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Oxidative Dehydrogenation of Hydrocarbons

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Experimental data are examined and the present state of the theory of the oxidative dehydrogenation reactions of hydrocarbons is discussed. Fundamental varieties of oxidative dehydrogenation have been considered as a function of dehydrogenating agent and the involvement of the solid surface in the process. Attention is concentrated on the elucidation of the process characteristics, the reaction mechanisms, and the nature of the active surface.
The bibliography includes 196 references.

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I. INTRODUCTION

The abstraction of a hydrogen atom from the dehydrogenated molecule in the oxidative dehydrogenation reaction proceeds under the influence of an oxidant which binds hydrogen into a chemical compound. The most thoroughly investigated dehydrogenating agents (oxidants) are oxygen and iodine, under the influence of which hydrogen is removed from the hydrocarbon molecule with formation of water and hydrogen iodide respectively. Hydrocarbons belonging to different homologous series, namely paraffins, naphthenes, aromatic alkyl-substituted compounds, etc., undergo oxidative dehydrogenation. This process arises from a comparatively recently established and successfully developing series of studies. It makes it possible to synthesise very effectively olefins and diene monomers from more saturated hydrocarbons. The study of the oxidative dehydrogenation reactions as a new and unusual variety of partial oxidation of organic compounds is also of independent theoretical interest.

Various data concerning the oxidative dehydrogenation have been published in a number of reviews [1-8]. Oxidative dehydrogenation reactions are exothermic. The equilibrium yields of lower olefins are higher compared with the usual dehydrogenation of the same hydrocarbons. The dehydrogenation of olefins and aromatic alkyl-substituted hydrocarbons is achieved with high yields of products and selectivity in the presence of oxygen and solid catalysts, while the dehydrogenation of paraffins can be carried out similarly in the presence of iodine and oxygen or solid acceptors of hydrogen iodide.

The oxidative dehydrogenation of butenes to butadiene (or the similar dehydrogenation of isopentenes to isoprenes),

$$C_nH_{2n} + {}^1/_2O_2 \rightarrow C_nH_{2n-2} + H_2O\,, \qquad (1)$$

is a heterogeneous-catalytic reaction. Paraffinic hydrocarbons are oxidised by oxygen in the gas phase by a radical-chain mechanism with low yields of olefins in accordance with the overall equation

$$C_nH_{2n+2} + {}^1/_2O_2 \rightarrow C_nH_{2n} + H_2O\,. \qquad (2)$$

The use of iodine-containing substances makes it possible to achieve fairly readily the dehydrogenation of C_4–C_5 paraffins to diolefins. Iodine, reduced via the reaction

$$C_nH_{2n+2} + I_2 \rightarrow C_nH_{2n} + 2HI \qquad (3)$$

or

$$C_nH_{2n+2} + 2I_2 \rightarrow C_nH_{2n-2} + 4HI \quad (n \geqslant 4)\,, \qquad (4)$$

can be regenerated by oxidising with oxygen the hydrogen iodide formed:

$$2HI + {}^1/_2O_2 \rightarrow I_2 + H_2O\,, \qquad (5)$$

or by binding it to solid acceptors, for example constant-valence metal oxides:

$$MeO + 2HI \rightarrow H_2O + MeI_2\,, \qquad (6)$$

or variable-valence oxides:

$$Me_2O_3 + 6HI \rightarrow 2MeI_2 + 3H_2O + I_2\,. \qquad (7)$$

In the last case the oxide is partly reduced with liberation of iodine. The iodine sorbed by the acceptor can be regenerated by atmospheric oxygen via the reaction

$$MeI_2 + {}^1/_2O_2 \rightarrow MeO + I_2\,. \qquad (8)$$

Solid catalysts which are not HI acceptors but which are capable of greatly accelerating the oxidative dehydrogenation reactions of paraffins in the presence of iodine and oxygen are also known. The nature of the activity of these catalysts differs significantly from that of the usual heterogeneous catalysts.

Industiral processes for the synthesis of butadiene by the oxidative dehydrogenation of butenes in the presence of oxygen and solid catalysts and of n-butane in the presence of iodine, oxygen, and solid HI acceptors are being developed at the present time. A number of other unsaturated hydrocarbons can also be obtained in high yields with the aid of oxidative dehydrogenation.

II. DEHYDROGENATION OF PARAFFINIC HYDROCARBONS IN THE GAS PHASE

1. THE REACTIONS OF HYDROCARBONS IN THE PRESENCE OF INDIVIDUAL RADICAL-FORMING SUBSTANCES

(a) The Nature of the Additive and the Selectivity of the Decomposition Reaction

The reactions of hydrocarbons are influenced significantly by the addition of substances which decompose into radicals or facilitate the formation of free radicals in the reaction system. The acceleration of the decomposition of paraffins by the addition of oxygen, iodine, epoxyethane, nitrogen oxides, hydrogen sulphide, bromine, azomethane, tetramethylethylene, metal alkyls, peroxides, etc.[9-22] and the retardation of the decomposition following the addition of nitric oxide, olefins, oxygen, hydrogen sulphide, hydrogen bromide, amides, hydrides, alkali metal hydroborates, and certain other substances[12,14,17,23-31] have been noted in the literature.

According to modern ideas, the addition of substances promoting the formation of free radicals has a dual effect (accelerating and retarding) on the reaction. The acceleration of the reaction is attributed to the replacement of the step involving chain generation or propagation by faster steps involving a molecule of the additive or the radicals (atoms) formed on its decomposition, while the retardation of the reaction is attributed to the replacement of the more active radical by a less active one or by the involvement of the additive in the chain termination stages[17,32-34]. Depending on the nature of the radical-forming additives and the experimental conditions, the mode of decomposition of hydrocarbons can vary significantly. The change in selectivity may be attributed to the acceleration or retardation of the individual stages of the overall process, leading to the formation of a particular product. In the presence of certain substances (iodine, bromine, chlorine, hydrogen sulphide, oxygen, and nitrous oxide), the ratio of the dehydrogenation and cracking products increases† [10,15,21,35-37].

The influence of the addition of iodine, oxygen, nitric acid, and epoxyethane on the reactions of butane has been investigated[13] under the conditions usually employed in oxidative dehydrogenation: 530°C and dilution with an inert gas at an overall pressure of 1 atm. Under these conditions, the addition of oxygen, iodine, epoxyethane, and nitric acid accelerates the decomposition of n-butane: in the absence of these substances, there is no change in n-butane. Cracking is the principal mode of reaction in the presence of all the above radical-forming additives in amounts up to approximately 8%.

The available information about the additives investigated suggests that the reaction of n-butane is initiated via the following process:

$$C_4H_{10} + R \rightarrow \dot{C}_4H_9 + RH\,, \qquad (9)$$

where $R = \dot{I}$, O_2, NO_2 or $\dot{C}H_3$, and the activation energies ϵ are respectively ~25, 40, 23, and 10 kcal mole^{-1}.[17,19,38,39]

The mechanism of the decomposition of the butyl radical with formation of cracking products in the presence of small amounts of additives is apparently the same as in the absence of additives, as shown by the similarity of the composition of the decomposition products. The cracking products are formed via the unimolecular decomposition of the butyl radical and the interaction of lower alkyl radicals with the initial molecule:

$$\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6 \quad \varepsilon = 23\text{—}27 \text{ kcal mole}^{-1}, \qquad (10)$$

$$\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4\,, \qquad (11)$$

$$C_4H_{10} + \dot{C}H_3 \rightarrow \dot{C}_4H_9 + CH_4 \quad \varepsilon \simeq 9 \text{ kcal mole}^{-1}, \qquad (12)$$

$$C_4H_{10} + \dot{C}_2H_5 \rightarrow \dot{C}_4H_9 + C_2H_6\,. \qquad (13)$$

When much greater amounts of the additives are introduced (up to 15–30%), differences are observed in the mode of reaction depending on the nature of the radical-forming substance, which indicates the interaction of the butyl radical with the additive. In the presence of iodine, dehydrogenation takes place and in the presence of the same amount of the other compounds cracking products are formed.

The activation energies quoted for reaction (9) in which hydrogen atoms are abstracted show that the dehydrogenating action of the additives is not related to their activity with respect to the abstraction of hydrogen atoms. Evidently the formation of large amounts of olefins does not involve the abstraction of hydrogen atoms by the active species from the alkyl radical, i.e.

$$\dot{C}_4H_9 + R \rightarrow C_4H_8 + HR\,,$$

and takes place via addition reactions between them.

Thus the dehydrogenating action of iodine is associated with the properties of the intermediates formed during the interaction between the alkyl radical and the additive. The interaction of the butyl radical with iodine

$$\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_9I$$

or

$$\dot{C}_4H_9 + I_2 \rightarrow C_4H_9I + \dot{I}$$

leads to the formation of alkyl iodides, which readily decompose at temperatures below 300° with formation of an olefin and HI or an olefin, a paraffin, and iodine[40,41].

One principle of the action of effective dehydrogenating agents (radical-forming substances), which is apparently general, follows from the data presented: the dehydrogenating effect of radical-forming substances is due to their inability to form compounds with alkyl radicals, which readily decompose into olefins.

(b) Dehydrogenation in the Presence of Iodine.

The conversion of paraffinic hydrocarbons into olefins by reaction (3) at approximately 300°C proceeds according to Benson's data via the interaction of the alkyl radical with an iodine molecule and the decomposition of the iodide thus produced. For example, the following equations may be formulated for the dehydrogenation of propane to propene[38]:

$$\begin{gathered} I_2 + M \rightleftarrows 2\dot{I} + M \quad \varepsilon = 35{,}5 \text{ kcal mole}, \\ C_3H_8 + \dot{I} \rightleftarrows \text{iso-}\dot{C}_3C_7 + HI \quad \varepsilon \simeq 25 \text{ kcal mole}^{-1}, \\ \text{iso-}\dot{C}_3H_7 + I_2 \rightleftarrows \text{iso-}C_3H_7I + \dot{I}\,, \\ \text{iso-}C_3H_7I \rightleftarrows C_3H_6 + HI\,. \end{gathered} \qquad (I)$$

The mechanism of the dehydrogenation of paraffins having a long chain with $C \geqslant 4$ [reaction (4)] has been examined by Raley et al.[15] According to their data,

†Cracking is understood in the present review as the decomposition of the hydrocarbon with rupture of the C–C bond.

paraffins are dehydrogenated to mono-olefins at approximately 300°C via the formation and decomposition of intermediate iodine compounds, as in Benson's mechanism. At higher temperaturss (500°C), the concentration of atomic iodine increases markedly and, according to the authors [15], the preferred pathway involves the formation of olefins via the direct abstraction of a second hydrogen atom by an iodine atom:

$$\dot{C}_nH_{2n+1} + \dot{I} \rightarrow C_nH_{2n} + HI .$$

According to Raley et al. [15], the dehydrogenation of a mono-olefin to a di-olefin proceeds similarly to the dehydrogenation of a paraffin to a mono-olefin. The reaction mechanism for n-butane is as follows:

$$\begin{gathered} I_2 + M \rightleftarrows 2\dot{I} + M , \\ C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI, \varepsilon = 25 - 27 \text{ kcal mole}^{-1} , \\ \dot{C}_4H_9 + \dot{I} \rightarrow C_4H_8 + HI , \\ C_4H_8 + \dot{I} \rightarrow \dot{C}_4H_7 + HI, \varepsilon \simeq 10 \text{ kcal mole}^{-1} , \\ \dot{C}_4H_7 + \dot{I} \rightarrow C_4H_6 + HI . \end{gathered} \qquad (II)$$

However, comparison of the above data for the reaction of n-butane in the presence of iodine and other radical-forming substances is inconsistent with the hypothesis that olefins are formed without an intermediate iodide. The intermediate formation of iodides has also been confirmed by experiments on the decomposition of the latter under dehydrogenation conditions [41].

