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PRINCIPLES OF THE PREPARATION OF BUTADIENE BY THE DEHYDROGENATION OF BUTANE AND BUTENE

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1. INTRODUCTION

The annual world production of buta-1,3-diene (divinyl), the most important monomer for the synthesis of many types of rubber, has long exceeded one million tons; the greater part of the butadiene is at present obtained by the catalytic dehydrogenation of n-butane and n-butene [1].

As a result of studies of the catalytic dehydrogenation of butane and butene, begun as early as the nineteen-thirties in the USSR and other countries, large factories were constructed in the USA during the Second World War for the production of butadiene by the single-stage dehydrogenation of butane in a vacuum, by the dehydrogenation of butene in the presence of water vapour†, and also by the two-stage dehydrogenation of butane according to the scheme: butane → butene → butadiene [1]. In the post-war years, several synthetic rubber factories were constructed in the USSR for the production of butadiene by the two-stage dehydrogenation of butane.

Because of their great practical importance, the dehydrogenation processes have been studied for many years in this country and abroad. The aim of studies of the dehydrogenation reactions is not limited to the solution of applied problems, however; the results of these studies have made an important contribution to the theory of heterogeneous catalysis. In particular, Balandin's multiplet theory of catalysis was developed in a study of the mechanism and kinetics of dehydrogenation reactions.

The number of papers devoted to the study of the dehydrogenation of hydrocarbons amounts to several hundred. The most detailed reviews are those of Kearby [2] and Lyubarskii [3]; the first of these covers the literature up to 1953, gives the equilibrium degrees of dehydrogenation at different temperatures, and describes industrial catalysts and methods of dehydrogenation; the second covers the literature up to 1957, describes in considerable detail the results of the development of catalysts for the dehydrogenation of alkanes, and gives data on the rate of dehydrogenation of butane, butene, and isopentane, obtained in the Karpov Physicochemical Institute.

The aim of the present paper is to review the accumulated material on the chemistry of the reactions taking place in the catalytic dehydrogenation of butane and butene, and on the equilibria and kinetics of these reactions.

† The use of water vapour achieves three results: the partial pressure of $n\text{-}C_4H_8$ is reduced, displacing the equilibrium towards the formation of C_4H_6, the necessary heat is supplied, and the deposited "carbon" is removed.

2. REACTIONS TAKING PLACE IN THE DEHYDROGENATION OF BUTANE AND BUTENE

In the catalytic dehydrogenation, many side reactions take place in addition to the main reactions involving the conversion of butane into butene and of butene into butadiene [4-6].

1. The main reactions are evidently:

$$n\text{-}C_4H_{10} \rightleftharpoons CH_3.CH_2.CH{=}CH_2 + H_2, \quad (1a)$$

$$n\text{-}C_4H_{10} \rightleftharpoons cis\text{-}MeCH{=}CHMe + H_2, \quad (1b)$$

$$n\text{-}C_4H_{10} \rightleftharpoons trans\text{-}MeCH{=}CHMe + H_2, \quad (1c)$$

or, overall,

$$n\text{-}C_4H_{10} \rightleftarrows n\text{-}C_4H_8 + H_2, \quad (1)$$

where $n\text{-}C_4H_8$ represents the equilibrium mixture of n-butene isomers;

$$EtCH{=}CH_2 \rightleftharpoons C_4H_6 + H_2, \quad (2a)$$

$$cis\text{-}MeCH{=}CHMe \rightleftharpoons C_4H_6 + H_2, \quad (2b)$$

$$trans\text{-}MeCH{=}CHMe \rightleftharpoons C_4H_6 + H_2, \quad (2c)$$

or, overall,

$$n\text{-}C_4H_8 \rightleftarrows C_4H_6 + H_2. \quad (2)$$

Let us now examine the side reactions.

2. The cracking of $n\text{-}C_4H_{10}$ in general cannot be described by a single stoichiometric equation, since the stoichiometric coefficients (and possibly even the composition of the reaction products) may depend on the temperature, degree of decomposition, and type of catalyst; these problems have been little discussed in the literature, however. It is stated [7] that the thermal cracking of $n\text{-}C_4H_{10}$ at 520°C and a degree of transformation up to 25% is described by the following reactions, which can be regarded as primary reactions:

$$15\ n\text{-}C_4H_{10} \rightarrow 10\ C_3H_6 + 10\ CH_4, \quad (3a)$$

$$\rightarrow 4\ C_2H_4 + 4\ C_2H_6, \quad (3b)$$

$$\rightarrow n\text{-}C_4H_8 + H_2, \quad (3c)$$

(that is, $15n\text{-}C_4H_{10} \rightarrow 10C_3H_6 + 10CH_4 + 4C_2H_4 + 4C_2H_6 + n\text{-}C_4H_8 + H_2$).

3. The cracking of $n\text{-}C_4H_{10}$ during its catalytic dehydrogenation to butene on one of the catalysts [5] takes place according to the equation

$$n\text{-}C_4H_{10} \rightarrow 0.12H_2 + 0.49CH_4 + 0.39C_2H_4 + 0.38C_2H_6 + 0.49C_3H_6 + 0.01C_3H_8 + 0.12C_4H_8, \quad (3d)$$

but on the catalyst used in the USSR it is described approximately by the equation [6]

$$n\text{-}C_4H_{10} \rightarrow 0.62CH_4 + 0.13C_2H_4 + 0.44C_2H_6 + 0.04C_3H_6 + 0.2C_3H_8 + 0.3(C_5+). \quad (3e)$$

4. The cracking of $n\text{-}C_4H_8$. A characteristic feature of the primary reactions involved in the thermal cracking of $n\text{-}C_4H_8$ is their much greater variety. Analysis of published data[8-14] indicates that at temperatures up to 600°C and small degrees of transformation in the thermal decomposition of but-1-ene and but-2-ene, the products are H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, and liquid hydrocarbons. The highest thermal stability is shown by but-2-ene.[13] The following can be regarded as the primary reactions in the thermal decomposition of $n\text{-}C_4H_8$:

$$n\text{-}C_4H_8 \rightleftarrows C_4H_6 + H_2, \quad (4a)$$
$$n\text{-}C_4H_8 + H_2 \rightarrow C_2H_4 + C_2H_6, \quad (4b)$$
$$n\text{-}C_4H_8 \rightarrow 2\,C_2H_4, \quad (4c)$$
$$n\text{-}C_4H_8 + H_2 \rightarrow CH_4 + C_3H_6, \quad (4d)$$
$$3n\text{-}C_4H_8 \rightarrow CH_4 + C_3H_6 + C_8H_{14}, \quad (4e)$$

The greater part of the $n\text{-}C_4H_8$ decomposes according to reaction (4d). It is suggested[5] that the cracking of $n\text{-}C_4H_8$ in its dehydrogenation on one of the catalysts (in the presence of water vapour) takes place according to the equation

$$n\text{-}C_4H_8 \rightarrow 0.25H_2 + 0.27CH_4 + 0.15C_2H_4 + 0.31C_3H_6 + 0.5C_4H_6 + 0.08 + 0.08(C_5+) + 0.1C. \quad (4)$$

5. Transformation of butadiene. The main reaction of C_4H_6 at 400–700°C and atmospheric pressure is its dimerisation[15] and this reaction is apparently the primary reaction:

$$2\,C_4H_6 \rightleftarrows C_8H_{12}. \quad (5a)$$

In the presence of dehydrogenation catalysts, this reaction is accompanied by the decomposition of butadiene (or its dimer) with the formation of lighter hydrocarbons and carbonaceous deposits ("carbon"); the following equations were found for two different catalysts for the dehydrogenation of $n\text{-}C_4H_8$:

According to the data of Beckberger and Watson[5]

$$C_4H_6 \rightarrow 0.56CH_4 + 0.07C_2H_4 + 0.58C_3H_6 + 1.49C, \quad (5b)$$

according to our data[16]

$$C_4H_6 \rightarrow 0.098CH_4 + 0.024C_2H_4 + 0.017C_3H_6 + 0.68C_4H_8 + 1.08C. \quad (5c)$$

The last equation was obtained[16] on the basis of the composition of the products of the decomposition of C_4H_6 on passage over a catalyst at 560–600°C and molar ratio $C_4H_6 : H_2O = 1:10-1:30$.

6. Isomerisation of $n\text{-}C_4H_{10}$ and $n\text{-}C_4H_8$. The following reactions are observed in the catalytic dehydrogenation

$$n\text{-}C_4H_{10} \rightleftharpoons iso\text{-}C_4H_{10}, \quad (6a)$$
$$n\text{-}C_4H_8 \rightleftharpoons iso\text{-}C_4H_8. \quad (6b)$$

7. Reactions of water vapour. In the dehydrogenation of butene in the presence of water vapour (the usual industrial conditions) the "carbon" formed on the catalyst — for example, according to reactions (5b) or (5c) — reacts with water vapour. It is assumed[17] that the following reactions take place in the interaction between water vapour and carbon (in particular during its gasification):

$$C + H_2O \rightleftarrows CO + H_2, \quad (7a)$$
$$C + 2\,H_2O \rightleftarrows CO_2 + H_2, \quad (7b)$$
$$CO_2 + H_2 \rightleftarrows CO + H_2O, \quad (7c)$$
$$C + 2H_2 \rightarrow CH_4, \quad (7d)$$

and a number of others. Two generally similar equations have been given for the reaction of water vapour with "carbon" deposited in the catalytic dehydrogenation of $n\text{-}C_4H_8$; one of these is[5]

$$H_2O + 0.512C \rightarrow 0.488CO_2 + 0.024CO + H_2, \quad (7e)$$

and the other is[16]

$$H_2O + 0.5068C \rightarrow 0.4931CO_2 + 0.0137CO + H_2. \quad (7f)$$

8. Reduction of the oxides of the catalyst. As shown below, many of the catalysts used in industry for the dehydrogenation of butane and butene contain the oxides of metals with variable valency — chromium and iron. The higher-valency oxides formed during their regeneration, that is, in the high-temperature calcination in a current of oxygen-containing gas, are converted into lower-valency oxides during the dehydrogenation in a reducing medium. For example[18],

$$CrO_3 \xrightarrow{C_nH_m} Cr_2O_3 + H_2O + CO_2 + CO,$$

and similarly for iron oxide

$$Fe_2O_3 \xrightarrow{C_nH_m} Fe_3O_4 \rightarrow FeO + H_2O + CO_2 + CO$$

Reduction may also be brought about by the hydrogen formed in the dehydrogenation, but analysis of the products[18,19] indicates that, for example, the CrO_3 in the aluminium–chromium catalyst is reduced chiefly by hydrocarbons. Other views have been put forward regarding the chemistry of the reduction of aluminium–chromium catalysts (with added potassium oxide); for example, it is suggested[20] that K_2CrO_4 is formed in the regeneration and that the following reaction takes place during dehydrogenation

$$2\,K_2CrO_4 + 2\,Al_2O_3 \xrightarrow{H_2} 4\,AlOOK + Cr_2O_3 + H_2O.$$

9. Reactions during the regeneration of the catalysts. The chief reactions in the regeneration of dehydrogenation catalysts are the combustion of the carbonaceous deposits and the change of the oxides of the catalysts from a lower valency to a higher valency. In particular, it has been shown[18,21-25] that in the regeneration of chromium and aluminium–chromium catalysts, Cr_2O_3 is converted into CrO_3; in addition, solid solutions of oxygen in chromium oxide may be formed.

