.2	
2-Methylbut-2-ene	»	»	540	2.0 »	27.7	
Mixture of methylbutenes	»	»	540	2.0 »	26.5	
ditto	Cr—Al	190	600	860—2000 h^{-1}	35	148
»		1:2.3–3.3	600	5 h^{-1}	30.6	164—166
»	Cr—Al of firm "UOR"	80	630	2.95 h^{-1}	35.6	167
»	ditto	80	660	1.53 h^{-1}	47.5	
»	Al—Cr—K	1:7 (diluent: N_2)	625	10 h^{-1}	30	168
2-Methylbut-2-ene	1707	1:14	665	500 h^{-1}	35.5	141
Mixture of methylbutenes	CaNi—phosphate	1:15—20	635	85—400 h^{-1}	35.3	144
2-Methylbut-2-ene		1:2.5—3	560 and 620	4.5—5.5 h^{-1}	20.4 and 41.3	164
2-Methylbut-1-ene		»	ditto	ditto	17.5 and 39	
3-Methylbut-1-ene		»	»	»	15.5 and 31.8	
n-Pentenes	mixed oxide	1:2.6—3.5	540—640	3—8 h^{-1}	12.3—25.6	169

Balandin and coworkers have studied the dehydrogenation of methylbutenes in the presence of water vapour[165,166]. It was found that the greatest yields of isoprene were obtained when the methylbutenes were diluted with water vapour in the ratio 1 : (2.3–3.3) by weight. With lower dilution ratios the yield of isoprene decreases, and the amounts of light hydrocarbons and carbon dioxide formed increase. In addition to the main reaction in which the methylbutenes are dehydrogenated to isoprene, demethanisation also occurs with the formation of butene and butadiene; the methylbutenes are hydrogenated to isopentane and isoprene is decomposed with the formation of light hydrocarbons and carbon dioxide. At 600°C and a space velocity of 5 h^{-1}, in the presence of water vapour, the yield of isoprene is 30.6% of the methylbutenes passed through. The activation energy for the dehydrogenation of a mixture of methylbutenes to isoprene was 23.3 kcal $mole^{-1}$.[165]

Mamedaliev and coworkers[170] dehydrogenated a mixture of methylbutenes in a semi-technical apparatus with a 0.5 litre reactor using K-16 Catalyst at 540°C and a space velocity of 2 h^{-1}, with water vapour as a diluent in the ratio of 7–10 moles per mole of starting material; they obtained a catalysate containing 23% of isoprene. The yield of isoprene on the methylpentenes passed is not stated. Kearby[141] dehydrogenated 2-methylbut-2-ene at a somewhat higher temperature (665°C) in the presence of Catalyst 1707 and water vapour (in the ratio 1 : 14) as a diluent and obtained a high yield (35.5%) of isoprene with a selectivity of 71%. Britton and Dietzler obtained a similar yield on calcium–nickel–phosphate catalyst at 635°C, the starting hydrocarbons being diluted with water vapour[144].

The dehydrogenation of normal pentenes has been studied by Grosse and coworkers[132], by Guyer[123], and by Bogdanova and others[169].

A number of workers have carried out the dehydrogenation of isopentane. Bogdanova and coworkers[171] have shown that, on an oxide catalyst at 580–620°C, and with a space velocity of feed of 5.5 h^{-1} and a 1 : 3 dilution with water vapour, comparatively low yields (4–8%) of isoprene are obtained. Mamedaliev and coworkers[172,173] studied the dehydrogenation of an isopentane fraction on Catalyst K-5 at 600–615°C with hydrogen as diluent; they found that the best yields of dienes (8.2–8.8%), on the basis of isopentane passed through, are obtained when the isopentane is diluted 1 : (3–4) with hydrogen. Higher yields of isoprene have been obtained on a catalyst developed at the All-Union Research Institute for Synthetic Rubber (VNIISK)[174]. The process was carried out at a low partial pressure of isopentane, obtained by using nitrogen as a diluent. It was shown that an increase in temperature or an increase in the degree of dilution leads to an increased content of diene hydrocarbons in the catalysts. The yield of diene hydrocarbons at 575°C, a space velocity of 1.1 h^{-1}, and a 1 : 4 dilution with nitrogen is 14.5%. High yields of isoprene (26–28.5% based on isopentane passed through) were obtained by Kolupaeva and coworkers[175] in the dehydrogenation of isopentane on an aluminochromium catalyst, previously activated in a stream of hydrogen, at a temperature of 600°C, a pressure of 100 mmHg, and a space velocity

