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Oxidative Dehydrogenation of Hydrocarbons

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I. INTRODUCTION

In recent years the oxidative dehydrogenation reactions, whereby olefins and diene monomers can be made from the corresponding more saturated hydrocarbons, have been attracting increasing attention. The essential feature of the oxidative dehydrogenation reaction consists in the partial oxidation of the hydrogen in the organic molecules without affecting the hydrocarbon skeleton. In the usual dehydrogenation of saturated hydrocarbons the conversion of the latter into unsaturated hydrocarbons is limited by the position of the equilibrium in the reversible reaction

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n-2} + 2H_2. \quad (1)$$

The extent of dehydrogenation of hydrocarbons can be sharply increased if the equilibrium is displaced by binding the hydrogen in the form of water, for example:

$$C_nH_{2n+2} + O_2 \rightleftarrows C_nH_{2n-2} + 2H_2O \quad (2)$$

or as hydrogen iodide:

$$C_nH_{2n+2} + 2I_2 \rightleftarrows C_nH_{2n-2} + 4HI. \quad (3)$$

Iodine is much more active as a dehydrogenating agent than oxygen and oxidative dehydrogenation using iodine can be of practical interest in those cases where the dehydrogenation is coupled with an effective iodine regeneration process. The iodine consumed in reaction (3) can be regenerated, for example, by the oxidation of the resulting hydrogen iodide with oxygen:

$$2HI + {}^1/_2O_2 \rightarrow H_2O + I_2 \quad (4)$$

or, as is usually done, the hydrogen iodide is first trapped by solid acceptors, for example, metal oxides, with formation of the corresponding iodides:

$$MO + 2HI \rightleftarrows H_2O + MI_2. \quad (5)$$

On heating in a stream of air, metal iodides readily decompose with evolution of elemental iodine:

$$MI_2 + {}^1/_2O_2 \rightarrow MO + I_2. \quad (6)$$

In contrast to normal dehydrogenation, oxidative dehydrogenation reactions are exothermic.

II. OXIDATIVE DEHYDROGENATION OF OLEFINS

A considerable amount of the available literature on the oxidative dehydrogenation of olefins refers to the conversion of n-butenes into divinyl and of isopentenes into isoprene. The oxidative dehydrogenation of mono-olefins into diolefins is a typical heterogeneous catalytic reaction.

Under certain conditions a high selectivity of the reaction

$$C_4H_8 + {}^1/_2O_2 \rightleftarrows C_4H_6 + H_2O \qquad (7)$$

is attained on suitable catalysts. Small amounts of furan, carbon monoxide, carbon dioxide, acetone, propene, ethylene, formaldehyde, and other substances are formed as side-products. Reaction (7) is an oxidative process and not dehydrogenation with subsequent oxidation of hydrogen. Hydrogen is either completely absent from the reaction system or is not oxidised under the experimental conditions. The oxidation of butane under these conditions is much slower than that of butenes and it is converted preferentially into carbon monoxide and carbon dioxide. Under the normal experimental conditions for the oxidative dehydrogenation of n-butenes into divinyl, thermal reactions virtually do not occur in a Pyrex reactor; a steel reactor favours the formation of carbon dioxide.

1. CHEMICAL COMPOSITION OF THE CATALYSTS

A fairly large number of catalyst recipes have been proposed for the dehydrogenation of mono-olefins in the presence of oxygen: molybdates or tungstates of bismuth [1-7], cobalt, vanadium, tin, titanium [8], tellurium [9], phosphoric acid on alumina [3,5,10], phosphates of bismuth, iron [11,12], strontium, nickel, chromium, calcium [13,14], tungsten, vanadium [15], and indium [16], phosphomolybdate and phosphotungstate of bismuth [17,18], mixed oxides of antimony and tin [3-5,19-24], mixed oxides of titanium [25], mixed oxides of tin and arsenic with selenium and tellurium [19], mixed oxides of iron with aluminium and chromium [26], basic halides of iron, cobalt, magnesium, and manganese [27,28], gold and platinum [29], and others [30].