10. Reactions leading to the formation of carbonaceous deposits. Important reactions in the dehydrogenation of butane and butene are those leading to the formation of carbonaceous deposits, which contain an appreciable quantity of hydrogen in addition to carbon[26] and which would be more correctly called tarry deposits. There are grounds for assuming[6,26-28] (the nature of the change in the composition of the carbonaceous deposits with change in the dehydrogenation conditions, and the formation of benzene, toluene, styrene, and other aromatic and cyclic hydrocarbons as side-products) that the so-called "carbon" deposited on the catalyst is formed not according to reactions (5b) or (5c) but according to the scheme:

$2C_4H_6 \rightarrow$ (vinylcyclohexene) $\rightarrow$ ... (polycondensation, dehydrogenation, cracking) ... $\rightarrow$ polycyclic hydrocarbons $\rightarrow$ ("tars" or "carbons").

11. Other reactions. The above list does not exhaust all the reactions taking place in the dehydrogenation of butane and butene, but these are the most important[6]. Other reactions which evidently take place in the dehydrogenation of n-C_4H_{10} and n-C_4H_8 are the dehydrogenation of the iso-C_4H_{10} formed by the isomerisation of n-C_4H_{10}, and the cracking of iso-C_4H_{10} and iso-C_4H_8, but the part played by these reactions is slight.

3. REACTION EQUILIBRIA

The equilibrium constant for the chemical reaction is calculated from the familiar equation

$$RT\ln K_{p_T} = -\Delta G^\circ_T = -\Delta H^\circ_T + T\Delta S^\circ_T,$$

and the degree of transformation x is related to K_p by an equation which depends on the form of the stoichiometric equation for the reaction. Methods for calculating the thermodynamic quantities and their values at different temperatures have been described in a number of familiar works[29-32], so that here we shall give for most reactions only the final equations for calculating the values of $\log K_p$ and the necessary data confirming the applicability of these equations; for some reactions we shall give the most reliable tabulated data.

1. The reaction n-$C_4H_{10} \rightleftharpoons$ n-$C_4H_8 + H_2$. The experimental and calculated data on the equilibrium for the dehydrogenation reaction have been reviewed[29].

Comparison of the values of K_p and x calculated on the one hand[2,6] from the latest and now generally accepted thermodynamic data, and on the other hand[6] from the empirical equations proposed by various authors, shows that the most satisfactory equations are those of Korobov and Frost[33]:

$$\begin{aligned}\log K_{p_{1-a}} &= \frac{-6586}{T} + 6.685,\\ \log K_{p_{1-b}} &= \frac{-6209}{T} + 6.639,\\ \log K_{p_{1-c}} &= \frac{-5992}{T} + 6.112.\end{aligned} \qquad (1)$$

The equilibrium constant for the overall reaction (1) is:

$$K_{p_1} = K_{p_{1-a}} + K_{p_{1-b}} + K_{p_{1-c}},$$

and the degree of transformation is

$$x_1 = \left(\frac{K_{p_1}}{K_{p_1} + P_{\text{total}}}\right)^{0.5}.$$

In the range 760–900°K, more accurate values of K_{p_1} are obtained from the equation[6]:

$$\log K_{p_1} = \frac{-30\,500}{4.575T} + 7.574. \qquad (2)$$

The values of K_p and x_1 calculated from Eqns. (1) and (2) are compared in Table 1 with the calculated values obtained[2] from thermodynamic data[32].

When side reactions take place simultaneously, the equilibrium degrees of dehydrogenation will differ from the values given in Table 1. When only the reaction $C_4H_{10} \rightleftharpoons C_4H_8 + H_2$ takes place and the degree of dehydrogenation is x_1, the partial pressures of the components are:

$$P_{C_4H_{10}} = \frac{1-x_1}{1+x_1}P_{\text{total}}, \qquad P_{C_4H_8} = P_{H_2} = \frac{x}{1+x}P_{\text{total}}.$$

TABLE 1. Equilibrium constants and equilibrium extents to which reaction (1) takes place at $P_{\text{total}} = 1$ atm.

T, °K	According to Eqn. (1)		According to Eqn. (2)		Calculations from thermodynamic data (Ref. 32)	
	K_{p_1}	x_1	K_{p_1}	x_1	K_{p_1}	x_1
760	0.0563	0.231	0.057	0.23	0.063	0.235
780	0.0945	0.296	0.106	0.31	0.105	0.309
800	0.1454	0.356	1.179	0.39	0.174	0.389
820	0.2258	0.433	0.282	0.47	0.282	0.47
840	0.3403	0.504	0.429	0.55	0.429	0.55
860	0.5069	0.580	0.667	0.63	0.667	0.63
880	0.7407	0.652	1.00	0.71	1.00	0.71
900	1.063	0.720	1.630	0.79	1.480	0.78

Substituting these values in the equation $K_{p_1} = \frac{P_{C_4H_8}P_{H_2}}{P_{C_4H_{10}}}$, we obtain

$$x_1 = \left(\frac{K_{p_1}}{K_{p_1} + P_{\text{total}}}\right)^{0.5}.$$

When side-reactions take place, the total number of reaction products is not $1 + x_1$ but α_1; since some of the n-C_4H_8 formed is used up in secondary reactions, the number of moles of n-C_4H_8 becomes equal to $x_1\gamma_1$ (where γ_1 is the selectivity of the dehydrogenation), and the quantity of hydrogen increases to $x_1\gamma_1\beta_1$, where β_1 is a coefficient for the excess of hydrogen, equal to $P_{H_2}/P_{C_4H_8}$. Substituting these values in the equation for the equilibrium constant, we obtain

$$x_1 = \frac{-K_{p_1}\alpha_1 + \sqrt{K_{p_1}\alpha_1(4\gamma_1^2\beta_1 P_{\text{total}} + K_{p_1}\alpha_1)}}{2\gamma_1^2\beta_1 P_{\text{total}}}.$$

2. The reaction n-$C_4H_8 \rightleftharpoons C_4H_6 + H_2$. Fairly accurate values of K_{p_2} and x_2 can be found from the equations[5]

$$\log K_{p_2} = \frac{-28\,000}{4.575T} + 5.70121, \qquad (3)$$

or[6]

$$\log K_{p_2} = \frac{-30\,500}{4.575T} + 6.33, \qquad (4)$$

as can be seen from Table 2, which gives the values of K_{p_2} and x_2, calculated[6] from these equations and found[2] from thermodynamic data[32].

The equation giving the dependence of x on K_p shows that with decrease in the total pressure (on dilution with an inert gas) the equilibrium degrees of dehydrogenation of butane and butene increase; the influence of reduced pressure is shown below for reaction (2):

	P = 1 atm						
T, °K	800	820	840	860	880	900	920
x_2	0.10	0.127	0.158	0.194	0.234	0.28	0.329
	P = 0.1 atm						
x_2	0.304	0.375	0.45	0.53	0.608	0.678	0.74
	P = 0.05 atm						
x_2	0.41	0.496	0.582	0.663	0.734	0.793	0.84

TABLE 2. Equilibrium constants and equilibrium extents to which reaction (2) takes place at P_{total} = 1 atm.

T, °K	According to Eqn. (3)		According to Eqn. (4)		Calculations (Ref. 2) according to published data (Ref. 32)	
	K_{p_2}	x_2	K_{p_2}	x_2	K_{p_2}	x_2
800	0.0112	0.106	0.00971	0.092	0.0102	0.10
820	0.0174	0.131	0.0159	0.124	0.0164	0.127
840	0.0263	0.159	0.0248	0.155	0.0256	0.158
860	0.0380	0.189	0.0378	0.19	0.0392	0.194
880	0.0550	0.229	0.0567	0.231	0.0585	0.234
900	0.0776	0.268	0.0838	0.278	0.0855	0.280
920	0.1096	0.307	0.121	0.32	0.1222	0.329

The equilibrium degree of dehydrogenation with allowance for side-reactions‡ is here equal to [6]:

$$x_2 = \frac{-K_{p_2}(\lambda+\alpha_2)+\sqrt{K_{p_2}^2(\lambda+\alpha_2)^2+4K_{p_2}(\lambda+\alpha_2)(P_{total}\gamma_2^2\beta_2)}}{2\gamma_2^2\beta_2 P_{total}}.$$

Equilibrium for the Dehydrogenation of Butane-Butene Mixtures. In the single-stage method for the preparation of butadiene, a butane–butene mixture is dehydrogenated (at reduced pressure). The term "single-stage" is a technological description (the process takes place in a single reaction vessel and only $n\text{-}C_4H_{10}$ is used up), but in actual fact the reaction takes place [34] according to the scheme

$$n\text{-}C_4H_{10} \rightarrow n\text{-}C_4H_8 \rightarrow C_4H_6.$$

The equilibrium degrees of dehydrogenation of a $n\text{-}C_4H_{10}$ + $n\text{-}C_4H_8$ mixture in the presence of an inert diluent were first calculated by Bogdanov [35]. The calculation of the equilibrium composition in the dehydrogenation of $n\text{-}C_4H_{10}$ + $n\text{-}C_4H_8$ at reduced pressure can be approached as follows [6]. Let us assume that $n\text{-}C_5H_{10}$: $n\text{-}C_4H_8$ = m : n and that $m + n = 1$. Let y_1 and y_2 be the numbers of moles of $n\text{-}C_4H_8$ and C_4H_6 formed. The equilibrium mixture will then contain the following numbers of moles:

$$n\text{-}C_4H_{10} = m - y_1;\ n\text{-}C_4H_8 = n + y_1 - y_2;\ C_4H_6 = y_2;\ H_2 = y_1 + y_2,$$

and a total of $1 + y_1 + y_2$ moles.