of 0.4 h^{-1}. They showed that when the pressure is reduced the proportion of isoprene in the reaction products is increased in comparison with the proportion of the isopentanes. The yield of normal C_5-hydrocarbons is less than 1%. The studies mentioned here were made in a flow system with a stationary catalyst layer.

Chang and coworkers[26] studied the kinetics of dehydrogenation of isopentane on aluminochromium oxide catalysts in a fluidised bed at 500–600°C and a pressure of 100–500 mmHg. Although the equilisation of concentrations in the fluidised bed leads to inhibition of the process and an increase in the proportion of side-reactions, fairly high yields of isoprene were obtained per pass: at 600°C, 100 mmHg, and a contact time of 2.2 s, the yield of isoprene was 15.8% based on the amount of isopentane passed through. These workers found that the observed activation energy of the dehydrogenation reaction was 44 kcal $mole^{-1}$. The kinetics of dehydrogenation of isopentane have also been studied by Shirokov[176], using an aluminochromium catalyst at 471–521°C and 0.2–1 atm. He found that the kinetics of the reaction could be represented by the following equation:

$$W = k\frac{C_1}{C_2^{0.4}},$$

where C_1 and C_2 are the concentrations of isopentane and methylbutenes at the reactor outlet. The activation energy of the process was 38 kcal $mole^{-1}$, a value differing only slightly from the more recent values given above[26].

Like butadiene, isoprene can be prepared from isopentane by two methods: single-stage and two-stage. In the two-stage method, isopentane is dehydrogenated to methylbutenes on one catalyst; the methylbutenes are then separated from the reaction products and dehydrogenated on another catalyst to isoprene. The isolation of the methylbutenes from the catalysate is a complex problem because of the closeness of the boiling points of the components and the difficulty of separating the azeotropic mixtures formed. Isoprene can be obtained in one stage by the dehydrogenation of isopentane–methylbutene mixtures. The process is carried out on a single catalyst and it is not necessary to separate the methylbutenes from the isopentane. The difficulty of the single-stage process lies in the selection of suitable catalysts and in finding the conditions under which the dehydrogenation of isopentane to methylbutenes proceeds simultaneously with the dehydrogenation of the methylbutenes to isoprene; the conversion of isopentane into methylbutenes must not be less than the conversion of methylbutenes into isoprene. Isoprene is separated from the catalysate obtained in the dehydrogenation of isopentane–methylbutenes mixtures, and isopentane is added. The quantity of isopentane is adjusted so that the conversion of isopentane exceeds the conversion of methylbutenes. The isopentane–methylbutenes mixture is again subjected to dehydrogenation. The extent to which the process is single-stage (φ) is determined[177] by the ratio of the concentration of methylbutenes in recycle (σ') to the concentration of methylbutenes in the initial isopentane–methylbutene mixture (σ):

$$\varphi = \frac{\sigma'}{\sigma} \times 100.$$

A value of φ necessary for operation of the single-stage process may be achieved at certain ratios of the process parameters. A number of workers have obtained the ratio of conversion of isopentane and methylbutenes needed for single-stage dehydrogenation (Table 5); isopentane is consumed in the formation of isoprene, but at the same time there is a slight increase in the amount of methylbutenes[174]. The results of Mavity and Zetterholm[167] and those of Fridshtein and coworkers[174] on the dehydrogenation of methylbutenes and mixtures of methylbutenes and isopentane show that the yields of isoprene increase with decreasing pressure, or increasing dilution with nitrogen, and also with increasing temperature, and when the isopentene content of the starting material is increased. But as the temperature is increased, or the content of methylbutenes in the mixture is reduced, the selectivity of the process is reduced, and more coke is formed[174,178]. Increasing the contact time beyond 0.6 s does not increase the yield of isoprene, because this also increases the rate of secondary reactions (dimerisation and decomposition of isoprene, and coke formation). Isopentane has been dehydrogenated in a single-stage by Houdry's method[179] on a semi-technical apparatus with recycling of the unreacted products. The mixture subjected to dehydrogenation contained 16.6% of methylbutenes; the yield of isoprene was 12.1 wt.% based on the amount of mixture passed through, and 51.8 wt.% based on the amount converted.