A more complete mechanism of the dehydrogenation of n-butane has been proposed by Chekhov et al. [42]:

$$\begin{gathered} I_2 + M \rightleftarrows 2\dot{I} + M , \\ C_4H_{10} + I \rightleftarrows \dot{C}_4H_9 + HI , \\ \dot{C}_4H_9 + I_2 \rightleftarrows C_4H_9I + \dot{I} , \\ C_4H_9I + \dot{I} \rightleftarrows C_4H_8 + HI + \dot{I} , \\ C_4H_9I \rightleftarrows C_4H_8 + HI , \\ C_4H_8\text{-}1 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI , \\ C_4H_8\text{-}2 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI , \\ \dot{C}_4H_7 + I_2 \rightleftarrows C_4H_7I + \dot{I} , \\ C_4H_7I + \dot{I} \rightleftarrows C_4H_6 + HI + \dot{I} , \\ C_4H_7I \rightleftarrows C_4H_6 + HI , \end{gathered} \qquad (III)$$

which involves, in conformity with scheme (I), stages in which iodides are formed and, in conformity with scheme (II), stages in which intermediate butenes are formed. Scheme (III) leads to the following equation for the rate of consumption of b-butane, which is close to the experimental equation:

$$w = k\,[C_4H_{10}]\,[I_2]^{1/2}/(1 + \beta),$$

where β characterises the reversibility of the reaction. The activation energy for the reaction at 380–535°C is 43 kcal mole^{-1}. [43]

The dominant products of the reactions of higher paraffins with iodine are aromatic hydrocarbons:

$$C_nH_{2n+2} + 4I_2 \rightleftarrows C_nH_{2n-6} + 8\,HI \; (n \geqslant 6) .$$

By analogy with catalytic dehydrocyclisation and oxidative dehydrogenation of lower paraffins to diolefins, the aromatisation of $C \geqslant 6$ paraffins presumably proceeds via the following consecutive stages: paraffin → mono-olefin → diene → triene → cyclohexadiene → aromatic hydrocarbon [44].

(c) Reactions of Paraffinic Hydrocarbons in the Presence of Oxygen

One of the products of the high-temperature oxidation of paraffins by oxygen is an olefin with the same number of carbon atoms. However, the yields of dehydrogenation products are small. The main reaction pathway is cracking and, in the presence of high oxygen concentrations, also complete oxidation.

Most workers have adopted nowadays the mechanism of the formation of olefins by reaction (2) involving the successive abstraction of two hydrogen atoms from the paraffin molecule [45-51]:

$$C_nH_{2n+2} + O_2 \rightarrow \dot{C}_nH_{2n+1} + H\dot{O}_2 \; \varepsilon \simeq 40 \text{ kcal mole}^{-1} .$$
$$\dot{C}_nH_{2n+1} + O_2 \rightarrow C_nH_{2n} + H\dot{O}_2 .$$

Appleby et al. [10] proposed a mechanism for the conversion of n-butane in the presence of oxygen, according to which cracking products are formed via the unimolecular decomposition of the butyl radical [reactions (10)–(13)]. The mechanism involves stages in which butene is formed and also chain propagation and termination stages with participation of the $H\dot{O}_2$ radical:

$$\begin{gathered} C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2 , \\ \dot{C}_4H_9 + O_2 \rightarrow C_4H_8 + H\dot{O}_2 , \\ H\dot{O}_2 + C_4H_{10} \rightarrow H_2O_2 + \dot{C}_4H_9 , \\ 2\,H\dot{O}_2 \rightarrow H_2O_2 + O_2 , \\ H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/_2O_2 , \\ 2\,H\dot{O}_2 \xrightarrow{\text{wall}} H_2O + 1{,}5\,O_2 , \\ \dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6 , \\ \dot{C}H_3 + C_4H_{10} \rightarrow CH_4 + \dot{C}_4H_9 , \\ \dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4 , \\ \dot{C}_2H_5 + C_4H_{10} \rightarrow C_2H_6 + \dot{C}_4H_9 . \end{gathered} \qquad (IV)$$

Scheme (IV) leads to a kinetic equation whose order is 1.5 with respect to butane and 0.5 with respect to oxygen, in agreement with experimental data in the presence of small amounts of added oxygen. However, this scheme does not agree with the kinetic equations for oxygen : butane ratios greater than 0.08–0.1, which involve higher orders with respect to butane and oxygen under these conditions [51]. Furthermore, scheme (IV) does not include reactions with participation of reactive $\dot{O}H$ radicals present in the hydrocarbon–oxygen reaction system (the activation energy for the abstraction of a hydrogen atom by the $\dot{O}H$ radical from the n-butane molecule should be not more than 8 kcal mole^{-1}) nor does it include reactions involving the formation of extensive oxidation products. With increase of the concentration of oxygen, its interaction with butyl radicals becomes more significant. We have proposed [51] a mechanism for the formation of cracking and far-reaching oxidation products of n-butane, which includes, in contrast to scheme (IV), reactions involving the formation, isomerisation, and decomposition of peroxy-radicals, a chain propagation stage with participation of the $\dot{O}H$ radical and unimolecular $\dot{O}H$ termination, as well as the overall formaldehyde oxidation reaction:

$$\begin{gathered} C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2 , \\ \dot{C}_4H_9 + O_2 \rightarrow C_4H_8 + H\dot{O}_2 , \\ C_4H_{10} + H\dot{O}_2 \rightarrow \dot{C}_4H_9 + H_2O_2 , \\ H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/_2O_2 , \\ \dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6 , \\ \dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4 , \\ C_4H_{10} + \dot{C}H_3 \rightarrow \dot{C}_4H_9 + CH_4 , \end{gathered}$$

$$
\begin{gathered}
C_4H_{10} + \dot{C}_2H_5 \rightarrow \dot{C}_4H_9 + C_2H_6 , \\
\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2 , \\
n\text{-}C_4H_9\dot{O}_2 \rightarrow \dot{C}_4H_8O_2H , \\
\dot{C}_4H_8O_2H \rightarrow C_3H_6 + CH_2O + \dot{O}H , \\
C_4H_{10} + \dot{O}H \rightarrow \dot{C}_4H_9 + H_2O , \\
CH_2O + O_2 \rightarrow CO_2 + H_2O , \\
iso\text{-}C_4H_9\dot{O}_2 \rightarrow \dot{C}_3H_4CH(O_2H)CH_3 , \\
\dot{C}_3H_4CH(O_2H)CH_3 \rightarrow C_3H_4 + CO + \dot{O}H + CH_4 , \\
\dot{O}H \xrightarrow{\text{wall}} \text{termination} .
\end{gathered}
\qquad (V)
$$

Scheme (V) leads to kinetic equations for cracking and extensive oxidation, which are of second order with respect to butane and of third order with respect to oxygen, in agreement with experimental data.

2. DEHYDROGENATION OF PARAFFINIC HYDROCARBONS IN THE PRESENCE OF IODINE AND OXYGEN

The dehydrogenation of paraffins in the joint presence of iodine and oxygen was first investigated by Raley et al.[15], who concluded that the role of oxygen consists in regenerating iodine via reaction (5). They proposed a reaction mechanism for 500°C:

$$
\begin{gathered}
I_2 + M \rightleftarrows 2\dot{I} + M , \\
C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI , \\
\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_8 + HI , \\
C_4H_8 + \dot{I} \rightarrow \dot{C}_4H_7 + HI , \\
\dot{C}_4H_7 + \dot{I} \rightarrow C_4H_6 + HI , \\
2\,HI + {}^1/_2\,O_2 \rightarrow I_2 + H_2O , \\
\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2 ,
\end{gathered}
\qquad (VI)
$$

$C_4H_9\dot{O}_2$ – cracking and extensive oxidation products.

However, further investigations showed that the role of oxygen is not limited to its participation in the oxidation of hydrogen iodide [reaction 5].[1,52,53] The role of oxygen and iodine depends on the reactant concentration ratios. At concentrations close to those employed by Raley et al. (equimolar iodine/hydrocarbon ratio, amount of oxygen much less than that of iodine), oxygen reacts mainly with hydrogen iodide, since the dissociation energy of the H–I bond (71.3 kcal mole^{-1}) is much smaller than that of the C–H bond in the paraffin (89–95 kcal mole^{-1}).

With decrease of the amount of iodine in the system and increase of the concentration of oxygen, one of the functions of the latter becomes the generation of the active radicals $\dot{O}H$, $\dot{C}H_3$, etc., as happens in the reaction of n-butane in the absence of iodine (see above). Calculation based on the kinetic equation of the collision theory assuming that the pre-exponential factors are the same showed that the rates of abstraction of a hydrogen atom by an oxygen molecule,

$$C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2 , \qquad (O)$$

and an iodine atom,

$$C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI , \qquad (i)$$

are comparable at approximately 500°C, provided that the concentration of atomic iodine is approximately 10^4 times smaller than that of molecular oxygen:

$$\frac{w_0}{w_i} = \frac{a_0\, e^{-40/RT}\,[C_4H_{10}]\,[O_2]}{a_i\, e^{-25/RT}\,[C_4H_{10}]\,[\dot{I}]} \simeq 10^{-4}\,\frac{[O_2]}{[\dot{I}]} .$$

This ratio of w_0 and w_i can obtain in the presence of an excess of oxygen by one or two orders of magnitude relative to molecular iodine, since the equilibrium degree of dissociation of iodine molecules into atoms is approximately 10^{-2} at 530°C, while under the conditions of the reacting system the equilibrium is apparently not attained.

The fact that w_0 and w_i are comparable implies the dominant role of oxygen in the formation of alkyl radicals, since the reactions of oxygen with a hydrocarbon involve the formation of considerable amounts of species more active than iodine and oxygen ($\dot{O}H$, $H\dot{O}_2$, $\dot{C}H_3$, etc.). This conclusion is confirmed by kinetic data for the conversion of n-butane in the presence of equimolar amounts of oxygen and small amounts of iodine[52-54].

The role of iodine introduced in small amounts consists mainly in its participation in the stages determining the selectivity of the reaction, i.e. in the stages of further transformation of butyl radicals and not their generation. This is indicated, in particular, by the fact that the addition of iodine up to approximately 7% relative to butane increases the fraction of dehydration products, but has little influence on the degree of conversion of the hydrocarbon[53,55]. Apart from its participation in the formation of dehydrogenation products, the role of iodine consists in inhibiting cracking, which may occur in consequence of the replacement of active radicals by less active species, for example as a result of the replacement of alkyl or hydroxy-radicals by iodine atoms[18]. When larger amounts of iodine are introduced into the system, the reaction of atomic iodine with the initial butane begins to play an increasing role:

$$C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI ,$$

as a result of which the rate of conversion of butane increases.

The above considerations may be applicable also to the subsequent two hydrogen abstraction stages: its abstraction from the butene molecule and from the butenyl radical. Butene is known to be oxidised in the presence of oxygen at high temperatures with high degrees of conversion, the first stage of the reaction consisting of the formation of the butenyl radical[9], and in the absence of iodine or special catalysts, for example bismuth molybdate (see below), appreciable amounts of butadiene are not formed.

Until recently, there have been few data on the mechanism of the regeneration of iodine by oxygen [reaction (5)]. In the development of the mechanism of the dehydrogenation of butane in the presence of iodine and oxygen (see below), the present author proposed a radical HI oxidation stage:

$$HI + O_2 \rightarrow \dot{I} + H\dot{O}_2 , \qquad (14)$$

the activation energy of which was estimated as approximately equal to the heat of reaction (approximately 20 kcal mole^{-1}).