The partial pressures are

$$P_{C_4H_{10}} = \frac{m-y_1}{1+y_1+y_2}P_{total};\quad P_{C_4H_8} = \frac{n+y_1-y_2}{1+y_1+y_2}P_{total};$$

$$P_{C_4H_6} = \frac{y_2}{1+y_1+y_2}P_{total};\quad P_{H_2} = \frac{y_1+y_2}{1+y_1+y_2}P_{total}.$$

‡ $\lambda = H_2O/C_4H_8$ mole mole^{-1}.

The equilibrium constant for the reaction

$$n\text{-}C_4H_{10} \rightleftharpoons n\text{-}C_4H_8 + H_2,$$

is

$$K_{p_1} = \frac{(n+y_1-y_2)(y_1+y_2)}{(1+y_1+y_2)(m-y_1)}P_{total},$$

and the equilibrium constant for the reaction

$$n\text{-}C_4H_8 \rightleftarrows C_4H_6 + H_2,$$

is

$$K_{p_2} = \frac{(y_1+y_2)y_2}{(1+y_1+y_2)(n+y_1-y_2)}P_{total}.$$

Dividing the first equation by the second and introducing the symbols $\frac{n+y_1}{y_2} = a$ and $\frac{1}{y_2} = b$, we obtain

$$b = \frac{(1+a)P_{total} - K_{p_2}(a^2-1)}{K_{p_1}m(a-1)+nP_{total}}, \quad (5)$$

$$b = \frac{K_{p_2}(a-1)^2}{K_{p_1}} + a. \quad (6)$$

This system can be solved graphically. For this purpose, Eqn. (6) is used to construct curves giving the dependence of b on a for different temperatures; points are plotted on the resulting graph in accordance with Eqn. (5) (separately for each temperature and pressure). The equilibrium compositions calculated [6] in this way for the dehydrogenation of a $n\text{-}C_4H_{10}$ + $n\text{-}C_4H_8$ mixture are given in Table 3.

Thus industrially acceptable yields of butadiene can be achieved at a temperature above 570°C and a pressure less than 125 mmHg at a concentration of $n\text{-}C_4H_8$ in the original mixture not less than 30%.

3. Cracking of $n\text{-}C_4H_{10}$. The results of calculations [36] of the equilibrium composition of the products obtained when only the primary reactions (3a)–(3c) take place indicate that under the conditions of dehydrogenation of $n\text{-}C_4H_{10}$ (500–600°C) its equilibrium degree of cracking amounts to about 70–75%.

TABLE 3. Equilibrium $n\text{-}C_4H_{10}$ + $n\text{-}C_4H_8$ + C_4H_6 composition for dehydrogenation of $n\text{-}C_4H_{10}$ + $n\text{-}C_4H_8$ mixture.

Original $n\text{-}C_4H_{10}$ + + $n\text{-}C_4H_8$ mixture	T, °K	P_{total} = 760 mmHg			250 mmHg			125 mmHg			95 mmHg		
		$n\text{-}C_4H_{10}$	$n\text{-}C_4H_8$	C_4H_6	$n\text{-}C_4H_{10}$	$n\text{-}C_4H_8$	C_4H_6	$n\text{-}C_4H_{10}$	$n\text{-}C_4H_8$	C_4H_6	$n\text{-}C_4H_{10}$	$n\text{-}C_4H_8$	C_4H_6
100:0	830	0.468	0.508	0.024	0.226	0.676	0.098	0.122	0.704	0.174	0.094	0.698	0.208
	850	0.378	0.58	0.042	0.162	0.698	0.14	0.082	0.673	0.245	0.063	0.643	0.294
	870	0.306	0.626	0.068	0.117	0.692	0.191	0.057	0.619	0.324	0.046	0.572	0.382
	890	0.246	0.649	0.105	0.088	0.66	0.252	0.044	0.542	0.414	0.035	0.492	0.472
80:20	830	0.404	0.561	0.035	0.213	0.678	0.109	0.128	0.685	0.186	0.104	0.681	0.215
	850	0.33	0.617	0.053	0.158	0.691	0.151	0.194	0.653	0.253	0.073	0 630	0.297
	870	0.279	0.642	0.079	0.12	0.68	0.20	0.07	0.599	0.331	0.055	0.560	0.385
	890	0.217	0.65	0.118	0.096	0.642	0.262	0.056	0 524	0.42	0.044	0.471	0.485
70:30	830	0.368	0.589	0.043	0.201	0.68	0.119	0.128	0.678	0.194	0.108	0.671	0.221
	850	0.302	0.636	0.062	0.152	0.687	0.161	0.094	0.645	0.261	0.080	0.677	0.303
	870	0.247	0 663	0.090	0.118	0.672	0.21	0.072	0.589	0.339	0.060	0.550	0.39
	890	0.20	0.671	0.129	0.096	0.633	0.271	0.058	0.514	0.428	0.047	0.464	0.489
60:40	830	0.329	0.618	0.053	0.184	0.686	0.13	0.122	0.673	0.205	0.105	0.663	0.232
	850	0.27	0.657	0.073	0.141	0.688	0.171	0.092	0.636	0.272	0.080	0.605	0.315
	870	0.22	0.679	0.101	0.113	0.667	0.22	0.071	0.579	0.350	0.061	0 539	0.40
	890	0.18	0.679	0.141	0.092	0.627	0.281	0.058	0.503	0.439	0.048	0.455	0.497

4. Cracking of $n\text{-}C_4H_8$. The equilibrium extents to which the primary reactions involved in the cracking of $n\text{-}C_4H_8$ take place can be calculated from the equations:

$$x_{4b} = \frac{(K_{p_{4b}})^{0.5}}{1+(K_{p_{4b}})^{0.5}}; \quad x_{4c} = \left(\frac{K_{p_{4c}}}{K_{p_{4c}}+4}\right)^{0.5};$$

$$x_{4d} = \frac{(K_{p_{4d}})^{0.5}}{1+(K_{p_{4d}})^{0.5}}; \quad x_{4e} = \frac{\sqrt[3]{K_{p_{4e}}}}{1+\sqrt[3]{K_{p_{4e}}}},$$

while that for reaction (4) can be found graphically. Calculations[6] from thermodynamic data[29] showed that in the range 520–630°C reactions (4), (4b), and (4e) are almost completely displaced to the right; the degree of transformation according to reaction (4d) varies from 94.7% to 92.3% and the degree of transformation according to reaction (4c) varies from 46.6% to 80.8%.

5. Transformation of C_4H_6. The temperature dependence of the equilibrium constant for the dimerisation of C_4H_6 is given by the equation[5]:

$$R\ln K_{p_{5a}} = \frac{-34\,825}{T} + 5.968 + 11.0755\log T + 10^{-4}T - 1.288\times 10^{-6}T^2.$$

The equilibrium degrees of dimerisation, calculated[6] from the equation

$$x_{5a} = \left[1 - \frac{1}{(1+4K_{p_{5a}})^{0.5}}\right],$$

are given in the following table

T, °K	800	820	840	860	880	900
x_{5a}	0.891	0.861	0.818	0.767	0.707	0.633

The cracking reactions (5b) and (5c) at 500–600°C are almost completely displaced to the right.

6. Isomerisation reactions. Equations for calculating the equilibrium constants for the isomerisation reactions in the gaseous phase are summarised in Table 4.

All these equations show satisfactory agreement with calculations using the latest thermodynamic data.

TABLE 4. Equations for the temperature dependence of the equilibrium constants of the isomerisations (in the gaseous phase).

Reaction	Equation	Temp. range, °C	Ref.
$n\text{-}C_4H_{10} \rightleftarrows Me_2C{=}CH_2$	$\log K_{p_{6a}} = \frac{358+93}{T} - 0.802+0.055$	—	33
	$\log K_{p_{6a}} = \frac{2318}{4.575T} - 0.929$	150	37
$n\text{-}C_4H_8 \rightleftarrows Me_2C{=}CH_2$	$\log K_{p_{6b}} = \frac{304}{T} - 0.528\pm 0.020$	265—426	38
$EtCH{=}CH_2 \rightleftarrows MeCH{=}CHMe$	$\log K_p = \frac{619.3}{T} - 0.335$	200—380	39
$EtCH{=}CH_2 \rightleftarrows$ *cis*-$MeCH{=}CHMe$	$\log K_p = \frac{387}{T} - 0.393$	200—380	39
$EtCH{=}CH_2 \rightleftarrows$ *trans*-$MeCH{=}CHMe$	$\log K_p = \frac{606}{T} - 0.524$	200—380	39

With increase in temperature the equilibrium is displaced towards the formation of $n\text{-}C_4H_8$; the equilibrium composition of the $n\text{-}C_4H_8$ mixture changes little with temperature[40]:

T, °K	800	820	840	860	880	900
$EtCH{=}CH_2$	0.303	0.312	0.32	0.328	0.336	0.344
cis-$MeCH{=}CHMe$	0.297	0.294	0.292	0.289	0.288	0.285
trans-$MeCH{=}CHMe$	0.40	0.394	0.388	0.383	0.376	0.371

7. Reactions of water vapour. The equilibrium constants for reactions (7a) to (7d) can be calculated using the following simplified equations[17]:

$$\log K_{p_{7a}} = \frac{-6830}{T} + 1.75\log T + 2.5, \quad (7a)$$

$$\log K_{p_{7b}} = \frac{-4300}{T} + 1.75\log T + 0.8, \quad (7b)$$

$$\log K_{p_{7c}} = \frac{-2150}{T} + 2.3, \quad (7c)$$

$$\log K_{p_{7d}} = \frac{-8919}{T} + 9.01. \quad (7d)$$

The equilibrium extents to which all these reactions take place increase with temperature and, for example, amount to 50–60%[33] at 600°C and stoichiometric ratio of the reacting substances; under the conditions of the dehydrogenation of butene, however, because of the large excess of water vapour (and also hydrogen) relative to the quantity of "carbon" on the catalyst, the equilibria for reactions (7a), (7b), (7c), (7e), and (7f) are almost completely displaced to the right.