To determine the optimal conditions for the dehydrogenation of isopentane–methylbutenes mixtures when the process is operating in one stage, Bol'shakov[180] studied the effect of temperature, space velocity, pressure, and content of methylbutenes in the mixture on the main characteristics of the process on Catalyst K-N. Table 6 gives his results.

In the same paper, Bol'shakov reported that when the partial pressure of the hydrocarbons is reduced by dilution with an inert gas such as nitrogen, the main characteristics of the single-stage process are impaired in comparison with dehydrogenation under vacuum. Thus, when nitrogen was used as a diluent, the yield of isoprene was 15% based on the amount of mixture passed through, and 50% based on the amount of mixture converted, the process being 100% single stage; under similar conditions but with the application of reduced pressure, the yield of isoprene increased to 17.7% based on the amount passed through, and 65% based on the amount of mixture converted, the process being single stage to the extent of 116%.[180]

Gorin and coworkers made a somewhat different approach to the dehydrogenation of isopentane–methylbutene mixtures[163]. In order greatly to simplify the two-stage scheme for the preparation of isoprene from isopentane, these workers proposed that dehydrogenation conditions

TABLE 5. Dehydrogenation of isopentane–methylbutene mixtures under single-stage conditions (according to data from different authors).

Temperature, °C	Pressure (mmHg) or dilution with nitrogen (molar ratio)	Space velocity, h^{-1}	Conc. of methylbutenes in initial mixture, wt.%	Conc. of isoprene in catalysate, wt.%	Yield of isoprene, wt.%: on hydrocarbons passed	Yield of isoprene, wt.%: on hydrocarbons decomposed	Conc. of methylbutenes, wt.%: in catalysate after separation of isoprene	Conc. of methylbutenes, wt.%: in catalysate recycle	Degree of single-stage operation	Reference
630	80	606	15	13.4	12.8	74.1	19.4	16.0	107	167
575	1:3	450	30	17.5	15.7	60.6	40.2	30.1	100	177
575	1:4	1350–1100	25	—	14.5–14.0	67–70	—	—	single-stage conditions achieved	174
600	100	0.4 (liquid)	21.4	—	27	61.5	—	21.4	ditto	178

TABLE 6. Optimal conditions for single-stage dehydrogenation of isopentane to isoprene on Catalyst K-N.

Partial pressure, mmHg	190
Temperature, °C	575
Space velocity, h^{-1}	450
Content of methylbutenes in mixture, %	27—28

should be so chosen that the ratio of methylbutenes to isopentane in the catalysate after separation of isoprene would be the same as the ratio of these compounds in the initial mixture. After separation of the isoprene from the reaction mixture, the mixture obtained can be sent for dehydrogenation having been mixed with a fresh portion of isopentane–methylbutene mixture of the same composition obtained in the first stage of the dehydrogenation of isopentane. The experiments showed that, at 580°C and a pressure of 190 mmHg, dehydrogenation of n-butane and butene [sic. pentane and pentene? (Ed. of Translation)] on a catalyst gives a catalysate containing 15–18% of isoprene (Table 7). The ratio of the methylpentenes to the isopentane in the initial mixture is the same as that in the catalysate (40 : 60).

Bogdanova and coworkers [171] studied the dehydrogenation of a prepared mixture of isopentane and methylbutene ($C_5H_{10} : C_5H_{12} = 1 : 1$) and of a catalysate (ratio 1 : 1.3) obtained on an aluminochromium catalyst after the first stage of the dehydrogenation of isopentane. These workers consider that the best results are obtained at 600–620°C, with a space velocity for the mixture 5–6 h^{-1} and a 1 : 3 dilution with water vapour. Under these conditions, the yield of isoprene is 38–40% based on isopentenes passed through and 88–92% based on the amount of mixture reacting.