The following mechanism has been proposed recently for the oxidation of hydrogen iodide at temperatures in the range 100–200°C [56]:

$$
\begin{gathered}
HI + O_2 \rightleftarrows \dot{I} + H\dot{O}_2 , \\
HI + H\dot{O}_2 \rightleftarrows \dot{I} + H_2O_2 , \\
2\,\dot{I} + M \rightleftarrows I_2 + M .
\end{gathered}
$$

The activation energy was found to be close to 20 kcal mole^{-1}. The reaction is inhibited by the product (iodine).

On the basis of the conclusions reached concerning the role of the individual reactants and about the intermediate formation of iodides and butenes[13,41], the present author

proposed a mechanism for the dehydrogenation of n-butane to butadiene in the presence of oxygen and iodine for small iodine/oxygen ratios [52,53]:

$$
\begin{aligned}
&I_2 + M \rightarrow 2\dot{I} + M\,,\\
&C_4H_{10} + O_2 \rightarrow \dot{C}_4H_9 + H\dot{O}_2\,,\\
&C_4H_{10} + H\dot{O}_2 \rightarrow \dot{C}_4H_9 + H_2O_2\,,\\
&C_4H_{10} + \dot{O}H \rightarrow \dot{C}_4H_9 + H_2O\,,\\
&C_4H_{10} + \dot{C}H_3 \rightarrow \dot{C}_4H_9 + CH_4\,,\\
&C_4H_{10} + \dot{C}_2H_5 \rightarrow \dot{C}_4H_9 + C_2H_6\,,\\
&\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_9I\,,\\
&\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2\,,\\
&\dot{C}_4H_9 \rightarrow \dot{C}H_3 + C_3H_6\,,\\
&\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4\,,\\
&C_4H_9I \rightarrow C_4H_8 + HI\,,\\
&C_4H_9\dot{O}_2 \rightarrow \dot{O}H + \text{cracking and extensive oxidation products,}\\
&C_4H_8 + H\dot{O}_2 \rightarrow \dot{C}_4H_7 + H_2O_2\,,\\
&C_4H_8 + \dot{O}H \rightarrow \dot{C}_4H_7 + H_2O\,,\\
&C_4H_8 + \dot{C}H_3 \rightarrow \dot{C}_4H_7 + CH_4\,,\\
&C_4H_8 + \dot{C}_2H_5 \rightarrow \dot{C}_4H_7 + C_2H_6\,,\\
&\dot{C}_4H_7 + \dot{I} \rightarrow C_4H_7I\,,\\
&C_4H_7I \rightarrow C_4H_8 + HI\,,\\
&HI + O_2 \rightarrow \dot{I} + H\dot{O}_2\,,\\
&2\dot{I} + M \rightarrow I_2 + M\,,\\
&2\dot{C}_4H_7 \rightarrow \text{termination,}\\
&H_2O_2 \rightarrow H_2O + {}^1/_2O_2\,.
\end{aligned}
\qquad \text{(VII)}
$$

On the assumption of a steady state, scheme (VII) leads to an equation for the rate of dehydrogenation of n-butane to butadiene which is close to that obtained experimentally for low degrees of conversion:

$$w = k\,[C_4H_{10}]^{0.4}\,[I_2]^{0.6}\,[O_2]^{0.4}$$

and to an activation energy which is close to the experimental value (approximately 35 kcal mole^{-1}).

A mechanism for the dehydrogenation of n-butane in the presence of iodine and oxygen was also proposed[42,57] by Chekhov and coworkers. It includes, apart from the stages comprised in scheme (III) in the absence of oxygen, also a stage with its participation:

$$
\begin{aligned}
&I_2 + M \rightleftarrows 2\dot{I} + M\\
&C_4H_{10} + \dot{I} \rightleftarrows \dot{C}_4H_9 + HI\,,\\
&\dot{C}_4H_9 + I_2 \rightleftarrows C_4H_9I + \dot{I}\,,\\
&C_4H_9I + \dot{I} \rightleftarrows C_4H_8 + HI + \dot{I}\,,\\
&C_4H_9I \rightleftarrows C_4H_8 + HI\,,\\
&C_4H_8\text{-}1 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI\,,\\
&C_4H_8\text{-}2 + \dot{I} \rightleftarrows \dot{C}_4H_7 + HI\,,\\
&\dot{C}_4H_7 + I_2 \rightleftarrows C_4H_7I + \dot{I}\,,\\
&C_4H_7I + \dot{I} \rightleftarrows C_4H_6 + HI + \dot{I}\,,\\
&C_4H_7I \rightleftarrows C_4H_6 + HI\,,\\
&2\,HI + {}^1/_2O_2 \rightarrow I_2 + H_2O\,, \qquad (a)\\
&\dot{C}_4H_9 + O_2 \rightarrow C_4H_8 + H\dot{O}_2\,, \qquad (b)\\
&\dot{C}_4H_9 + O_2 \rightarrow C_4H_9\dot{O}_2\,, \qquad (c)\\
&C_4H_9\dot{O}_2 \rightarrow \text{cracking and extensive oxidation products}\,: \qquad (d)
\end{aligned}
\qquad \text{(VIII)}
$$

According to scheme (VIII), the role of oxygen consists, apart from stages (*b*), (*c*), and (*d*) in scheme (VI), in abstracting a hydrogen atom from the butyl radical [reaction (*b*)].

Adel'son et al.[58] proposed the following mechanism for the conversion of isopentane in the presence of iodine and oxygen:

$$
\begin{aligned}
&I_2 + M \rightleftarrows 2\dot{I} + M\,, && (a)\\
&\text{iso-}C_5H_{12} + \dot{I} \rightleftarrows \text{iso-}\dot{C}_5H_{11} + HI\,, && (b)\\
&\text{iso-}\dot{C}_5H_{11} + I_2 \rightleftarrows \text{iso-}C_5H_{11}I + \dot{I}\,, && (c)\\
&\text{iso-}C_5H_{11}I \rightleftarrows \text{iso-}C_5H_{10} + HI\,, && (d)\\
&\text{iso-}C_5H_{10} + \dot{I} \rightleftarrows \text{iso-}\dot{C}_5H_9 + HI\,, && (e)\\
&\text{iso-}\dot{C}_5H_9 + I_2 \rightleftarrows \text{iso-}C_5H_9I + \dot{I}\,, && (f)\\
&\text{iso-}C_5H_9I \rightleftarrows \text{iso-}C_5H_8 + HI\,, && (g)\\
&\text{iso-}C_5H_{12} + H\dot{O}_2 \rightarrow \text{iso-}\dot{C}_5H_{11} + H_2O_2\,, && (h)\ (\text{IX})\\
&\text{iso-}\dot{C}_5H_{11} \rightarrow \dot{C}H_3 + C_4H_8\,,\\
&\text{iso-}\dot{C}_5H_{11} \rightarrow \dot{C}_2H_5 + C_3H_6\,,\\
&2\,H\dot{O}_2 \rightarrow H_2O_2 + O_2\,,\\
&2\,HI + {}^1/_2O_2 \rightarrow I_2 + H_2O\,, && (p)\\
&\text{iso-}\dot{C}_5H_{11} + O_2 \rightarrow \text{iso-}C_5H_{10} + H\dot{O}_2\,, && (r)\\
&\text{iso-}\dot{C}_5H_{11} + O_2 \rightarrow \text{iso-}C_5H_{11}\dot{O}_2\,, && (s)\\
&\text{iso-}C_5H_{11}\dot{O}_2 \rightarrow CO + H_2O + \text{decomposition products.} && (t)
\end{aligned}
$$

The stages in which isopentane is dehydrogenated to isopentenes [reactions (*a*)–(*d*)] are analogous to those in the dehydrogenation of propane via Benson's mechanism (I), while the stages involving the dehydrogenation of isopentenes to isoprene [reactions (*e*)–(*g*)] are analogous to those in the dehydrogenation of isopentane to isopentene. Apart from the reactions included in the previous scheme or processes analogous to them [reactions (*p*)–(*t*)], the role of oxygen consists in the participation of the oxygen-containing radical $H\dot{O}_2$ in the formation of butyl radicals [reaction (*h*)].

Each of the last three mechanisms of the oxidative dehydrogenation of C_4–C_5 paraffins in the presence of iodine and oxygen [mechanisms (VII)–(IX)] can give a satisfactory quantitative agreement with experimental reaction rates for a reasonable choice of constants for the fundamental stages[54,57,58]. Nevertheless, none of them can claim to be complete. Thus the only reaction of oxygen in scheme (VIII), apart from the regeneration of iodine and the formation of side products, is abstraction of a hydrogen atom from the butyl radical. However, in the presence of iodine, which is much more selective in relation to dehydrogenation than oxygen, this stage hardly plays a significant role. On the other hand, the reactions of the most active radicals ($\dot{O}H$, $\dot{C}H_3$, $\dot{C}_2H_5$, and $H\dot{O}_2$) were not taken into account in this mechanism. For this reason, the applicability of scheme (VIII) to the reaction in the presence of large amounts of oxygen is unlikely. In scheme (IX) for the dehydrogenation of isopentane, the involvement of oxygen is represented by a large number of reactions. However, this scheme also does not include chain propagation reactions with participation of lower alkyl or hydroxy-radicals. In the present author's mechanism (VII) published previously, the reactions of butane in the presence of oxygen and comparatively small amounts of added iodine are represented by the reactions of oxygen-containing lower alkyl radicals with hydrocarbon molecules. However, it does not include certain reactions with participation of iodine, which are present in other schemes: the interaction of atomic iodine with hydrocarbon molecules and of hydrocarbon radicals with molecular iodine.

In later studies, Adel'son and coworkers[59,60] introduced a further series of reactions into scheme (IX), in particular the interaction of hydrocarbon molecules with the methyl radical:

$$\dot{C}H_3 + \text{iso-}C_5H_{12} \rightarrow CH_4 + \text{t-}\dot{C}_5H_{11},$$

$$\dot{C}H_3 + \text{iso-}C_5H_{10} \rightarrow CH_4 + \text{iso-}\dot{C}_5H_9,$$

and of isopentane with the hydroxy-radical:

$$\dot{O}H + \text{iso-}C_5H_{12} \rightarrow H_2O + \text{t-}\dot{C}_5H_{11}.$$

However, in order to devise a sufficiently complete detailed mechanism for the reaction in this extremely complex system, which is subject in addition to the influence of the surface (this will be discussed below), further studies are necessary and it is first essential to revise the kinetic data for the fundamental stages of the dehydrogenation process and concomitant reactions.

III. DEHYDROGENATION REACTIONS IN THE PRESENCE OF SOLID CATALYSTS

1. DEHYDROGENATION OF OLEFINS IN THE PRESENCE OF OXYGEN

(a) Certain Experimental Data

The available information about the chemical compositions of the catalysts of the oxidative dehydrogenation of olefins in the presence of oxygen [reaction (1)] and the yields of products is given in the reviews published previously[1,8,61]. High yields of butadiene and isoprene were obtained in the presence of many catalysts having different compositions. Most of them (bismuth–molybdenum, antimony–tin, etc.) were known previously as catalysts of incomplete oxidation. However, certain catalysts of the oxidative dehydrogenation of olefins are similar in composition to the catalysts of ordinary dehydrogenation (for example, the mixed nickel, calcium, and chromium phosphate).