It is impossible to examine the equilibria for the oxidation or reduction of the metal oxides usually present in dehydrogenating catalysts, since usually the form of compound in which the oxides are actually present in the catalyst and the reactions involved in the conversion of the metal from one valency state to another are still unknown.

4. CATALYSTS

There have been many attempts to use different combinations of oxides as catalysts for the dehydrogenation of alkanes, particularly butane, but only the aluminium–chromium oxide catalysts promoted with potassium oxide have found industrial application[2]. The optimal concentration of Cr_2O_3 in catalysts for the dehydrogenation of $n\text{-}C_4H_{10}$ to $n\text{-}C_4H_8$ is apparently close to 10%.[2] Many properties of these catalysts (the optimal concentration of chromium oxide, the influence of promoting additives, methods of preparation, the porous structure of the Al_2O_3 and the catalysts, the influence of the catalyst particle size, the degree of dispersion of the chromium oxide, and the relationship between the catalytic activity and the electrical conductivity) have been described in detail[3]. A characteristic property of aluminium–chromium catalysts is their sensitivity to the poisoning effect of water; thus in the dehydrogenation of isobutane the activity of the catalyst begins to decrease at a concentration of water vapour in the original gas greater than 1 mg litre^{-1}, but the activity also decreases with decrease in the moisture content of the isobutane (below 1 mg litre^{-1}).[41] This feature (the decrease in activity in the total absence of water) has unfortunately not yet been explained. An extremely important feature of aluminium–chromium catalysts is the change in their activity during dehydrogenation; the yield of butene[19] increases sharply in the first few minutes after regeneration, reaches a maximum (see

Fig. 1§), and then decreases¶. The reduced activity in the first minutes is attributed[16] to poisoning of the catalyst by the water formed by the reaction of the excess (relative to Cr_2O_3) of oxygen with the hydrocarbons. The activity of the catalyst increases as this excess of oxygen is used up and the water (and also CO_2) is desorbed. The decrease in the activity of the catalyst after the maximum is usually attributed to an increase in the deposition of carbon, although this is unlikely to be the only cause.

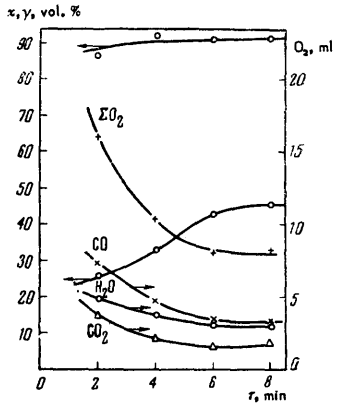


Fig. 1. Change in the yield of n-C_4H_8, selectivity, and quantity of combined oxygen during dehydrogenation of butane for 8 min at 570° and a space velocity of 1000 h^{-1}:
x — yield of n-C_4H_8; γ — selectivity;
O_2 — quantity of oxygen in H_2O, CO_2, and CO;
ΣO_2 — total quantity of O_2; τ — duration of dehydrogenation.

Many papers have been devoted to the study of the influence of the oxidation and reduction of aluminium–chromium[18,22,24,25,43] and also chromium[44–46] catalysts on their activity in dehydrogenations (of butane or cyclohexane). In most of this work it has been shown unambiguously that after reduction (with sufficient desorption of water) the activity of the catalysts increases†; if, however, the desorption of the water formed during the reduction is inadequate, the activity of the catalyst may even decrease as a result.

The compositions of the industrial catalysts for the dehydrogenation of butene are more varied than those of the catalysts for the dehydrogenation of butane; the compositions and properties of these catalysts are given in Table 5.

At present, the chief catalyst used in Canada and Britain is Dow-B, and the chief catalysts used in the USA are Shell-205, Dow-B, and Phillips-1490.[47] The chief advantages of the Shell catalysts are: prolonged operation without regeneration, low dilution with water vapour, durability, and mechanical strength; a disadvantage of the catalysts is their low selectivity[48]. High yields and selectivity are the chief advantages of the catalyst Dow-B,[49] although this catalyst also has many disadvantages (sensitivity to poisoning by most oxides and metals, higher yields of carbonyl compounds and alkynes, and shorter operational life[48]).

Method of dehydrogenation may be mentioned briefly. Three methods for dehydrogenating butane to butene are known[50–55]: in tubular periodic-action reactors with external heating and immobile catalyst, in assemblies with moving catalyst spheres, and in assemblies with a fluidised bed of fine catalyst particles.

In all countries the dehydrogenation of butene on the industrial scale is carried out in reactors without external heating on an immobile catalyst[1]. The single-stage dehydrogenation of butane to buta-1,3-diene is carried out[1] at reduced pressure in a system of reactors, each of which

§ An earlier paper[19] gave data on the change in the yields only at 505°; analogous data have been obtained at 570° and 590°.

¶ The same relationships were observed in the dehydrogenation of isopentane[42,114].

† An increase in the activity of the aluminium–chromium catalyst as a result of its reduction by hydrogen was also observed[42] in the dehydrogenation of pentane and isopentane.

TABLE 5. Composition and properties of some industrial catalysts for the dehydrogenation of butene*.

Catalyst (firm's designation)	Composition, %	Conditions of use (in industrial reactors)	Characteristics		References
			yield of C_4H_8, mole %	selectivity, mole %	
No. 1707	72.4MgO + 4.6CuO + 18.4Fe_2O_3 + 4.6K_2O	630°, space velocity (with respect to C_4H_8) 400 h^{-1}, dilution to molar ratio $C_4H_8 : H_2O$ = 1 : 10, duration of dehydrogenation 1 h, duration of regeneration 1 h	20.2	73	1, 47
Shell-105	90Fe_2O_3 + 4Cr_2O_3 + 6K_2CO_3	620°, space velocity 400 h^{-1}, dilution to molar ratio 1 : 10, duration of dehydrogenation without regeneration about one week	19–20.3	69–72	1, 2, 47, 48
Shell-205	same as Shell-105, but with higher K_2CO_3 content	621–677°, space velocity 500 h^{-1}, dilution to molar ratio 1 : 8, dehydrogenation for 24 h, regeneration for 1 h	19.5–20.5	73–75	1, 2, 47
Phillips-1490	unknown	649°, dilution to molar ratio 1 : 10, operation for one year without regeneration	20.5	76	47
Dow-B	$Ca_3Ni(PO_4)_6$ stabilised with 2% Cr_2O_3 on carrier	593–677°, space velocity 125–175 h^{-1} dilution to molar ratio 1 : 20, dehydrogenation for 15–30 min, regeneration for 15–50 min	42.5–49.5	90–94**	49, 94

* See also Ref. 94.

** Maximal yield and selectivity.

is periodically switched over to dehydrogenation, regeneration, and preliminary operations (blow-through, evacuation, etc.). In the dehydrogenation the temperature of the catalyst (mixed with inert packing) is reduced by 15–20 deg and this supplies the heat required for the process. The operational conditions are chosen in such a way that the heat of dehydrogenation is equal to the heat of regeneration[47,56]. Many sources point out the need to purge the catalyst with hydrogen after regeneration[57].

5. REACTION RATES

The study of the rates of the reactions taking place in the dehydrogenation of n-C_4H_{10} and n-C_4H_8 involves many difficulties associated with the complexity (large number of reactions) and non-steady nature (change in activity during a single cycle) of the process.

An outstanding contribution to the study of the mechanism and kinetics of the catalytic dehydrogenation of organic compounds has been made by the work of Balandin and his school. On the basis of the principles of the multiplet theory of catalysis, he developed the mechanism of dehydrogenations[58,59], proposed a general equation for the rate of dehydrogenation of organic compounds[60,61], made a detailed study of the rate of dehydrogenation of n-C_4H_8 on chromium and mixed oxide catalysts[62–65], obtained general relationships[66] for the dehydrogenation of n-C_4H_{10}, and studied the dehydrogenation[67–69] of n-C_4H_{10} + n-C_4H_8 mixtures. Important studies of the kinetics of the dehydrogenation of n-C_4H_{10} and n-C_4H_8 have been carried out by Kagan, Lyubarskii, Pshezhetskii, and their coworkers[3]. Let us now examine the equations for the rates of individual reactions.

Rate of Dehydrogenation

The reaction n-$C_4H_{10} \rightleftharpoons$ n-$C_4H_8 + H_2$. The equations at present known for the rate of dehydrogenation of n-butane to butene are given in Table 6.

TABLE 6. Equations for the rate of dehydrogenation of n-C_4H_{10} to n-C_4H_8 over aluminium–chromium catalysts.