Satisfactory results have also been obtained in the dehydrogenation of isopentane–methylbutene mixtures (60 : 40) diluted with benzene in the molar ratio 1 : 3.[163] Isopentane–methylbutene mixtures (70 : 30) have also been diluted with nitrogen–hydrogen mixtures [174] containing 0 to 50% of hydrogen. In the presence of hydrogen, the concentration of unsaturated hydrocarbons changes little, but the concentration of alkadienes decreases, as does also the degree of coke formation. Thus, as might be expected, the presence of hydrogen in the starting mixture has an inhibitory effect on the formation of isoprene.

A very important characteristic of the isopentane dehydrogenation process is the amount of coke deposited on the catalyst, which is determined by the temperature and duration of the experiment [181]. The amount of coke deposited increases with the methylbutene content of the mixture, and the coke is removed by the hydrogen. Tyuryaev and Balashova have suggested the following mechanism for coke formation [181]: isoprene → cyclic dimer → ... (polycondensation, decomposition, dehydrogenation)... → polycyclic hydrocarbons.

TABLE 7.

Temperature, °C	Space velocity, h^{-1}	Yield of catalysate, wt. %	Content of isoprene in catalysate, wt. %	Yield of isoprene, wt. %		Ratio $C_5H_{12} : C_5H_{10}$ in catalysate
				on mixture passed through	on mixture decomposed	
580	6	92.6	18.4	17.2	70.0	61.3:38.7
580	8	95.6	15.0	14.3	77.1	60.5:39.5

VI. DEHYDROGENATION OF C_6-HYDROCARBONS

Alkadienes have been prepared from C_6-alkanes and mono-alkenes on catalysts used for the dehydrogenation of butane and butenes to butadiene, the hydrocarbon being diluted with water vapour, hydrogen, or nitrogen [27,182–184].

Nazarov and coworkers [182] found that, on Catalysts K-12, K-16, and K-18, which are used for the conversion of butenes to butadiene, at temperatures of 600–675°C, space velocities of 1000–2000 h^{-1}, and a 1 : 8 water-vapour dilution, 2,3-dimethylbut-2-ene is converted into 2,3-dimethylbuta-1,3-diene. The yield of alkadiene on Catalyst K-16 is 20–23% based on the quantity of alkene passed through, and 40–50% based on the amount that reacts. Under similar conditions [181], on this catalyst, 2-methylpent-3-ene gives 10–13% of diene hydrocarbons (isoprene and 2,3-dimethylbuta-1,3-diene), calculated on the amount of hydrocarbon passed through.

A group of workers [183,184] dehydrogenated 2,3-dimethylbutane and its mixtures with 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene (containing 54% of alkenes) on Catalyst K-5 at 630°C, a space velocity of 2 h^{-1}, and 1 : 4 hydrogen dilution. These workers pointed out that the yield of alkenes and alkadienes (12–14% of starting material) does not depend on the position of the double bond in 2,3-isomers present in the starting mixture. When a mixture of 2,3-dimethylbutane with 2,3-dimethylbutenes (40%) diluted 1 : 8 by volume with water vapour is dehydrogenated on Catalyst K-16, a yield of 12–12.2% of alkadienes is obtained [184]. Timofeeva and coworkers [185] studied the dehydrogenation of 2,2-methylbutane on an aluminochromopotassium catalyst at 500°C, a space velocity of 0.72 h^{-1} at atmospheric pressure, with helium as an inert diluent. Comparison of the results showed that dilution increases the yield of 3,3-dimethylbut-1-ene in comparison with dehydrogenation at atmospheric pressure from 8–9 to 10–12%. Other workers, who carried out the reaction in vacuum on an aluminochromium catalyst also obtained ~10 wt.% of alkene [186].

Thus, in the dehydrogenation of the C_6 hydrocarbons described above, because of side-reactions, fairly low yields of unsaturated dehydrogenated products are obtained, although higher yields are thermodynamically possible. It is well known that the equilibrium yield of dehydrogenation products increases with increasing molecular weight [5–7].