Aromatic alkyl-substituted hydrocarbons also undergo heterogeneous-catalytic oxidative dehydrogenation in the presence of oxygen; however, the optimum catalysts for these substances have a composition different from that of the catalysts for the dehydrogenation of olefins. The high yields of styrene in the dehydrogenation of ethylbenzene in the presence of aluminium oxide are striking[62].

Among binary systems of the type MoO_3–oxide of a Group V element (bismuth, arsenic, phosphorus, and antimony) deposited on α-Al_2O_3, the molybdenum–bismuth catalyst is the most active[63]. Its optimum composition without a carrier or on carriers for the dehydrogenation of C_4–C_5 olefins lies within the limits of the ratio Bi : Mo = 0.5–2.[64-69]. Among catalysts having the composition M_mO_n–Sb_2O_4 (where M = Fe, Sn, Mn, V, Cr, Ni, Co, or Cu), the Fe_2O_3–Sb_2O_4 catalyst (atomic ratio in the range $1/16 \leqslant Fe/Sb \leqslant 1/4$) has the best parameters for the dehydrogenation of butene[70] and is followed in this respect by SnO_2–Sb_2O_4 (optimum composition $1/4 \leqslant Sn/Sb \leqslant 4/1$).[71-73] In the presence of the bismuth–molybdenum catalyst, the rate of dehydrogenation of but-1-ene is higher than that of but-2-ene [74,75] and the rate of dehydrogenation of 3-methylbut-1-ene is higher than those of the dehydrogenation of the remaining two isopentene isomers[76,77]. The rates of dehydrogenation of 3-methylbut-1-ene, 2-methylbut-2-ene, and 2-methylbut-1-ene at 386° in the presence of the catalyst with the atomic ratio Mo : Bi = 1 are in the proportions 4.3 : 1.2 : 1.[77]

The dependence of the reactivity of olefins on their molecular structure in the presence of other catalysts has been investigated comparatively little, but it is clear that it can differ significantly from that in the presence of the bismuth–molybdenum catalyst. Thus the yields of isoprene in the presence of the iron–zinc–chromium catalyst in the dehydrogenation of isopentenes decrease in the sequence 2-methylbut-2-ene > 2-methylbut-1-ene > 3-methylbut-1-ene.[78] The reactivities of the isopentene isomers decrease in the same sequence in the presence of phosphoric acid deposited on silica gel[79].

In the presence of the bismuth–molybdenum catalyst, a zero reaction order with respect to oxygen and a nearly first order with respect to mono-olefins is observed over a fairly wide range of concentrations and experimental conditions[80-82]. A zero order with respect to oxygen obtains also with increase of oxygen concentration above a limiting value, which is usually much lower than the concentration of the hydrocarbon. A zero reaction order with respect to oxygen has likewise been observed in the presence of the iron–chromium–zinc and phosphoric acid catalysts[83,84], but has not been found in the presence of the iron–antimony and antimony–tin catalysts even at oxygen concentrations exceeding by several factors of ten the concentration of the olefin. In the presence of low product concentrations, reaction orders close to 1/2 with respect to mono-olefins and oxygen have been found for these catalysts[85].

With decrease of temperature from 420° to 350°C, the apparent activation energy for the dehydrogenation of but-1-ene in the presence of the bismuth–molybdenum catalyst in a stirred reactor increases from 11 to 36 kcal mole^{-1},[86] which has attributed to the inhibition of the reaction by butadiene[87]. Dehydrogenation in the presence of these catalysts may be inhibited by added water and unsaturated carbonyl compounds[88,89], which can be attributed, like the poisoning by butadienes, to the blocking of active centres.

(b) The Dehydrogenation Mechanism

Oxidative dehydrogenation of mono-olefins has nowadays come to be regarded as a reaction analogous to allylic oxidation: the oxidation of propene to acrolein and oxidative ammonolysis[66,87,90-92]. According to the mechanism of Adams and Jennings[93], the oxidative dehydrogenation in the presence of the bismuth–molybdenum catalyst proceeds via an intermediate allyl complex, for example:

$$CH_2=CH-CH_2-CH_3 \quad \text{or} \quad CH_3-CH=CH-CH_3 \xrightarrow{(a)} \rightarrow \underbrace{H_2C=CH=CH-CH_3}_{Z} \xrightarrow[+Z_1-O]{(b)} \underbrace{H_2C=CH=CH-CH_2}_{Z} \rightarrow$$

$$\xrightarrow{(c)} Z\,(H_2C=CH-CH=CH_2) \xrightarrow{(d)} H_2C=CH-CH=CH_2. \qquad (X)$$

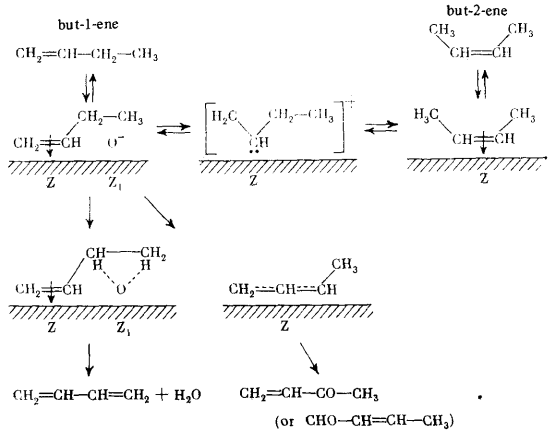
The rate limiting stage is believed to be the dissociative adsorption of the initial olefin.

According to the data of Margolis and Krylov[92,94], who also treat oxidative dehydrogenation as a reaction analogous to allylic oxidation, the stage involving the interaction between the surface hydrocarbon radical and the adsorbed oxygen [reaction (*b*)] is more complex than shown in scheme (X) and includes the formation of an intermediate positively charged hydrocarbon–oxygen complex containing an excess of carbon atoms relative to

oxygen atoms. The rate-limiting stage of the dehydrogenation process is believed to be the formation of the hydrocarbon–oxygen complex.

However, the analogy between the oxidation of propene to acrolein and the oxidative dehydrogenation of butenes is not observed in all cases. This is shown by a number of facts. There are catalysts in the presence of which the oxidation of propene to acrolein and oxidative ammonolysis proceed satisfactorily, while oxidative dehydrogenation takes place to only a slight extent [for example copper (I) oxide[95] and the vanadium–molybdenum catalyst[96]]. On the other hand, other catalysts are more or less active in oxidative dehydrogenation, but allylic oxidation does not take place in their presence [the iron–zinc–chromium, antimony–chromium[97], copper (II) oxide, manganese–molybdenum, vanadium–bismuth, and other[96] catalysts]. However, only partial specificity of catalytic activity to oxidative dehydrogenation reactions and reactions involving oxidation to acrolein is observed even in the presence of bismuth–molybdenum catalysts. Thus the β-phase is most active in the former reactions while the α- and γ-phases are most active in the latter[99]. In the oxidative dehydrogenation of butenes, the products contain small amounts of methyl vinyl ketone and crotonaldehyde, which must be regarded as very close analogues of acrolein formed via the allylic mechanism. However, the relative yields of butadiene and unsaturated carbonyl products in the presence of the same catalyst differ appreciably for different butene isomers[100]. In the oxidation of isopentene isomers, the reactivity series with respect to unsaturated carbonyl compounds and isoprene do not agree. For example, the rate of partial oxidation in the presence of Cu_2O decreases in the sequence 2-methylbut-1-ene > 2-methylbut-2-ene ≥ 3-methylbut-1-ene, while the rate of oxidative dehydrogenation in the presence of the same catalyst decreases in the sequence 3-methylbut-1-ene > 2-methylbut-1-ene > 2-methylbut-2-ene.[95]

Alkhazov et al.[101] proposed a mechanism for the oxidative dehydrogenation of butenes with the intermediate formation of the surface butene π-complex; the allyl complex is regarded as an intermediate in the formation of products containing the carbonyl group:



(XI)

According to scheme (XI), the dehydrogenation of but-2-ene can occur only after its preliminary isomerisation to but-1-ene. Scheme (XI) is therefore difficult to apply to the catalysts (iron–antimony[102] and uranium–antimony[103]) in the presence of which but-2-ene is dehydrogenated, but butenes are not isomerised.

The available data suggest that the oxidative dehydrogenation of mono-olefins can proceed via different mechanisms. One of the manifestations of these features is probably the dependence of the relative reactivity of isopentene isomers on the chemical composition of the catalyst. The differences in the mechanisms can consist in the formation of different surface intermediates. Thus in the presence of CuO the rate of oxidative dehydrogenation of 2-methylbut-1-ene and 2-methylbut-2-ene is almost independent of the addition of other mono-olefins (pent-1-ene or 3-methylbut-1-ene), i.e. there is no competition between the hydrocarbons as regards adsorption[98]. This shows that the dehydrogenation reaction on CuO bypasses the isopentene chemisorption stage. The pre-catalytic effect involving an enhancement of the adsorption of butenes under the influence of the adsorption of oxygen has not been observed in the presence of the iron–zinc–chromium catalyst. This effect, indicating the formation of an oxygen–hydrocarbon complex, has been observed in the presence of other catalysts of the oxidative dehydrogenation of butenes (molybdenum–bismuth, antimony–tin, and antimony–chromium). The above findings imply, according to the authors[97], that, in contrast to other catalysts, oxygen does not react with the butene molecule in the presence of the iron–zinc–chromium catalyst and its role consists in oxidising the hydrogen split off from the butene. This may also be the mechanism of the oxidative dehydrogenation of butenes on palladium[104].

During the oxidative dehydrogenation reaction in the presence of the bismuth–molybdenum catalyst, oxygen in the catalyst lattice is consumed. This involves partial reduction of the higher oxides of bismuth and molybdenum to lower oxides. The active oxidised form of the catalyst is maintained by the supply of oxygen from the gas phase. The catalyst dehydrogenation and reduction reactions proceed at comparable rates[105]. Thus the rate of the overall oxidative dehydrogenation process is determined within certain concentration limits by the rate of reduction, which is of first order with respect to butene and of zero order with respect to oxygen. Analogous results, indicating the oxidative dehydrogenation of but-1-ene via alternate oxidation and reduction, have been obtained in the presence of the antimony–tin[106] and iron–antimony[107] catalysts. With increase of the degree of reduction, its rate decreases rapidly, while the rate of oxidation rises. The steady state in the process corresponds to the surface of the iron–antimony catalyst being reduced approximately to the extent of 55%.[107]

The oxidation-reduction mechanism for the reactions of butenes, including side and secondary reactions, can be represented schematically as follows (Boreskov et al.[102]):

$$
\begin{gathered}
K(O) + C_4H_8 \rightleftarrows K(OC_4H_8)\,, \\
K(OC_4H_8) \rightarrow K(C_4H_6) + H_2O \xrightarrow{\text{fast}} C_4H_6 + K(r)\,, \\
K(OC_4H_8) \xrightarrow{+x_1K(O)} \nu_1CO_2 + \nu_1H_2O + (x_1+1)K(r)\,, \\
K(O) + C_4H_8 \rightleftarrows K(OC_4H_8)\,, \\
K(OC_4H_8) \xrightarrow{+x_2K(O)} \nu_2CO_2 + 3/4\nu_2H_2O + (x_2+1)K(r)\,, \\
K(r) + O_2 \rightarrow K(O_2^-) \xrightarrow[\text{fast}]{+K(r)} 2K(O)\,,
\end{gathered}
\qquad \text{(XII)}
$$

where K(O) and K(r) are respectively the oxidation and reduction sites on the catalyst surface, x_1 and x_2 are coefficients, and ν_1 and ν_2 are stoichiometric coefficients. An interaction of the hydrocarbon molecule with the catalyst surface more extensive than the formation of the intermediate surface butene is not taken into account in scheme (XII). On the assumption that the surface is homogeneous and that there is no mutual influence of the

adsorbed species, but without the postulate that adsorption equilibrium is reached and that a rate-limiting stage is present, scheme (XII) leads to a kinetic equation for the overall conversion of butene with a reaction order of 1/2 with respect to butene and oxygen, in agreement with experimental results. The oxidation-reduction mechanism with alternate oxidation and reduction evidently cannot occur in the presence of catalysts such as Al_2O_3 by virtue of the very nature of this catalyst.