No.	Rate equations	Temperature range, deg	Apparent activation energy E_1, kcal mole^{-1}	Refs.
1	$\frac{dx_1}{d\tau} = k_d \exp\left(h - \frac{1}{RT}\right) E_1 \cdot \frac{P_1}{\Sigma z_r \cdot P_r}$	—	—	59,60
2	$-\frac{dP_1}{d\tau} = \frac{k_1 P_1}{1 + k_1/k_2 P_1 + k_3/k_4 P_2}$	260–500	—	70
3	$-\frac{dC_1}{d\tau} = k_1 \frac{C_1}{C_2^{0.5}} - k_{hydr} C_2^{0.5} \cdot C_3$	460–500	40.0±1.0	71,72
4	$\ln \frac{D}{D-M} = a\tau^b$	500–550	—	73
5	$\frac{dx_1}{d(W/F)} = \frac{k_1 (P_1 - P_2 P_3/Kp)}{(1 + k_1' P_1 + k_2' P_2 + k_3' P_3)^2}$	570 480–550	36.0 43.9	4 53
6	$\frac{dx_1}{d(W/F)} = k_1 \frac{P_1}{P_2^{0.5}} \left(1 - \frac{P_2 P_3}{K_p P_1}\right)$	510–550	41.4±2.2	83,115

Note. According to data[116] obtained in a flow-circulation assembly, the rate of dehydrogenation of n-C_4H_{10} on a reduced aluminium–chromium–potassium catalyst at 525–570° is described by the equation

$$k_1 P_1 \left(1 - \frac{P_2 P_3}{K_p P_1}\right), \quad E = 46 \pm 3 \text{ kcal mole}^{-1}.$$

In these equations, the left-hand side gives expressions for the rate of dehydrogenation; P_1, P_2, P_3, and P_4 are the partial pressures of n-C_4H_{10}, n-C_4H_8, H_2, and C_4H_6 respectively; C_1, C_2, C_3, and C_4 the concentrations of the reagents (in the same order as in the case of P_i); $k_d = \frac{k_0 \alpha}{h - 1/RT}$, in which k_0 is a constant, and h and α the coefficients in the function for the distribution of the active centres of the catalyst with respect to activation energies $\Phi(E) = \alpha \exp(hE)$; z_r the relative adsorption coefficients for the reacting substances, and P_r their partial pressures; k_1, k_2, and k_3 — in Eqn. (2) — the rate constants for the elementary reactions (formation and decomposition of the surface radical) or, in Eqn. 5 (with primes) the constants of the adsorption equilibrium for n-C_4H_{10}, n-C_4H_8, and H_2; k_1 — in Eqns. (3), (5), and (6) — the rate constant; W the weight of catalyst; F the rate of supply of butane; x_1 and M the degrees of dehydrogenation; D the maximum degree of dehydrogenation attainable on a given catalyst at a given temperature; τ the duration of contact, and a and b coefficients.

Equation 1 was proposed by Balandin, who claims[61] that it expresses the rate of dehydrogenation of hydrocarbons, alcohols, and amines over metallic and oxide catalysts at pressures which are not too low and at a distance from equilibrium. This equation is readily transformed into Frost's equation[75] for monomolecular irreversible reactions. Let us demonstrate this. For a given catalyst, the quantity $k_d \exp(h - 1/RT).E = \varphi(T) = K$. Replacing the partial pressures by the degree of dehydrogenation x_1 and integrating from 0 to x_1, we obtain

$$k\tau = \int_0^{x_1} \frac{\frac{1-x_1}{1+x_1} z_1 + \frac{x_1}{1+x_1} z_2 + \frac{x_1}{1+x_1} z_3}{\frac{1-x_1}{1+x_1}} dx = \int_0^{x_1} \left[z_1 + (z_2 + z_3) \frac{x_1}{1-x_1} \right] dx_1 = (z_2 + z_3) \int_0^{x_1} \left(\frac{z_1}{z_2 + z_3} + \frac{x_1}{1-x_1} \right) dx_1,$$

from which

$$\frac{K}{z_2 + z_3} \tau = \frac{z_1}{z_2 + z_3} x_1 - \ln(1 - x_1) - x_1 = \ln \frac{1}{1-x_1} - \left(1 - \frac{z_1}{z_2 + z_3}\right) x_1.$$

Introducing the symbols

$$\frac{K}{z_2 + z_3} = k_1 \text{ and } 1 - \frac{z_1}{z_2 + z_3} = \beta,$$

we obtain

$$k_1 \tau = \ln \frac{1}{1-x_1} - \beta x_1.$$

An analogous transformation[106] in more general form was given earlier[59,61].

Equation 2 (Pshezhetskii, Lyubarskii, and coworkers) is analogous in form to the first equation of Balandin, but the coefficients of the equations (for the partial pressures of the reagents) are interpreted in different ways. According to Pshezhetskii, Lyubarskii, and coworkers[70], these coefficients give the ratio of the rate constants of the elementary stages of the reaction; according to Balandin[60,61], these coefficients are the relative constants of the adsorption equilibrium for the reagents, as confirmed by the much higher value of the constants for the adsorption equilibrium compared with the value of the dehydrogenation rate constant[76].

The equation of Pshezhetskii and Lyubarskii is also readily transformed into Frost's equation. Integration of this equation gives[70]:

$$\left(\frac{k_1}{k_2}-\frac{k_3}{k_4}\right)P_1^0\alpha-\left(1+\frac{k_3}{k_4}\right)P_1^0\ln(1-\alpha)=\frac{k\omega}{V},$$

where P_1^0 is the initial partial pressure of C_4H_{10}, $\alpha = \frac{P_1^0 - P_1}{P_1}$ the degree of transformation; V the rate of flow of gas, and ω the free volume of the catalyst. Dividing both sides of the equation by $\left(1+\frac{k_3}{k_4}P_1^0\right)$ and introducing the symbols

$$\frac{\left(\frac{k_1}{k_2}-\frac{k_3}{k_4}\right)P_1^0}{1+\frac{k_1}{k_2}P_1^0}=-\beta \text{ and } \frac{k_1}{1+\frac{k_3}{k_4}P_1^0}=K,$$

we obtain

$$K\frac{\omega}{V}=\ln\frac{1}{1-\alpha}-\beta\alpha.$$

The value of β here is in fact negative, since[70] $\frac{k_3}{k_4} \gg \frac{k_1}{k_2}$ (for example[70], at 500°, $k_1/k_2 = 3.8$ and $k_3/k_4 = 100$).

Equations 1 and 2 are applicable only for low degrees of dehydrogenation, since they make no allowance for the back reaction.

Equation 3 (Lyubarskii and Pshezhetskii) is an empirical equation; it makes allowance for the reverse reaction of hydrogenation[72] and is more conveniently written in the form (retaining the symbols used in the original[72]):

$$w=k_1\frac{C_1}{C_2^{0.5}}\left(1-\frac{C_2C_3}{K_CC_1}\right),$$

since $k_1/k_{hydr} = K_C$ is the equilibrium constant. In this form the equation is applicable up to equilibrium.

Equation 4 (Obolentsev and coworkers[73]) is of characteristic form‡ and is also distinguished by the fact that as $\tau \to 0$ the reaction rate also tends to 0; the existence of an induction period for this example is difficult to explain although for the thermal dehydrogenation of ethane the form of the kinetic curve apparently indicates the existence of an induction period[78].

Equation 5 was derived, on the basis of a general method[79], from the Langmuir isotherm. In the derivation it was assumed[4] that the dehydrogenation involves two active centres; the equation makes allowance for the back reaction.

Equation 6[6,74,115] is analogous to the Lyubarskii–Pshezhetskii equation. Some of the data for its derivation are given in Figs. 2 and 3§. The experiments were carried out in a flow assembly with an immobile catalyst layer (particle size 0.7 mm) at maximal activity. In the range 510–550°C, the apparent activation energy is 41.4 ± ± 2.2 kcal mole^{-1}, and in the range 550–570°C E = 15.7 ± ± 0.7 kcal mole^{-1}.[83,115] The observed decrease in the value of E here is due to retardation by internal diffusion.

The establishment of the kinetic relationships for dehydrogenation in a fluidised catalyst bed is extremely important. From the general relationship[80] it follows that

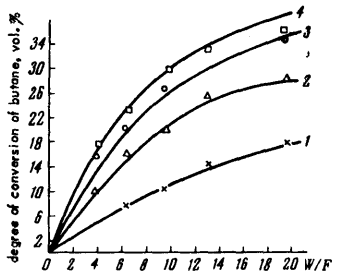


Fig. 2. Dependence of the degree of conversion of n-C_4H_{10} on the rate of supply and temperature (°C): 1) 510°; 2) 530°; 3) 550°; 4) 570° (atmospheric pressure).

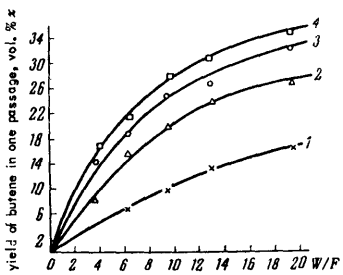


Fig. 3. Dependence of the yield of n-C_4H_8 on the rate of supply of butane and temperature (for numbering see Fig. 2).

the degree of dehydrogenation in a reactor containing a fluidised bed is less than that in a reactor containing an immobile layer, and that this difference increases with increase in the linear velocity and decrease in the particle size of the catalyst in the fluidised bed; this is due to the fact that some of the gas slips through the fluidised bed in the form of bubbles[74]. The rate of dehydrogenation in this reactor¶ is given by an equation of the same type, with the introduction of a coefficient φ which makes allowance for the change in the reaction rate as a result of the fact that some gas slips through[74]:

$$\frac{dx_1}{d(w/F)}=\varphi k_1\frac{P_1}{P_2^{0.5}}\left(1-\frac{P_2P_3}{K_pP_1}\right),$$

in which

$$\varphi=\left[1-\left(\frac{w-w_{cr}}{w}\right)^2\right]^{0.5},$$

where w is the linear velocity of the gas in the reactor and w_{cr} the rate of the start of formation of the fluidised bed; other conditions being equal, w_{cr} depends on the particle size[6].

The reaction n-$C_4H_8 \rightleftharpoons C_4H_6 + H_2$. The published kinetic equations for this reaction are given in Table 7; the symbols are the same as those used earlier. It can be seen that some of the equations in Table 7 are

‡ An equation of this type was justified by Kazeev[77].