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Certain conclusions can be drawn from the literature survey on the conversions of alkanes and alkenes at low pressures.

It is thermodynamically more advantageous to dehydrogenate alkanes and alkenes for the purpose of obtaining alkadienes at temperatures above 600°C and very low pressures. However, because of technological difficulties and increased cracking at high temperatures, the process cannot be carried out under these conditions. It is therefore expedient to carry out the dehydrogenation at 550–600°C and a pressure of 100–200 mmHg. Low partial pressures are obtained by evacuation, or by the use of inert diluents.

The use of nitrogen, methane, or carbon dioxide as a diluent greatly increases the volume of the contact gas, and this makes the condensation and separation of the reaction products very complicated. Water vapour has a number of advantages compared with the diluents mentioned above: it can be easily separated from the reaction products, it also serves as a heat carrier, and since it reacts with coke deposited on the catalyst, no special regeneration of the catalyst is necessary. In the dehydrogenation of mono-alkenes and alkadienes in the presence of water vapour, the most active catalysts were found to be those based on oxides of magnesium, iron, zinc, and phosphates of calcium and nickel. Other catalysts, even those that are active dehydrogenation catalysts, for example, aluminochromium catalysts, are rapidly deactivated in the presence of water vapour. For this reason, dehydrogenations of alkane and alkene hydrocarbons and their mixtures on aluminochromium catalysts are carried out in the presence of inert diluents, such as nitrogen, or under vacuum. The use of low pressures produced by evacuation in the dehydrogenation process is more effective than dehydrogenation in the presence of diluents, although operation under vacuum requires that the plant should be hermetically sealed to prevent air being sucked in. Most of the catalysts described in the literature for the dehydrogenation of alkanes, alkenes, and their mixtures at low pressures are not sufficiently selective. Further development of these processes therefore requires that a search should be made for new and more effective catalysts.

Kinetic studies of the dehydrogenation processes considered here have permitted elucidation of the most probable mechanism for the reactions and, in a some instances, have made it possible to select the optimal conditions for the process. However, a number of kinetic studies have been made at an unsatisfactory level, and the kinetics of the processes dealt with require extensive study with the use of the most modern methods.

The dehydration of C_4–C_5 hydrocarbons at low pressures has been widely adopted in the synthetic rubber industry, and a tendency has been noted to extend work still further in the field of single-stage dehydrogenation under vacuum of alkanes or mixtures of alkanes and alkenes to give alkadienes.

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CALCULATION OF THE ACTIVATION ENERGY OF CHEMICAL REACTIONS ON THE BASIS OF THE ADDITIVITY PRINCIPLE

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1. INTRODUCTION

A great mass of experimental data has now accumulated in the literature on chemical kinetics and urgently requires generalisation and classification. However, to appraise this mass of disconnected and often contradictory facts is quite a complex task, made difficult by the fact that the theoretical premises and the methods of calculation of the kinetic parameters for most chemical reactions are still in an "embryonic" state.

The now generally accepted theoretical treatment of the nature of the elementary act of a chemical reaction is based on the "activated complex" method developed by Eyring[1] and by Evans and Polanyi[2]. It is based on the concept that the configuration of the atoms of a system, whilst changing continuously during the course of a reaction, passes through some critical intermediate configuration, which has received the name of "activated complex" or "transition state". A quite important concept introduced in this method is the potential-energy surface with a saddle point corresponding to the "transition state". The height of this point in comparison with the initial system gives the activation energy of the chemical reaction.

In its quantitative aspect the activated complex method frequently allows the pre-exponential factors in the Arrhenius equation to be calculated satisfactorily[3]. The accuracy of the results thus obtained is approximately one order of magnitude.

As regards calculations of activation energy, the results obtained so far have been much more modest. The most developed theory is that for the simplest system of three hydrogen atoms, which corresponds to reaction (1):

$$H\cdot + H_2 \rightarrow H_2 + H\cdot \qquad (1)$$

Many studies[4-12] have been devoted to quantum-mechanical calculations of system (1), but it is only very recently that the use of computer techniques has allowed agreement