In the presence of the spinel zinc–chromium ferrite catalyst, oxidative dehydrogenation also occurs without the involvement of lattice oxygen. The catalyst is not reduced during the reaction. This is suggested by the finding that, in the absence of oxygen, the yield of butadiene is very low. It amounts to not more than several per cent of the yield in the presence of oxygen and falls to zero after the consumption of 1–2 oxygen monolayers [108]. According to the mechanism proposed by the authors [108] for the converson of butene in the presence of the zinc–chromium ferrite catalyst, the first hydrogen atom is abstracted at an active centre consisting of an iron(III) cation with participation of adsorbed oxygen:

$$[A] + C_4H_8 + Fe^{3+} + O_a^- \rightarrow (C_4H_7Fe)^{3+} + OH^- ,$$

while lattice oxygen is involved in the abstraction of the next hydrogen atom:

$$(C_4H_7Fe)^{3+} + O_L^{2-} \rightarrow C_4H_6 + Fe^{2+} + OH .$$

Here [A] is an anionic vacancy associated with Fe^{3+}, O_a^- is an adsorbed oxygen radical, and O_L^{2-} is the lattice oxygen. The oxygen involved in the reaction is regenerated by the following processs:

$$2OH^- \rightarrow H_2O + O_L^{2-} + [A] ,$$

$$Fe^{2+} + 1/2O_2 \rightarrow Fe^{3+} + O_a^- .$$

Boreskov et al. [109] observed in the presence of the same specimens of the iron(III) oxide catalyst the occurrence of the dehydrogenation reaction via different mechanisms, one of which was the oxidation-reduction mechanism. Depending on the oxygen content in the reaction mixture, the catalyst operating in the steady state consists of magnetite on which the oxidation-reduction reaction takes place or α-Fe_2O_3 on which the hydrogenation mechanism is different from the oxidation-reduction mechanism.

(c) The Nature of the Active Surface of the Catalyst

In many cases, the catalytic activities in the oxidation of propene to acrolein, oxidative ammonolysis, and oxidative dehydrogenation of olefins are found to vary in parallel. For example, all three reactions proceed satisfactorily in the presence of bismuth–molybdenum or antimony–tin catalysts. The optimum compositions of the bismuth–molybdenum catalyst for these reactions are similar. However, as noted above, the specificities of the catalysts in relation to the above reactions are frequently not the same.

Data concerning the influence of chemical composition on catalytic properties agree with the hypothesis that the oxidative dehydrogenation of olefins can proceed via different mechanisms, one of which is analogous to allylic oxidation. In this case, the oxidative dehydrogenation reactions can probably proceed both on active centres for partial oxidation and on other centres.

A correlation is observed between the catalytic properties and the physicochemical characteristics associated with the mobility of the lattice oxygen and the strength with which the hydrocarbon adsorbed on the surface is retained. In order to characterise the mobility of oxygen, parameters such as the susceptibility of the catalysts to reduction [105,110], the diffusion of the bulk-phase lattice oxygen to the catalyst surface [111], the activation energy for the isotope exchange of the lattice oxygen with labelled molecular oxygen [66], and finally the energies of the bonds between oxygen and the catalyst surface, calculated from the heats of oxidation and reduction of the catalyst [112] or from data for the thermal desorption of oxygen from the catalyst surface [113], have been used. The most important conclusion reached in these studies is that the mobility of oxygen must have a definite optimum value for selective oxidation. When the mobility of oxygen is low, the catalyst is inactive, while an excessively high mobility entails the formation of products of the complete oxidation of the hydrocarbon.

The oxygen on the catalyst surface is as a rule inhomogeneous as regards the strength of its binding to the surface; the activity and selectivity of the catalytic action depend on the strength of this binding [112,114]. Thus the removal of 10–12% of the oxygen monolayer from the surface of the calcium-nickel phosphate catalyst leads to a decrease of the degree of conversion of butene and an increase in the selectivity with respect to butadiene [115].

According to Marshneva's data [113], weakly bound oxygen, involved in the complete oxidation reaction, has binding energies of 4–9 kcal mole^{-1} on different catalysts. On the other hand, the energy spectrum of the surface oxygen on the bismuth–molybdenum and iron–antimony catalysts for oxidative dehydrogenation lies in the region above 61 kcal mole^{-1}.

The relation between the catalytic properties and the strength of binding of the hydrocarbon to the surface is manifested by the correlations between the reactivity and ionisation potentials [77,78]. Since the adsorbed hydrocarbon species are charged, the ionisation potentials can be regarded as a measure of the capacity of the hydrocarbons for adsorption on the catalyst surface. On the bismuth–molybdenum and antimony–tin catalysis, the reactivity increases, while on the catalysts with iron oxides it diminishes with increase of the ionisation potential [78].

The catalytic properties of individual oxides in mixed catalysts based on them have been compared [101]. Systems comprising mixtures of oxides, one of which is moderately active in relation to extensive oxidation (bismuth, tin, manganese, and indium oxides) and the other is active with respect to the isomerisation of but-1-ene to but-2-ene (molybdenum, tungsten, antimony, and phosphorus oxides), are active in the oxidative dehydrogenation of butenes. The ability of the catalysts to promote isomerisation apparently reflects in a definite manner the optimum energy of binding of the olefin to the catalyst.

There are still few data concerning the nature of the active centres responsible for chemisorption and catalysis in oxidative hydrogenation reactions. The most active incomplete oxidation catalysts are mixed oxides with a definite ratio of the cations (for example Bi : Mo = 2 : 1–1 : 2). Hence follows the hypothesis that allylic oxidation requires the obligatory presence in the catalyst of a doublet consisting of two ions of different kinds on which the hydrocarbon and oxygen are adsorbed respectively [95,116–118]. The presence of paired centres in oxidation catalysts is indicated by the finding that, at high dilutions of the transition metal oxide by a non-transition metal oxide (down to transition metal concentrations of the order

of 1% and less), the catalytic activity diminishes, in contrast, for example, to the catalyst of the usual dehydrogenation, whose activity increases under the conditions of such dilution[94].

Various hypotheses have been put forward concerning the site of adsorption and the nature of the bond between the hydrocarbon and the surface of the catalyst of allylic oxidation. According to Sachtler and de Boer[110,119], the allyl group is retained on the surface as a result of the formation of a carbon–oxygen σ bond between one of the carbon atoms and a surface oxygen ion. Other workers[105] believe it to be more likely that the allyl group is bound to a transition metal ion as a result of the formation of a π-complex, while the hydrogen atom is linked to an oxygen atom. If the hydrocarbon is adsorbed on metal ions, the cations retaining the hydrocarbon in bismuth–molybdenum catalysts may be Mo^{6+} [94,105] or Bi^{3+}.[116,120]

In the general case, the presence of cations of different kinds is not an obligatory condition for the oxidative dehydrogenation of olefins. This is demonstrated by the occurrence of dehydrogenation in the presence of catalysts such as silica gel or phosphoric acid on carriers[79,121] and also by the possible occurrence of reactions via an impact mechanism between the adsorbed oxygen and gas-phase olefin molecules (CuO, see above).

The optimum strength of the binding of oxygen to the surface is attained for a definite lattice structure. It is suggested that such a structure may be formed by oxygen ions bound to cations by double bonds[122–125]. This hypothesis is supported by the correlation between the selectivity and the number or strength of the Mo=O double bonds in molybdate catalysts[126,127]. The strength of binding of the complexes to the surface, the degree of deformation of the C–H bonds, and the mobility of oxygen depend on the nature of the positive lattice ions, which is probably the cause of the differences between the reaction mechanisms on catalysts of different chemical compositions. For example, in the presence of the iron–zinc–chromium catalyst, on which there is no interaction between the adsorbed hydrocarbon and oxygen according to Krylova et al.[97], dissociative adsorption apparently takes place on the catalyst cations, similar to the behaviour in the usual catalytic dehydrogenation.

In the presence of catalysts such as phosphoric acid or alumina, the yields of oxidative dehydrogenation products are correlated with their acidic properties[128,129], which probably play a significant role in the nature of their acidity. The phosphoric acid catalyst contains protic and aprotic centres and is poisoned by butylamine. Alumina is a strong aprotic acid. The acid centres of the catalysts can serve as the adsorption sites for the reactant and for the formation of intermediate surface compounds[128,130].

2. DEHYDROGENATION OF PARAFFINIC HYDROCARBONS IN THE PRESENCE OF OXYGEN, HALOGENS, AND SULPHUR COMPOUNDS

(a) Reaction in the Presence of Oxygen

Table 1 presents certain typical data for the formation of the dehydrogenation products of paraffinic hydrocarbons in the presence of oxygen and solid catalysts. Compared with the reaction under similar conditions but in the absence of catalysts (see, for example, Skarchenko[1]), there is a sharp increase of the yields of diolefins.

The overall conversion into dehydrogenation products increases to a lesser extent, although in some cases (n-butane) it may exceed severalfold the yields of these products in the empty reactor. The difference between the reaction in the presence and absence of the catalyst is nevertheless not large enough to rule out the occurrence in the presence of the catalyst of gas-phase reactions, which apparently make a significant contribution to the overall conversion of the hydrocarbon.

Table 1. The formation of dehydrogenation products from paraffinic hydrocarbons in the presence of oxygen and solid catalysts.

Initial hydrocarbon	Catalyst	Molar ratio C_nH_{2n+2}:O_2:N_2(or H_2O)	Temp., °C	Yields of products*, mole %		Selectivity w.r.t. dehydrogenation products, mole %	Refs.
				monoolefins	diolefins		
Ethane	mixed Zn, Pb, and Na oxides	1:0.4:0	770	30	—	85	131
Propane	mixed Na, V, and Al oxides	1:0.3:1.2	490	17	—	79	132
n-Butane	Na phosphomolybdate	1:1:0	600	5	17	78	133
n-Butane	nickel–molybdenum	1:1:8	560	4	11	66	134
n-Butane	mixed Ni, Mg, and P oxides	1:1:14	593	4	14	44	135
n-Butane	mixed Ni, Sn, P, and K oxides	1:1:10	595	7	20	65	136
Isopentane	mixed Fe, Ni, and Sb oxides	1:1:20	538	1	7	44	137

*The yields of products are expressed in mole % relative to the initial hydrocarbon.

The surface of the reactor walls has a significant influence on the oxidation of paraffinic hydrocarbons regardless of whether complete or incomplete oxidation, dehydrogenation, or cracking predominates[1,11,12,41,138–141]. The influence of the solid surface on radical-chain reactions is usually attributed to its involvement in chain initiation and termination processes[11,12,17]. The termination of oxidation chains on the surface may involve the capture of $\dot{O}H$, $\dot{H}O_2$, $\dot{C}H_3$ etc. radicals. The conversion may be initiated on an active surface centre via the reaction[11]

$$C_nH_{2n+2} \xrightarrow{+(O_2)_{ads}} \dot{C}_nH_{2n+1}\,. \qquad (15)$$

However, the initiation and termination of chains on the surface is apparently only the simplest instance of the influence of the surface on the rate of radical-chain reactions. The influence of the surface may be attributed also to its involvement in chain branching of propagation. For example, according to Norikov et al.[139], in the oxidation of n-butane the surface of quartz catalyses the isomerisation of an unstable intermediate (s-butylperoxy-radical), which leads to the formation of one of the products of incomplete oxidation–acetaldehyde.