§ The experimental data are given in detail elsewhere[6].

¶ The results of the dehydrogenation of n-C_4H_{10} in a fluidised bed in small experimental assemblies have been described by Aliev et al.[95]

TABLE 7. Equations for the rate of the reaction $n\text{-}C_4H_8 \rightleftharpoons C_4H_6 + H_2$ over various oxide catalysts.

No.	Equations	Catalyst	Conditions	E_a, kcal mole^{-1}	Refs.
1	$\frac{dx_2}{d\tau} = \frac{k_2 C_2}{C_2 + z_3 C_3 + z_4 C_4}$	chromium, chromium oxide	pressure 180–350 mmHg, 535–559°C 550–600°C	34.34–34.14 26.26–27.93	63
2	$\frac{d(H_2)}{d\tau} = \frac{104{,}5\,[C_4H_8]}{[C_4H_8] + 9.5\,[C_4H_6] + 0.82\,[H_2]}$	ditto	dilution to molar ratio $n\text{-}C_4H_8 : H_2O = 1:10$, 560°C	19.1	64
3	$-\frac{dP_2}{d\tau} = \frac{k_2 P_2}{1 + k_2/k_5 P_2}$	aluminium–chromium	dilution with nitrogen, $P_2 = 0.1$–0.3 atm, 450–500°C	27±1	70
4	$-\frac{dC_2}{d\tau} = k_2 C_2^{0.2}$	ditto	ditto	27±1	81
5	$\frac{dx_2}{d(W/F)} = \frac{k_2 (P_2 - P_3 P_4 / K_p)}{(1 + k_2' P_2 + k_3' P_3 + k_4' P_4)^2}$	No. 1707	dilution with water vapour, 640–668°C	17.6	5
6	$-\frac{dC_2}{d\tau} = k_2 C_2^8$	not indicated	dilution with water vapour, 570–630°C	not calculated	82
7	$\frac{dx_2}{d(W/F)} = k_2 P_2^{0.35}\left(1 - \frac{P_3 P_4}{K_p P_2}\right)$	industrial oxide	dilution with water vapour, 580–620°C	24.8	6,16

similar in form to the equations for the rate of dehydrogenation of $n\text{-}C_4H_{10}$; only equations 5 and 7 make allowance for the reverse hydrogenation reaction.

Equations 1 and 2 (Balandin, Bogdanov, and coworkers[63,64]) are identical; the numerical coefficients are given for 560° and P_{total} = 180–350 mmHg. The difference between equation 3 (Pshezhetskii and coworkers[70]) and Balandin's equation is in a term making allowance for retardation by the reaction products. Shcheglova and Pshezhetskii[81] did not detect this retardation, apparently because of differences in the experimental procedures: in the study of the retarding influence of C_4H_6 its concentration in the original mixture[81] did not exceed the quantity formed by dehydrogenation of pure $n\text{-}C_4H_8$; in the work by Balandin and coworkers[63,64], the quantity of C_4H_6 added was 3–10 times greater than the quantity of C_4H_6 formed. It should be emphasised that in these experiments of Balandin and coworkers[63], as in the dehydrogenation of butane[62], a decrease in the value of E with increase in temperature was observed.

Equation 5 is completely analogous to the corresponding equation for the rate of dehydrogenation of butane, so that all that was previously said regarding this equation is applicable to the equation for the rate of dehydrogenation of $n\text{-}C_4H_8$.

Equation 6 [82] was derived from experimental data obtained on a large-scale assembly in a tubular reactor with 8 litres of catalyst. It appears that some methodological factors associated with this are responsible for the unusual order of the reaction.

Equation 7 is applicable for a catalyst with maximal activity[6,16]. In fact, the activity of the industrial catalyst for which this equation was obtained does not remain constant throughout the operational period; the time dependence of the rate constants for the dehydrogenation of $n\text{-}C_4H_8$, calculated[6] from published data[16], is shown in Fig. 4. The temperature dependence of the maximal values of k_2 is given by the equation[16]:

$$\log k_2 = \frac{-24\,800}{4.575T} + 5.03,$$

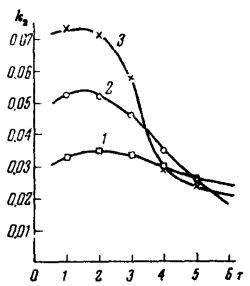


Fig. 4. Time dependence of the rate constants for the dehydrogenation of $n\text{-}C_4H_8$:
1) 580°; 2) 600°; 3) 620°; τ = duration of dehydrogenation, h.

and for any value of the time within the operational period from 1 h to 6 h the values are given by the equations[6] (for example, for 600°):

from 1 h to 4 h, $k_\tau = k_2 \times 0.9924\tau^{0.062} \exp(-0.0109\tau^{2.3})$,

from 4 h to 6 h, $k_\tau = k_2 \times 5.97\tau^{-1.88}$.

It is assumed[16] that the change in the activity of the dehydrogenation catalyst is due to a change in chemical composition under the influence of the reaction medium.

Dehydrogenation of butane–butene mixtures at reduced pressure. No mathematical description of the rate of dehydrogenation of $n\text{-}C_4H_{10}$ + + $n\text{-}C_4H_8$ mixtures at reduced pressure (that is, the rate of the single-stage dehydrogenation) has yet been published, but a number of papers have described fairly clearly the main regular features of this process.

On an aluminium–chromium catalyst, the rate of the reaction $n\text{-}C_4H_{10} \rightleftharpoons n\text{-}C_4H_8 + H_2$ is greater[67,70] than the rate of the reaction $n\text{-}C_4H_8 \rightleftharpoons C_4H_6 + H_2$. According to the data of Pshezhetskii et al.[70] the difference in the rates of these

reactions decreases with temperature and at 500°C $w_1 : w_2 = 2.7$; according to the data of Shcheglova and coworkers[67] the rate of the first reaction at 600°C is almost six times the rate of the second reaction. The establishment of the fact that the reactions involved in the formation of C_4H_6 from n-C_4H_{10} take place in succession is extremely important. It has been established[34] using ^{14}C that in the dehydrogenation of n-C_4H_{10} + n-C_4H_8 on an aluminium–chromium catalyst at 600°C and P_{total} = = 250 mmHg the rate of the reaction n-$C_4H_8 \rightarrow C_4H_6 + H_2$ is approximately twenty-five times the rate of the reaction n-$C_4H_{10} \rightarrow C_4H_6 + 2H_2$. From this work[34] it also follows that the rate of dehydrogenation of n-C_4H_{10} to n-C_4H_8 is smaller than the rate of dehydrogenation of n-C_4H_8 by a factor of about 2.5; the reasons for the discrepancy between these and other data[67,70] are not clear.

General relationships describing the influence of temperature, volume rate, pressure, and composition of the original n-C_4H_{10} + n-C_4H_8 mixture on the yield of butadiene and the selectivity of the process have been published[84,85]. They may be summarised as follows. Under the conditions studied[85] the yield of C_4H_6 increases with increase in temperature, increase in the concentration of n-C_4H_8 in the original mixture, and decrease in pressure. When the catalyst is purged for a short period with hydrogen after regeneration, the yield and selectivity increase appreciably (by 10–15%); the selectivity also increases with increase in the volume rate and with decrease in the temperature or pressure. An important characteristic of the process is the ratio of the quantities of n-C_4H_8 in the reaction products and in the original mixture. If this ratio is equal to unity, the butene is not used up and the process can be regarded as a single-stage process in the sense that only butane has to be added to the butane–butene mixture returned for recycling. This parameter, called the degree of single-stage character, increases with decrease in the concentration of butene in the original mixture, with decrease in the volume rate, with decrease in temperature, and with increase in pressure; purging of the catalyst with hydrogen also increases the degree of single-stage character (by 15–20%). Moreover, all the characteristics of the process also depend on the duration of the dehydrogenation[85]: the yield of butadiene at first increases, passes through a maximum, and then decreases†; the selectivity increases continuously and the degree of single-stage character decreases.

Reactions involved in the cracking of n-C_4H_{10} and n-C_4H_8. The catalytic and thermal cracking of hydrocarbons obeys a first-order equation. For n-butane the rate constant of the thermal decomposition (for a degree of transformation 7–9%, when secondary reactions can be neglected) is determined from the equation[86]:

$$\log k_c = \frac{-73\,900}{4.575T} + 17.05.$$

According to other data[87], for all straight-chain alkanes from C_3 to C_{10}, the activation energy of the primary thermal decomposition has an average value of 63 kcal mole^{-1}. According to more recent data[88], for n-C_4H_{10} E = = 58.7 kcal mole^{-1}; the same value was obtained in recently published work[89] in which the order of the reaction involved in the thermal decomposition of n-C_4H_{10} was found to be 3/2.

The rate of the cracking of butane in its catalytic dehydrogenation has been examined by a few authors[4,6,53]. It has been assumed[4] that the rates of the cracking of n-C_4H_{10} and n-C_4H_8 under dehydrogenation conditions are approximately equal; the cracking reaction is homogeneous and of first order. Since the kinetic data were obtained[4] for a single temperature (571°C) the equation obtained by Paul and Marek[86] is used for the cracking rate constant, although it is pointed out that the rate of cracking in the presence of an aluminium–chromium catalyst is slightly greater than the rate of thermal cracking (but by a factor of not more than 5–10). It is considered[5] that in the dehydrogenation of butene on catalyst No. 1707 the cracking of butane is also a first-order thermal reaction

$$\log k_c = \frac{-60\,000}{4.575T} + 15.2734,$$

the rates of the cracking of n-C_4H_{10} and n-C_4H_8 being approximately equal. The same assumption, made by Tyuryaev[6], is justified by the fact that on the highly selective catalyst used[6] only a comparatively small quantity of butane and butene decompose by cracking reactions (not more than 15% of the total butane reacting). With these assumptions, the rate of cracking is[83]:

$$\frac{dx_c}{d(W/F)} = k_c \frac{P_{C_4H_{10}} + P_{C_4H_8}}{P_{H_2}}.$$

For the dehydrogenation of butane on this catalyst[83,115]:

$$\log k_c = \frac{-40\,000 + 3600}{4.575T} + 7.0 \pm 1.0.$$

For dehydrogenation on another catalyst[53] the rate of cracking was given approximately by the equation

$$\frac{dx_c}{d(W/F)} = k_c(P_{C_4H_{10}} + P_{C_4H_8}), \text{ and } \log k_c = \frac{-38\,300}{4.575T} + 8.06.$$

Comparison of the cracking rate constants from this equation and from the equation for thermal cracking[87,88], shows that the rate of cracking increases slightly in the presence of the dehydrogenating catalyst.

There are very few papers on the thermal cracking of n-butene. The cracking of MeCH=CHMe has been studied in detail[8]. At 570–700°C and a degree of transformation in the range 5–12%, the rate of decomposition is described approximately by a first-order equation:

$$\log k_c = \frac{-53\,000 + 900}{4.575T} + 11.40.$$

The rate of the cracking of butene during its dehydrogenation on catalyst No. 1707 was mentioned above[5]; on another industrial catalyst[16] the cracking of n-C_4H_8 is negligibly small so that the study of this reaction is of no particular interest.

The decomposition of butadiene is an important reaction in the dehydrogenation of butene[5,6,63,90]. Work on the rate of thermal transformation of C_4H_6 has been reviewed[91]. The chief reaction involved in the thermal transformation of C_4H_6 at 400–700°C and atmospheric pressure[15] is polymerisation; the reaction is of second order with E = 28 kcal mole^{-1} and

$$\log k = \frac{-6400}{T} + 7.3 \pm 0.04.$$

† On the specimen studied[85], the yields of C_4H_6 were:

duration of dehydrogenation, min:	5	7	10	13
yield of C_4H_6 in one passage, mole %:	18	19	17	16

At reduced pressure [91,92], the chief reaction in the transformation of butadiene is dimerisation; the reaction is of second order [91] with

$$\log k = \frac{-26\,800}{4.575T} + 11.14.$$

In the dehydrogenation of n-C_4H_8 on catalyst No. 1707 [5] (with dilution by water vapour) decomposition of the butadiene formed involves chiefly catalytic cracking (5b) and thermal dimerisation; the rate of the first reaction is

$$r = \frac{kP_{C_4H_6}}{(1 + k_{C_4H_8}P_{C_4H_6} + k_{H_2}P_{H_2} + k_AP_A)^2},$$

with

$$\log k = \frac{-5000}{4.575T} + 0.2385,$$

(the subscripts A denote aromatic compounds). The dimerisation is a second-order reaction with

$$\log k = \frac{-25\,000}{4.575T} + 8.0632.$$

The dimer may also undergo cracking [5] with the formation of H_2, CH_4, C_2H_4, C_2H_6, and toluene; this reaction is a thermal reaction of first order, with

$$\log k = \frac{-31\,000}{4.575T} + 6.0323.$$

In the dehydrogenation of n-C_4H_8 on an industrial catalyst the cracking of C_4H_6 according to Eqn. (5c) is described by an equation of the same type [90] as that given by Beckberger and Watson [5] (with the exception of the term k_AP_A), or by the simpler equation [6]:

$$\frac{dx}{d(W/F)} = \frac{kP_{C_4H_6}}{(1 + aP_{C_4H_6})^2}.$$

The constants in these equations naturally depend on the form of equation used [6,90]. The activity of the catalyst with respect to the cracking reaction decreases during the operational period [90]. The time dependence of the rate constant is shown in Fig. 5; the curves are described by the equation

$$k_\tau = k\exp(-0.429\tau^{0.613}),$$

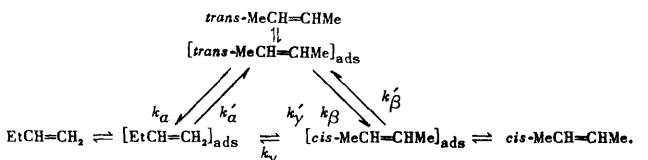
where τ is the duration of the operational period and k the rate constant for τ = 1 h.

Rate of carbon formation. As can be seen from Section 2, the quantity of "carbon" deposited on the catalyst in the dehydrogenation of n-butene is determined by the rate of decomposition of C_4H_6, for example, according to reactions (5b) or (5c); carbon formation in the dehydrogenation of n-butane must be regarded as an independent process [26]. Only one paper [26] has been published on the kinetics of carbon deposition on an aluminium-chromium catalyst in the dehydrogenation of n-C_4H_{10}; other papers [50,96,97] merely record the fact that "carbon" is formed or give values for the extent of carbon deposition on the catalyst under specific dehydrogenation conditions. The quantity of "carbon" formed in the dehydrogenation of butane is independent of the particle size of the catalyst and the volume rate of supply of butane and is determined by the equation [26]: $C_C = A\tau^{0.684}$, where C_C is the quantity of "carbon" as a percentage of the weight of catalyst, and τ the duration of dehydrogenation or the time for which the catalyst is present in the reactor, min‡,

$$\log A = \frac{-6620}{T} + 6.57.$$

The kinetic equation obtained [26] is analogous in form to equations found earlier for the rate of carbon formation in the cracking of petroleum products on an aluminosilicate catalyst [98] or in the dehydrogenation of cyclohexane on an aluminium–molybdenum catalyst [99].

The isomerisation of n-C_4H_{10} and n-C_4H_8. Although isomerisation in the dehydrogenation of n-butane and n-butene has been reported many times [47,73], there are no quantitative data on the rates of the reactions n-C_4H_{10} ⇌ iso-C_4H_{10} and n-C_4H_8 ⇌ $Me_2C{=}CH$ in the presence of dehydrogenating catalysts. The rate of the isomerisation $EtCH{=}CH_2$ ⇌ *trans*-MeCH=CHMe ⇌ *cis*-MeCH=CHMe on an aluminium–chromium catalyst has been studied in detail [93]. The following reaction mechanism has been proposed:



It is assumed [93] that the limiting stage is the surface reaction; on this basis, the rates of the individual reactions are:

$$-\frac{dP_1}{d\tau} = \frac{dP_t}{d\tau} + \frac{dP_c}{d\tau} = \frac{k_\alpha K_1P_1}{1 + K_1P_1} + \frac{k'_\gamma K_1P_1}{1 + K_1P_1},$$

$$-\frac{dP_c}{d\tau} = \frac{dP_1}{d\tau} + \frac{dP_t}{d\tau} = \frac{k_\gamma K_cP_c}{1 + K_cP_c} + \frac{k'_\beta K_cP_c}{1 + K_cP_c},$$

$$-\frac{dP_t}{d\tau} = \frac{dP_c}{d\tau} + \frac{dP_1}{d\tau} = \frac{k_\beta K_tP_t}{1 + K_tP_t} + \frac{k'_\alpha K_tP_t}{1 + K_tP_t}.$$

In these equations, P represents the partial pressures and K the adsorption equilibrium constants; the subscripts 1, c, and t refer to $EtCH{=}CH_2$, *cis*-MeCH=CHMe, and *trans*-MeCH=CHMe, and k and k' are the rate constants for the forward and back reactions. The following values were found for the activation energies (kcal mole^{-1}):

for $EtCH{=}CH_2$ ⇌ *trans*-MeCH=CHMe, E = 7.9;

for $EtCH{=}CH_2$ ⇌ *cis*-MeCH=CHMe, E = 5.0;

and for *trans*-MeCH=CHMe ⇌ *cis*-MeCH=CHMe, E = 12.6.

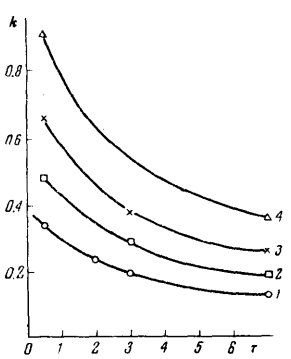


Fig. 5. Time dependence of the rate constants for the transformation of C_4H_6: 1) 560°; 2) 580°; 3) 600°; 4) 620°.

‡ According to data [117] published after the present manuscript was submitted, $C_C = A + B\tau$.

In the dehydrogenation of n-butane, the isomeric composition of the mixture of n-butenes obtained[6,50] is close to the equilibrium composition. The part played by skeletal isomerisation of n-C_4H_{10} and n-C_4H_8 in the dehydrogenation is small[6].

The reaction of water vapour with "carbon". Reactions (7e) and (7f), observed in the dehydrogenation of n-C_4H_8 (with dilution by water vapour), is of zeroth order both with respect to H_2O and with respect to the concentration of carbonaceous deposits on the catalyst[5,6];

$$\log k = \frac{-39\,000}{4.575T} + 5.09375, \text{ according to Beckberger and Watson (Ref. 5),}$$

or

$$\log k = \frac{-41\,600}{4.575T} + 8.02475, \text{ according to Tyuryaev (Ref. 6).}$$

The zeroth order with respect to water is attributed[6] to the very large excess of water vapour, and the order with respect to "carbon" probably depends on the reaction mechanism. The rate constant decreases with time[6] (see Fig. 6).

Reaction involved in the regeneration of the catalysts. Despite the importance of this question, the rate and chemistry of the processes taking place in the regeneration of dehydrogenating catalysts have been insufficiently studied. Thermograms have been obtained[23,101] for the regeneration of chromium catalyst specimens on which carbon was deposited during the decomposition of alcohols and dehydrogenation of cyclohexane; combustion of the carbonaceous deposits began at 240°. It was established[23,102] that the carbonaceous deposits contain components richer in hydrogen ("tars") and components with low hydrogen content ("coke").

The rate of combustion of carbonaceous deposits in the regeneration of aluminium–chromium catalysts has been little studied[6,100,103]. In the kinetic range (300–350°)[103] the combustion is of second order with respect to "carbon" and of first order with respect to oxygen, that is, $-\frac{dc}{d\tau} = kc^2P_{O_2}$, and E = 31.1 kcal mole^{-1}. The rate constant depends on the composition of the carbonaceous deposits: the value of k decreases with decrease in the hydrogen content; on the other hand, the hydrogen content of the carbonaceous deposits decreases with increase in the deposition of carbon on the catalyst. The rate of regeneration of aluminosilicate cracking catalysts obeys the same equation[104]; the value of E here is similar (26.6 kcal × × mole^{-1}).