One of the functions of the catalyst in the oxidative dehydrogenation of paraffins is evidently the inhibition of oxidative cracking and of far-reaching oxidation, which has been observed on the surface of quartz[12,41]. All this does not of course rule out the possibility of the simultaneous occurrence in the system of definite heterogeneous-catalytic oxidative and other reactions with formation of dehydrogenation products. One of the possible mechanisms of the heterogeneous-catalytic oxidative

dehydrogenation of n-butane (in the presence of cobalt molybdate) has been proposed by Boutry et al.[142] The dehydrogenation of paraffins cannot proceed via a mechanism analogous to the dehydrogenation of olefins in the presence of bismuth molybdate, since the latter does not catalyse the dehydrogenation of paraffins[74]. Dieolefins may be formed from the intermediate mono-olefins via the usual heterogeneous-catalytic mechanism. Indeed substances such as phosphates or molybdates dehydrogenate mono-olefins with high yields of dienes. This probably explains the finding that the yields of butadiene in the presence of catalysts become higher than the yields of butenes (Table 1).

Mono-olefins may be formed to some extent via the usual dehydrogenation mechanism: mixed oxides containing substances such as chromium, vanadium, nickel, zinc, etc. are dehydrogenation catalysts[143]. Jouy and Balaceanu[144] indicate the possible role of the interaction of oxygen with the hydrogen removed from the hydrocarbon molecule. Thus all the catalysts which they tested (platinum, aluminium–chromium, etc.) readily oxidised hydrogen and there was no dehydrogenation of paraffin in the absence of oxygen under these conditions.

(b) Dehydrogenation in the Presence of Iodine and Oxygen

The characteristics of the dehydrogenation of n-butane in the presence of solid catalysts were investigated by the present author[1,145,146]. The experiments were performed mainly at 530°C in the presence of small (up to 3–4% relative to the hydrocarbon and oxygen) amounts of iodine. The dehydrogenation reaction is accelerated by the reactor walls, broken quartz, and to a particularly large extent in the presence of certain metal oxides and halides and other compounds on a porous carrier. An analogy is observed between the occurrence of dehydrogenation in the presence of solid catalysts and in the empty reactor. Changes in process parameters such as temperature, contact time, and reactant ratio had approximately the same influence on the conversion of n-butane in the presence of solid catalysts as in the empty reactor. A marked influence, comparable to that of the chemical composition of the catalyst, is shown by factors which determine the surface/volume ratio and the distribution of the surface in the reaction zone.

These studies led to the conclusion[1,146] that oxidative dehydrogenation in the presence of oxygen and iodine is not a heterogeneous-catalytic reaction. The increase of the yield of dehydrogenation products under the influence of solid catalysts cannot be accounted for by the inhibition of a side or secondary reaction, since the catalytic effect of the surface is not necessarily accompanied by a significant change in the distribution of products and the rate of conversion of butadiene in the presence of catalysts is actually higher than in the empty reactor. The characteristics of the action of a solid surface can be explained in terms of the hypothesis that the active surface accelerates a slow stage occurring in the bulk-phase reaction without altering significantly its mechanism. The oxidation of hydrogen iodide and the activation of oxygen and iodine by the surface have been considered to be stages of this kind.

The oxidation of hydrogen iodide [reaction (5)] is accelerated by oxidative dehydrogenation catalysts, but this cannot explain the increase of the yield of butadiene, since the rate of reaction (5) under the experimental conditions greatly exceeded the rate of dehydrogenation[1,147]. To test the possibility of heterogeneous initiation via the reaction of the hydrocarbons with oxygen [reaction (15)], a study was made[41] of the influence of broken quartz packing on the conversion of n-butane in the presence of oxygen. It was found that, under conditions close to those in the dehydrogenation reaction (but without iodine), the quartz surface strongly inhibits the conversion of butane and this is incompatible with the hypothesis of heterogeneous initiation [reaction (15)] with participation of oxygen. The data obtained can be explained if it is assumed that iodine may be activated on the catalyst surface, for example as a result of an increase of the concentration of atomic iodine in the system (analogously to the assumption made by Semenov for the chlorination reaction[18]):

$$I_2 + L \rightarrow L - I + \dot{I}$$

or by the formation of a reactive chemisorbed iodine molecule.

The role of the catalyst consists in accelerating the reactions of hydrocarbon molecules and radicals with iodine. At the same time the solid catalyst may also have a negative influence on the process, accelerating the secondary reactions of the dehydrogenation products.

Oxidative dehydrogenation in the presence of oxygen, iodine, and solid catalysts has also been investigated by Adel'son and coworkers. In the majority of experiments isopentane (and in addition also isopentenes and isobutane) were dehydrogenated and iodine was taken in an amount of 10% relative to carbon and oxygen. The observed characteristics proved to be in many respects analogous to those described above for the dehydrogenation of n-butane. Thus the dehydrogenation of those catalysts is accelerated by the addition of broken quartz[148–150]. The catalytic effect of the surface has been explained by the acceleration of a slow stage of the process[150,151]. The role of the catalyst does not consist in activating oxygen, since the quartz surface inhibits the conversion of hydrocarbons in the absence of iodine[152,153]. However, in contrast to the results quoted above for the dehydrogenation of n-butane, the authors[150,151] concluded that, under the conditions of their experiments, the slowest reaction stage is the oxidation of hydrogen iodide [reaction (5)] and that the role of the catalyst is to accelerate it. It is noteworthy that unduly high activation energies for reaction (14), involving the abstraction of the hydrogen atom from the hydrogen iodide molecule (29 kcal mole^{-1} [150] and 25 kcal mole^{-1} [151]) were used in a comparative estimate of the rates of oxidation of hydrogen iodide and dehydrogenation[150,151] instead of the more reliable value of 20 kcal mole^{-1} (see above). This must have led to unduly low rates of oxidation of HI.

The ratio of the rate of oxidation of HI and dehydrogenation depends in general on the reactivity of the hydrocarbons and the reactant concentration ratios. With increase in the reactivity of the hydrocarbon and the concentration of iodine, which accelerates dehydrogenation and inhibits the oxidation of hydrogen iodide (see Section II), the above rate ratio can change significantly towards a reduced rate of reaction (5) and the acceleration of this reaction by the catalyst then becomes one of the causes of the increase of the yields of dehydrogenation products.

The dehydrogenation of n-hexane in the presence of iodine and oxygen is also accelerated by broken quartz and other active solid catalysts[145]. The main product of the iodine-induced dehydrogenation of n-hexane is benzene regardless of the presence of oxygen or solid catalysts. The preferential formation of the aromatic product takes place not only for appreciable degrees of conversion (above 30–40%) into dehydrocyclisation

products, as in the usual heterogeneous-catalytic processes[143], but also for low degrees of conversion (less than 10%).[145] If the aromatisation of paraffins in the presence of iodine proceeds via intermediate olefins (see above), the implication is that the difference between the reactivity of hexenes and hexane in iodine-induced dehydrogenation is very large.

(c) Dehydrogenation in the Presence of Chlorine- and Bromine-Containing Substances

Considerable advances have been made in recent years in the dehydrogenation of paraffins under the influence of chlorine, bromine, their compounds, and oxygen (Table 2). For the same halogen/hydrocarbon ratio, the yields of dehydrogenation products decrease in the sequence iodine > bromine > chlorine compounds. Mixtures of halogens are extremely effective. Juding from the available data[162,163], more effective dehydrogenation parameters are achieved in the presence of a mixture of iodine, bromine, and chlorine than when only one of the halogens is used. It follows from other patents[164-167] that higher yields of dienes and styrene were achieved in the dehydrogenation of olefins and ethylbenzene respectively than in the dehydrogenation of paraffins in the presence of the same amounts of the halogen. The main products of the dehydrogenation of n-hexane in the presence of HCl and oxygen for degrees of conversion up to 30% were hexenes (Table 2).

Table 2. The yields of products in the presence of HCl or bromine compounds, oxygen, and solid catalysts.

Initial hydrocarbon	Catalyst	Halogen-containing substance (X)	Molar ratio $C_nH_{2n}+2:X:O_2$	Temp., °C	Yields of products, mole %: mono-olefins	diolefins	benzene	Selectivity w.r.t. dehydrogenation products, mole %	Refs.
Ethane	Fe, Li, Ln chlorides-Al_2O_3	HCl	1:1:1	575	79	—	—	87	154
n-Butane	$CeCl_3$-SiO_3	HCl	1:2:1,5	560	30	32	—	80	155
n-Butane	Fe_2O_3-RbCl-SiO_2	HCl	1:2.3:1.3	585	28	33	—	76	156
n-Pentane	Fe_2O_3-KCl-SiO_2	HCl	1:1.7:1	525	32	11	—	87	157
Isopentane	mixed oxides and chlorides	HCl	1:1.4:1	500	27	20	—	79	158
n-Hexane	Fe_2O_3-CsCl-SiO_2 gel	HCl	1:0.6:0.7	521	23	4	2	50	159
n-Butane	Mg ferrite	HBr	1:0.16:1.2	525	3	51	—	80	160
Isopentane	$CoCl_2$-LiCl-$MgCl_2$-pumice	Br_2	1:0.1:1.9	500	21	17	—	71	161

In the presence of HCl and oxygen but without a catalyst, there is virtually no dehydrogenation. Thus at 550°C and for the butane : HCl : O_2 = 1 : 0.8 : 1 ratios, 38% of butenes and butadiene is formed in the presence of the $FeCl_3$–KCl–SiO_2 catalyst; in the absence of the catalyst, dehydrogenation products were not detected[168]. Dehydrogenation in the presence of HCl and O_2 apparently proceeds via a mechanism different than in the presence of chlorine, which is capable, in contrast to HCl, of interacting directly under the dehydrogenation conditions with the hydrocarbon in the gas phase via a radical-chain mechanism[169]. The role of the catalyst in the dehydrogenation of paraffins in the presence of chlorine may be to generate chlorine atoms by the cleavage of molecular chlorine, as has been assumed for the chlorination of hydrocarbons[18,169]. On the other hand, dehydrogenation in the presence of HCl and oxygen should probably be regarded as a heterogeneous-catalytic reaction.

Both in the presence of chlorine and in the presence of HCl and oxygen, hydrocarbons are probably dehydrogenated via intermediate organic chlorides. These products are formed on direct interaction of the hydrocarbons with chlorine[169]. In the presence of HCl, oxygen, and metal chloride as catalysts, methane and ethane undergo oxidative chlorination with formation of alkyl chlorides in accordance with the overall equation[170]

$$HCl + 1/2O_2 + RH \rightarrow RCl + H_2O .$$

It is also known that C_3–C_4 alkyl chlorides readily decompose above 300–400°C into olefins and HCl.[169]

There is a correlation between the activity of catalysts in relation to oxidative dehydrogenation and oxidation of HCl:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O . \qquad (16)$$

The activity increases for both reactions in the following series of metal compounds: Nb < Ce < Bi < (Mn, Fe, Co, Ni, Pd) < V < Cu.[171]

Ioffe and Kikot'[155] proposed a multistage mechanism for the dehydrogenation of n-butane to butadiene via the intermediate formation of alkyl and alkenyl chlorides, chlorine, and butenes:

$$\begin{aligned} &4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O , \\ &C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl , \\ &C_4H_9Cl \rightarrow C_4H_8 + HCl , \\ &C_4H_8 + Cl_2 \rightarrow C_4H_7Cl + HCl , \\ &C_4H_7Cl \rightarrow C_4H_6 + HCl , \end{aligned} \qquad (XIII)$$

where the rate-limiting stage is the oxidation of HCl [reaction (16)]. According to scheme (XIII), the hydrocarbon reacts with chlorine alone and the role of oxygen is limited to its involvement in the formation of chlorine [reaction (16)]. According to scheme (XIII), chlorine should be a much more active dehydrogenation agent than HCl, which has not been confirmed experimentally[168].