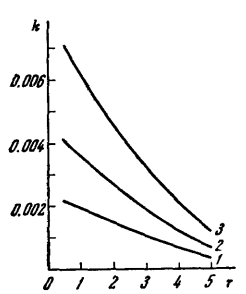


Fig. 6. Change in the rate constants for the reaction of water vapour with "carbon":
1) 560°; 2) 580°; 3) 600°.

In the regeneration of a catalyst for the dehydrogenation of butane in a fluidised bed[100] at 600–650°, the combustion takes place in the outer-diffusion range; the reaction rate is given by an equation of the same type

$$-\frac{dc}{d\tau} = k_d c^2 P_{O_2},$$

where k_d is the apparent rate constant, which depends on the rate of diffusion

$$\log k_d = \frac{-2800}{4.575T} + 0.14 \quad \text{or} \quad k_d = 0.0482(T/273)^{3/2}.$$

The rate of oxidation of an aluminium–chromium catalyst during regeneration is given by an equation of the form $C = A\tau^n$ where C is the CrO_3 concentration, wt.%, A the temperature coefficient, and τ the duration of the regeneration, min.[6,100] For the catalyst specimen studied[6,100], the reaction takes place in the kinetic range up to 550°C, after which diffusion retardation is observed; in the kinetic range, n = 0.098 and $\log A = \frac{-815}{T} + 0.766$.[6] An interesting feature is that integration of the equation proposed[105] for the rate of reduction of MoO_3 to MoO_2 during treatment of an aluminium–molybdenum catalyst with hydrogen, $\frac{1}{W_0}\frac{dW}{d\tau} = -a\tau^{-b}$, gives an equation of the same form with approximately the same exponents§.

The relationship between the activity and the concentration of sexivalent chromium after regeneration has been studied by a number of workers[18,22,24,25].

Rate of desorption of water. The change in the water content with time during regeneration of the catalyst for the dehydrogenation of n-butane is described satisfactorily by the equation[6,100]: $q/q_0 = A_1\tau^{0.61}$, where q_0 is the initial or equilibrium concentration of H_2O on the catalyst and q the concentration of H_2O, wt.%, at time τ, min.

The desorption rate constant also depends on the initial water content[6,100]:

for q_0 = 0.2–0.4 mg g^{-1}

$$\log A_1 = -\left(\frac{800}{T} + .49\right);¶$$

for q_0 = 0.1–0.2 mg g^{-1}

$$\log A_1 = \frac{-1680}{T} + 0.65;$$

for $q_0 < 0.1$ mg g^{-1}

$$\log A_1 = \frac{-3400}{T} + 2.61.$$

This relationship is attributed[6] to the fact that part of the water is adsorbed physically on the catalyst and part is

§ $\frac{dW}{W_0} = -a\tau^{-b}d\tau \frac{W}{W_0} = \frac{a}{1-b}\tau^{1-b}$. According to John and coworkers[105], b = 0.904, that is, 1 − b = 0.096 (compare with n = = 0.098).

¶ Misprint in Russian text (Ed. of Translation).

chemisorbed; on heating, the physically adsorbed water is desorbed first (with a smaller thermal effect). The magnitude of the apparent activation energy for the removal of chemisorbed water should be close to the activation energy of chemical reactions. This is confirmed by the results obtained[6]; from the last equation it follows that E = = 15.6 kcal mole^{-1}. With increase in the extent of the heat treatment of the catalyst, its activity for the dehydrogenation of butane increases[100].

There are no published data on the kinetics of carbon decomposition, combustion of carbonaceous deposits, and oxidation of catalysts for the dehydrogenation of butene.

6. NEW DEHYDROGENATION REACTIONS

The dehydrogenations examined up to the present are reversible; the yields of butene or buta-1,3-diene usually do not exceed 80% of the equilibrium degrees of dehydrogenation. This means that in the two-stage dehydrogenation the yields (of n-C_4H_8 in the first stage and of C_4H_6 in the second stage) cannot exceed about 45% and that the yield of C_4H_6 in the single-stage dehydrogenation of butane in a vacuum can at best reach 20%. Thus the scope of ordinary dehydrogenation methods is clearly limited.

Recent years have seen the discovery of other dehydrogenation reactions in which the hydrogen is bound in the form of water, for example[107]:

$$n\text{-}C_4H_8 + \tfrac{1}{2}O_2 \rightarrow C_4H_6 + H_2O.$$

These reactions, which may be called oxidative dehydrogenation reactions, are displaced almost completely to the right. On the basis of published data[107-113], these dehydrogenation reactions can be divided into three groups.

1. Dehydrogenation of alkenes on oxide catalysts in the presence of oxygen[107,108]. The reaction is carried out at 450–540° at a volume rate of supply of n-C_4H_8 equal to 200–600 h^{-1} with dilution by water vapour. In a reactor with an immobile layer of catalyst[107] (a mixture of oxides of metals from Groups V and VI of the Periodic System) the yield of C_4H_6 reaches 50% and the selectivity is about 90%. The chief side-reaction is extensive oxidation of the hydrocarbons (to CO_2 and CO); almost no hydrogen is present. In a reactor with a fluidised catalyst bed the yield of C_4H_6 could be increased[108] to 70% without loss of selectivity. It is reported[109] that catalysts based on bismuth tungstate, bismuth molybdate, and bismuth phosphate are active for the oxidative dehydrogenation of butene.

2. Dehydrogenation of alkanes to alkadienes in the presence of iodine[110,111,113]. The process is described by the following equations[110]

$$n\text{-}C_4H_{10} + 2I_2 \rightleftharpoons C_4H_6 + 4HI,$$
$$2HI + MO \rightarrow H_2O + MI_2,$$
$$MI_2 + \tfrac{1}{2}O_2 \rightarrow MO + I_2.$$

MnO_2 has been used as metal oxide[111]. The reaction is carried out at 520–550° at a molar ratio $C_4H_{10}:I_2 = 1:1.43$ in the presence of metal oxides which readily absorb the HI formed. The use of the oxides achieves two results: displacement of the dehydrogenation equilibrium to the right and regeneration of iodine. The quantity of iodine required[110] can be decreased by adding oxygen to the reaction mixture to bring about "internal regeneration" of iodine:

$$2HI + \tfrac{1}{2}O_2 \rightarrow I_2 + H_2O.$$

A C_4H_6 yield of 52% has been achieved[110] with a selectivity of 75%.

3. Dehydrogenation of alkanes on solid catalysts in the presence of oxygen. A number of patents[112] show that it is possible to carry out the reaction

$$n\text{-}C_4H_{10} + O_2 \rightarrow C_4H_6 + 2H_2O.$$

The catalysts consist of a mixture of metal oxides (for example, 97.5 Fe_3O_4 + 2.5 LiOH) or a mixture of metal halides (for example, 2.08 KBr + 1.09 r.e.e. chlorides + + 0.82 AgBr on α-Al_2O_3). In the first the original mixture (in moles): n-C_4H_{10} + 15H_2O + 0.85O_2 + 0.07I_2 + + 0.115Cl_2 is passed over a catalyst at 575°C and a liquid C_4H_{10} volume rate of 0.5 h^{-1}. Under these conditions the yield of C_4H_6 is 54% and the selectivity 66%.

Passage of a mixture with $C_4H_{10}:air:I_2:H_2O = 1:4.76:$ $:0.04:2.9$ (in moles) at 500°C over a catalyst of the second type gives a C_4H_6 yield of 48.7% and selectivity 79.1%.

Oxidative dehydrogenation reactions open up new possibilities for the preparation of alkadienes; the study of these reactions is of considerable scientific interest.

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THE ABSOLUTE RATE CONSTANTS OF THE ELEMENTARY STAGES OF RADICAL POLYMERISATION

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The elementary stages in a polymerisation radical chain reaction can in most cases be summarised as follows:

$$M \rightarrow M^{\cdot}, \quad (1)$$

$$M^{\cdot} + M \xrightarrow{k_p} MM^{\cdot}, \quad (2)$$

$$2M^{\cdot} \xrightarrow{k_t} P. \quad (3)$$

Reaction (1) is initiation, that is, formation of radicals from inactive molecules of the monomer M, reaction (2) is propagation of the reaction chain, leading to growth of the polymeric radical, and reaction (3) leads to the formation of the final reaction product — inactive polymer — and termination of the reaction chain.

Kinetic study of the polymerisation scheme (1) shows that for long reaction chains the dependence of the steady-stage reaction rate V_{st} on the elementary constants is given by the equation

$$V_{st} = I^{1/2} \frac{k_p}{k_t^{1/2}} [M]. \quad (4)$$

Thus the quantity $k_p/k_t^{1/2}$ can be determined from the reaction rate if the rate of initiation I is known. Methods for measuring rates of initiation have been described in detail[1]. $k_p/k_t^{1/2}$ can also be determined[2] from the dependence of the length of the polymer chain on the rate of polymerisation, given by the equation

$$\frac{1}{P_n} = \frac{k_M}{k_p} + \frac{k_t}{k_p^2} \frac{V_{st}}{[M]^2}, \quad (5)$$

where P_n is the number-average degree of polymerisation, usually determined from the viscosity of the polymer solutions, and k_M is the rate constant for chain transfer via the monomer. Schulz and coworkers[3] proposed equations which can be used to calculate the value of $k_p/k_t^{1/2}$ directly from the viscosity-average degree of polymerisation P_η. The value of $k_p/k_t^{1/2}$ can also be found by measuring the intensity of light scattering in the reaction vessel during the polymerisation[4].

The individual absolute values of the constants k_p and k_t cannot, however, be determined on the basis of Eqns. (4) or (5) alone. An additional equation relating these quantities depends on kinetic measurements of the lifetime of the radicals under non-steady reaction rate conditions.