Tarasova and Solomatina[168] proposed mechanisms for the dehydrogenation of butane to butenes:

$$\begin{aligned} C_4H_{10} + 1/2O_2 + HCl \rightarrow [C_4H_9Cl] + H_2O \\ \downarrow \\ C_4H_8 + HCl \end{aligned} \qquad (XIV)$$

and to butadiene:

$$\begin{aligned} C_4H_{10} + 2HCl + O_2 \rightarrow [C_4H_8Cl_2] + 2H_2O \\ \downarrow \\ C_4H_6 + 2HCl , \end{aligned} \qquad (XV)$$

According to these mechanisms, the reaction proceeds without the formation of intermediate chlorine. These mechanisms reflect to a greater extent the specific features of the process than mechanism (XIII). However, when butadiene is formed [mechanism (XV)], the absence of intermediate butene is doubtful. There are few experimental data concerning the conversion of paraffins into mono- and di-olefins in the absence of chlorine compounds. However, it is known that the dehydrogenation of butane in the presence of HCl and oxygen involves the formation of an appreciable amount of butenes, whose capacity for conversion into butadiene in the presence of the same catalyst is greater than that of butane[172]. At least a significant fraction of butadiene should therefore be formed via butenes.

Bromine compounds behave more like iodine compounds in oxidative dehydrogenation reactions than like chlorine compounds. In the presence of oxygen and HBr (in contrast to HCl and similarly to HI), dehydrogenation occurs also in the empty reactor[147,173]. Thus at 500°C and for the isopentane : oxygen : HBr = 1 : 1 : 2.1 ratios, 13% of isoprene is formed in the absence of the catalyst[173].

When the catalyst ($CoCl_2$, LiCl, and $MgCl_2$ on pumice) was introduced, the yield of isoprene rose to 26%.

In the joint presence of iodine and chlorine or bromine, the dehydrogenation of hydrocarbons apparently proceeds via a radical-chain mechanism. The acceleration of the reaction under the influence of the addition of the second halogen may be associated with the interaction between the halogens, which leads to the replacement of the slow reaction stages by faster stages. For example, when chlorine is added to the paraffin–iodine system, the comparatively slow formation of the alkyl radical on interaction with iodine

$$C_4H_{10} + \dot{I} \rightarrow \dot{C}_4H_9 + HI, \quad \varepsilon \simeq 25 \text{ kcal mole}^{-1}$$

is replaced by the rapid reaction [39]

$$C_4H_{10} + \dot{Cl} \rightarrow \dot{C}_4H_9 + HCl, \quad \varepsilon \simeq 1 \text{ kcal mole}^{-1}.$$

On the other hand, the formation of atomic chlorine in the presence of iodine is facilitated by the fact that it may not involve the dissociation of a chlorine molecule:

$$Cl_2 + M \rightarrow 2\dot{Cl} + M, \quad \varepsilon \simeq 57 \text{ kcal mole}^{-1}$$

but may proceed, for example, via the reaction

$$Cl_2 + \dot{I} \rightarrow ClI + \dot{Cl},$$

whose rate should be much higher.

(d) The Reaction of Hydrocarbons in the Presence of Sulphur Compounds

Appreciable yields of dehydrogenation products are reached in the presence of sulphur or sulphur compounds (H_2S, SO_2, COS, etc.) and solid catalysts [174–178]. In the dehydrogenation of ethane in the presence of H_2S and oxygen (with $C_2H_6 : H_2S : O_2 = 1 : 1.5 : 0.75$) and cadmium oxide on Al_2O_3 with a specific surface less than 1 $m^2\ g^{-1}$, the yield of ethylene was 77% for a selectivity of about 90%. [174] In the dehydrogenation of butane in a mixture with SO_2 on a bismuth–iron phosphate catalyst, the sum of butenes and butadiene formed was 38% for a selectivity of 38%, while in the dehydrogenation of isobutane on molybdenum sulphide the yield of isobutenes was 30% for a selectivity of 61%. [175]

Olefins with long C_4–C_5 chains are dehydrogenated with higher yields of products than the corresponding paraffins [175]. In the presence of sulphur (0.5 mole) and oxygen (1 mole per mole of hydrocarbon), ethylbenzene is converted into styrene with a yield exceeding 80% for a selectivity above 90%. [178,179] The degree of conversion of n-hexane in the presence of various catalysts and SO_2 reached 44–93%. [175] The dominant product for highest degrees of conversion was benzene (in a yield up to 54%). For moderate degrees of conversion, a considerable proportion of the products consisted of olefins, whose yields (up to 23–24%) exceeded those which are reached in the usual catalytic dehydrogenation [143,180]. Thus higher yields are reached in many instances in the dehydrogenation of hydrocarbons in the presence of sulphur compounds than in oxidation by oxygen or in the usual catalytic dehydrogenation.

There are reasons why dehydrogenation in the presence of sulphur compounds should be regarded as a process involving heterogeneous-catalytic reactions [178,185]. In the absence of the catalyst, the reaction proceeds to only a slight extent. Thus the dehydrogenation of n-hexane and cyclohexane (500°C, space velocity 0.5 h^{-1}) in a 1 : 1 mixture with SO_2 on alumina leads to the formation of up to 15 and 35% of benzene respectively. When alumina is replaced by quartz, the reaction hardly occurs. In the absence of sulphur dioxide, there is also no dehydrogenation on Al_2O_3. [182] During the reaction, SO_2 interacts directly with the hydrocarbon but not with the hydrogen evolved, since dehydrogenation ceases immediately after the removal of SO_2. Here SO_2 behaves as a hydrogen acceptor, being converted in the dehydrogenation reaction into hydrogen sulphide, for example:

$$C_4H_{10} + 1/3SO_2 \rightarrow C_4H_8 + 1/3H_2S + 2/3H_2O.$$

By accepting hydrogen, sulphur is similarly converted into hydrogen sulphide, for example via the reaction

$$C_4H_{10} + 1/2S_2 \rightarrow C_4H_8 + H_2S.$$

According to Pasternak and Vadekar [183], mixtures of H_2S and oxygen are more effective. During the oxidation of H_2S, which occurs simultaneously with the dehydrogenation reaction, the S_2 biradical as well as other active species ($H\dot{S}$, S_2^*) are formed and are probably involved in the intermediate dehydrogenation stages.

IV. DEHYDROGENATION IN THE PRESENCE OF SOLID ACCEPTORS OF HYDROGEN IODIDE

1. THE INFLUENCE OF THE CHEMICAL COMPOSITION OF THE HYDROGEN IODIDE ACCEPTOR

The influence of the chemical composition of the acceptor on the yield of n-butane, propane, and isopentane dehydrogenation products in the presence of iodine (but without oxygen) has been investigated [145]. The specimens were prepared by mixing ground oxide powders with a binder. In terms of the yields of the n-butane dehydrogenation products, the constant-valence metal oxides investigated can be arranged in the following sequence:

$$SrO \simeq CaO > ZnO > MgO. \qquad (17)$$

In the presence of variable-valence metal oxides, which are reduced on interaction with HI, the yields of butadiene decrease in the sequence

$$Mn_3O_4 \simeq Fe_2O_3 > Co_3O_4 > Ni_2O_3 > CuO > Cu_2O. \qquad (18)$$

Fairly high yields of butadiene were obtained only in the presence of Mn_3O_4 and Fe_2O_3. In the presence of the remaining variable-valence metal oxides, the main process is oxidation by the oxygen evolved from the lattices of the oxides as a result of their partial reduction by the hydrocarbon. In the dehydrogenation of propane and isopentane, the oxide acceptors investigated can be arranged, with slight deviations, in the same sequences in terms of the yields of products as in the dehydrogenation of n-butane.

The influence of the chemical composition of HI acceptors on the dehydrogenation of paraffinic hydrocarbons by oxygen supplied to the system has been investigated in a number of studies. The highest yields of isoprene in the presence of calcium, barium, strontium, zinc, nickel, iron, cobalt, copper, and manganese oxides have been obtained when alkaline earth metal and manganese oxides were used [184]. Alkali metal hydroxides deposited on carriers are extremely effective acceptors. In the dehydrogenation of isopentane in the presence of iodine and oxygen, the yield of isoprene decreases in the sequence [185]

$$NaOH > KOH > BaO > CaO > CuO \qquad (19)$$

(the oxides and hydroxides were deposited on Al_2O_3).

NaOH, KOH, and MnO_2 acceptors deposited on Al_2O_3 were investigated[186]. On sodium acceptors, it is possible to achieve higher yields of butadiene and a much smaller loss of iodine from the reactor than in the presence of the manganese acceptor[186]. However, a disadvantage of the sodium acceptor is the appreciable corrosion of the reaction apparatus. In the presence of the potassium acceptor, the loss of iodine from the reactor is smaller, but the yields of butadiene for the same amount of iodine are lower than in the presence of the sodium acceptor[187].

The influence of the chemical composition of HI acceptors in the dehydrocyclisation of n-hexane has been investigated[188]. The metal oxides were prepared by pressing their powders with added binder and potassium iodide. Tor the ratios $C_6H_{14}:I_2:O_2 = 1:{\sim}0.9:1$, the yields of benzene decreased in the sequence

$$Fe_2O_3 > Mn_2O_3 > CaO > ZnO > CuO > Co_3O_4 > Ni_2O_3 \qquad (20)$$

and in the presence of the last four oxides they were lower than in the reaction in the empty reactor.

Under optimum conditions, yields of benzene exceeding 60% were achieved in the dehydrocyclisation of n-hexane in the presence of an acceptor[189], but they do not exceed the yield of this product in the usual catalytic aromatisation. The yields of hexene in the presence of HI acceptors are even lower than in the empty reactor or in the presence of non-accepting solid catalysts. Considerable amounts of coke-like and tarry side products are formed.

The distribution of acceptors in sequences (17)–(20) apparently depends to a definite extent on the method of preparation of the specimens, the additives present, and the experimental conditions. For low amounts of iodine supplied (iodine/hydrocarbon = 0.1) and an equimolar amount of oxygen, the yields of butadiene obtained in the presence of active HI acceptors such as sodium hydroxide on Al_2O_3 are lower than in the presence of ground quartz[190] and only a mixture of the acceptor and quartz makes it possible to obtain higher yields of butadiene than on quartz. A similar effect has been observed in the dehydrogenation of isopentane. The fact that the replacement of quartz by an active HI acceptor for low amounts of iodine supplied leads to a decreased yield of diolefins can be accounted for, on the one hand, by the catalytic influence of quartz and, on the other hand, by the fact that the acceptor binds HI and removes a definite proportion of the iodine from the reaction sphere. The study of the time variation of the yield of diolefins showed that, after complete iodination, the acceptor has approximately the same influence on the reaction as the quartz packing.

2. THE BINDING OF HYDROGEN IODIDE BY SOLID ACCEPTORS

Reactions involving the absorption of HI [reactions (6) and (7)] belong to the class of exchange topochemical reactions:

$$\text{solid}_{(1)} + \text{gas}_{(1)} \rightarrow \text{solid}_{(2)} + \text{gas}_{(2)}$$

and exhibit properties characteristic of reactions of this type.

The comparative reactivities of a number of metal oxides in relation to HI have been investigated[191,192]. The oxides were prepared in two ways: by deposition in a thin layer on quartz plates and by the granulation of commercial preparations. The oxide grains (approximately 2 mm in size) were the same as those employed in experiments on oxidative dehydrogenation in the presence of iodine (see above). The average thickness of the layer of oxide deposited on plates was approximately 1–2 μm. The specific surfaces of the finished specimens did not exceed several $m^2\ g^{-1}$ and their pore volumes were in the range 0.1–0.3 $cm^3\ g^{-1}$. The experimental data for the oxides investigated are described by the kinetic equation

$$\alpha = kt^n \qquad (21)$$

or

$$1 - \sqrt[3]{1-\alpha} = kt^m, \qquad (22)$$

where α is the degree of conversion and n and m are constants. The reactions of the metal oxides with HI are retarded up to a complete arrest for degrees of conversion departing widely from equilibrium. The granulated constant-valence metal oxides can be arranged in the following sequence in terms of their reactivity for low (up to 1–2%) degrees of conversion:

$$SrO > BaO > CaO > ZnO > MgO, \qquad (23)$$

while variable-valence metal oxides can be arranged in the following sequence:

$$Mn_3O_4 > Co_3O_4 > CuO > Fe_2O_3 > Ni_2O_3. \qquad (24)$$

The rate of reaction of the granulated metal oxides with HI is much lower than that of the oxides deposited on plates. For all the oxides in the grains, except zinc oxide, the reaction virtually ceases under the conditions investigated when the degree of conversion is less than 5%. The degree of conversion reached for the same oxide on plates is between 10 and 95%. Thus the dependence of the reactivity of the oxides on their particle size is so great that it is manifested even more markedly than its dependence on the chemical nature of the oxide. The arrest of the reaction of the oxide with hydrogen iodide under conditions remote from equilibrium has been explained[192] in terms of the theory of impedance in topochemical reactions[193]. The ionic radius of I^- (2.2 Å) greatly exceeds that of O^{2-} (1.4 Å). The molar volume of the iodide formed is therefore much greater than that of the initial oxide, i.e. the volume of the reaction system greatly increases during the reaction. The molar volumes of the iodides of the metals investigated (calcium, magnesium, strontium, barium, manganese, nickel, and copper) are greater by a factor of 2.7–5.8 than those of the corresponding metal oxides. As a consequence of the increased volume of the system, the conversion of the oxide into the iodide entails an increase in the compactness of the outer layer of the specimen, which inhibits the diffusion of HI into the bulk of the oxide and the removal of water vapour, and, in the case of variable-valence oxides, also the removal of iodine from the reaction zone.

In the majority of experiments with oxides deposited on plates and with granulated oxides in all cases, the observed values of n and m in Eqns. (21) and (22) were smaller than unity and the apparent activation energies above 400°C did not exceed 10–11 kcal $mole^{-1}$,[194] which is characteristic of reactions occurring under conditions with diffusion-induced inhibition. The only exception (with respect to the values of m and activation energies) is ZnO on plates. The product of the reaction of ZnO with HI (zinc iodide) sublimes under the experimental conditions. The removal of the iodide from catalyst sites containing ZnO which has not reacted should lead to an increase with time

of the proportion of defects in the surface layer of the oxide and to the formation of transport pores, which is probably the cause of the pronounced S-shape of the kinetic curves for reactions involving the absorption of HI by zinc oxide and also the comparatively small extent of the diffusion-induced inhibition of this reaction [192]. The impedance phenomenon has a significant influence on the dehydrogenation process in the presence of oxides which are HI acceptors. The acceptor is rapidly exhausted, so that its large excess relative to the hydrocarbon is required.

3. FACTORS DETERMINING THE EFFICIENCY OF HYDROGEN IODIDE ACCEPTORS IN THE OXIDATIVE DEHYDROGENATION PROCESS

In order to elucidate the factors which determine the efficiency of HI acceptors, the yields of dehydrogenation products were compared with the rates and equilibria of the reactions of metal oxides with hydrogen iodide [41,145]. At temperatures in the range 300–530°C, the equilibrium degree of conversion of all the oxides investigated (BaO, SrO, CaO, ZnO, Cu_2O, etc.), except magnesium oxide, into the iodides is close to 100%, while for MgO it is not more than 10%. [145,194] The yields of diolefins in the oxidative dehydrogenation of n-butane and isopentane in the presence of magnesium oxide are also lower than on the remaining constant-valence metal oxides. However, no relation is observed for the latter oxides between the degree of approach to equilibrium in the reaction with HI and the yields of dehydrogenation products, since the equilibrium in the reaction involving the absorption of HI is almost completely displaced towards the formation of the iodide on virtually all the oxides‡.

Under the conditions of the dehydrogenation experiments, the acceptor : hydrocarbon weight ratio was 140 to 150. For low degrees of conversion (up to 1–2%), the rate of sorption of HI by the granulated metal oxides decreases in sequences (23) and (24) and the yield of butadiene decreases as a function of the chemical composition of the acceptor in sequences (17) and (18). Thus, for constant-valence metal oxides, there is a correlation between the reactivity in relation to HI and the yields of butadiene in the dehydrogenation of n-butane [sequences (17) and (23)]. In the presence of Mn_3O_4, the highest yields of butadiene are observed and the rates of binding of HI by this oxide are a maximum. However, for the remaining variable-valence metal oxides, no correspondence is observed between sequences (18) and (24). This can probably be accounted for by the catalytic influence of some of the above oxides, promoting the dehydrogenation and complete oxidation of the hydrocarbons [41].

The correspondence between the yields of dehydrogenation products and the reactivities of the acceptor in relation to HI is associated with the fact that the reaction involving the absorption of HI is not sufficiently fast under the dehydrogenation conditions to influence the rate and equilibrium of the dehydrogenation reaction, and the efficiency of the acceptor is determined by the rate of its reaction with HI. The observed impedance phenomenon and other experimental findings, in which a pronounced diffusion-induced inhibition of the reaction of the oxides with HI is manifested, demonstrates the particular importance of ensuring a sufficient degree of dispersion of the acceptor in order to improve its efficiency. Indeed, under the conditions usually employed in oxidative dehydrogenation (in the presence of a large excess of the acceptor relative to HI), the yield of dehydrogenation products begins to fall for degrees of conversion of the oxides into the iodides not exceeding several per cent [194,195].

When dehydrogenation with an HI acceptor proceeds in the presence of oxygen, the binding of HI is accompanied by the oxidation of the metal iodide by oxygen—reaction (8), involving the regeneration of iodine and the acceptor, takes place. The rate of dehydrogenation is therefore also important for the yields of the products of this reaction. According to Kolobikhin [187], the yields of butadiene on the potassium acceptor (KOH deposited on Al_2O_3) are much lower than on the sodium acceptor for the same content of iodine. At the same time, the rate of binding of hydrogen iodide on the potassium acceptor is apparently higher than on the sodium acceptor, as can be inferred from the loss of HI from the reactor. However, the rate of regeneration of the potassium acceptor is much lower than that of the sodium acceptor: under the conditions tested, the sodium acceptor is regenerated to the extent of 52% after 20 min, while the potassium acceptor is regenerated to the extent of only 8.7%. Thus the yields of the dehydrogenation products decrease with increase of the rate of regeneration of the acceptor.

In the study of granulated HI acceptors, a dependence of either the rate of absorption of HI or of the rate of dehydrogenation on their porous structure was not observed (although one must bear in mind that the pore volumes and the specific surfaces of the acceptors were small [192,194]). This can be explained by the fact that the increased compactness of the outer layer of the grain as a result of impedance is so great that the inner surface is blocked and hardly participates in the reaction. However, the dependence on the porous structure of the acceptor is manifested when a granulated acceptor is compared with one deposited on a carrier with a well developed porous structure (for example CaO on the KSK silica gel with a specific surface of about 100 $m^2 g^{-1}$). [1,196]

The influence of the inner surface of the acceptor on the conversion of the hydrocarbon is caused, on the one hand, by the increased rate of binding of HI and of the regeneration of the acceptor and, on the other, by the increased extent of the secondary reactions of the dehydrogenation products. In the presence of porous catalysts, isoprene undergoes a particularly extensive conversion. The yields of isoprene in the dehydrogenation of isopentane in the presence of porous acceptors as well as in the presence of porous non-accepting catalysts are therefore low.

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Studies in the field of the oxidative dehydrogenation of hydrocarbons have been carried out during the last decade mainly on the following lines.

1. The development of the theory and technology of industrial processes (iodine dehydrogenation of butane, oxygen dehydrogenation of butenes). The technological aspects of the problem were not considered in the present review.

‡For this reason, it is difficult to justify theoretically the hypothesis [184] of a relation between the yields of isoprene and the decrease of the free energy of binding of HI for the oxides of metals such as barium, strontium, zinc, manganese, etc.

2. The accumulation of data (mainly empirical data) on the yields of products and the selection of catalysts and process conditions for other oxidative dehydrogenation procedures, which are of clear practical interest and are likely to be applied on an industrial scale in the near future (dehydrogenation in the presence of chlorine and sulphur compounds, dehydrogenation of paraffinic hydrocarbons in the presence of oxygen and solid catalysts).

3. The search for new, previously unknown dehydrogenating agents and the associated development of ideas about the general principles of the action of dehydrogenating agents.

There is an extremely large variety of types of oxidative dehydrogenation processes. Those which have been most thoroughly investigated can be subdivided into two types to a first approximation: heterogeneous-catalytic reactions and radical-chain reactions catalysed by the surface. The dehydrogenation of olefins in the presence of oxygen belongs to the first variety, which may also include the dehydrogenation of paraffins in the presence of HCl or sulphur compounds and oxygen. Iodine dehydrogenation (in the presence or absence of oxygen) belongs to the second variety.

The accumulated experimental data show that, in dehydrogenation involving halogen compounds, there are analogies between the reactions of hydrocarbons belonging to different homologous series, the reactivity increasing with increased degree of unsaturation of the hydrocarbon. The influence of unsaturation in iodine dehydrogenation is so great that the dehydrogenation of C_4–C_5 paraffins leads to the almost exclusive formation of diolefins, while the dehydrogenation of C_6 paraffins yields aromatic products. The dehydrocyclisation of higher paraffins in the presence of chlorine and sulphur compounds and oxygen as well lead, like ordinary catalytic dehydrocyclisation, to the formation of a considerable amount of mono-olefins. In dehydration in the presence of oxygen, there is as a rule no similarity in the behaviour of paraffins and olefins.

Iodine dehydrogenation is employed in practice in an extremely complex system with gaseous and solid regenerators (acceptors); solid acceptors also exhibit a catalytic activity. The mechanism of iodine dehydrogenation in the presence of oxygen and an HI acceptor has been elucidated mainly by the separate investigation of the reaction in simplified and model systems (dehydrogenation in the presence of individual radical-forming substances, the influence of non-accepting catalysts, the reactions of acceptors with HI, etc.). The results can be regarded as a first approximation to the reaction mechanism involving the simultaneous occurrence of these processes in a real system.

Iodine dehydrogenation can be regarded merely as a first advance in the field of oxidative dehydrogenation of paraffins. Further development of methods for oxidative dehydrogenation should probably lead to the development of additional processes with more readily available and cheaper dehydrogenating agents, particularly agents based on chlorine or sulphur compounds. There already exists a definite theoretical basis, which makes it possible to direct the search for new systems of dehydrogenating agents (mixtures of radical-forming substances) along a rational pathway.

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