The application of certain solid catalysts is combined with the introduction into the reaction zone of halogen-containing [31-42] or sulphur-containing [43-46] compounds, which decompose under the reaction conditions with formation of halogens or sulphur dioxide. Thus mixed and pure oxides of iron, cobalt, nickel, manganese, vanadium, molybdenum, bismuth, tin, cadmium, and copper, magnesium phosphate, and many other compounds are recommended for the oxidative dehydrogenation of mono-olefins in the presence of halogen- or sulphur-containing compounds.

Despite the large number of catalysts tested, relatively few data have been published which would permit their comparison. Some typical results of tests of catalysts under optimum conditions are presented in Table 1. The data in Table 1 permit only a very restricted quantitative comparison of the catalysts, since the conditions of the tests, the composition of the raw material, and the method of preparation and treatment of the catalysts were not the same in most of the studies quoted. The yield of diolefins on a molybdenum–bismuth catalyst in the oxidative dehydrogenation of individual butene isomers increases in the series *trans*-but-2-ene, *cis*-but-2-ene, and but-1-ene, and in the dehydrogenation of isopentenes it increases in the series 2-methylbut-1-ene, 2-methylbut-2-ene, and 3-methylbut-1-ene.

High yields of divinyl (65–74%) with a selectivity of 83–91% were attained on many catalysts of various compositions. The same catalysts as those for the dehydrogenation of n-butenes proved to be preferable for the oxidative dehydrogenation of isopentenes to isoprene. The fact that on certain catalysts (mixed oxides of antimony and tin, phosphates) high yields of diolefins are attained at temperatures not higher than 400°C is also striking. The highest yields of diolefins and the highest selectivity are observed in the presence of iodine- and sulphur-containing compounds. Evidently, these additives themselves play a significant if not the main role in the dehydrogenation reaction. Fairly high yields of divinyl were obtained on quartz and silica gel, these catalysts being markedly inferior to those listed in Table 1 only as regards selectivity.

Kolobikhin and Emel'yanova [53] investigated the effect of the proportions of bismuth and molybdenum and also of the total content of bismuth and molybdenum oxides in the catalyst on its dehydrogenating capacity. The catalysts were made by impregnating silica gel for 1 h at room temperature with a complex solution of bismuth nitrate and ammonium molybdate in nitric acid. The optimum composition of the catalyst corresponded to the atomic ratio Bi : Mo = 0.7–0.9 and 18–20 wt.% of bismuth and molybdenum oxides. The silica gel was treated with steam and had a specific surface of 64 $m^2 g^{-1}$ and a pore volume of 0.82 $cm^3 g^{-1}$. An analogous study of bismuth–tungsten catalysts [54] showed that catalysts with the atomic ratio Bi : W = 0.67–1.5 exhibited the highest activity. The addition of phosphorus up to atomic proportions Bi : P : W = 12 : 1 : 12 increases the yields of divinyl.

Table 1. Oxidative dehydrogenation of certain unsaturated hydrocarbons on catalysts of various chemical compositions.

Catalyst	Initial hydrocarbon	Temperature, °C	Moles per mole of hydrocarbon: of oxygen	Moles per mole of hydrocarbon: of nitrogen, water, or other diluent	Yield of diolefins, %: with respect to starting material	Yield of diolefins, %: with respect to product	References
Bismuth molybdate	but-1-ene	460	1	4	74	91	1
Bismuth molybdate	*cis*-but-2-ene	494	1	4	70	82	1
Bismuth molybdate	*trans*-but-2-ene	493	1	4	66	83	1
Mixed Sb and Sn oxides	but-1-ene	405	1	8	69	90	20
Mixed Mo and Te oxides	but-1-ene	440	1	4	67	90	47
Ni, Ca, and Cr phosphates	but-1-ene	670	1	18	57	83	13
Bismuth tungstate	but-1-ene	470	1	4	51	78	6
Bismuth phosphate	but-1-ene	500	1	2	46	80	11
Indium phosphate	but-1-ene	490			44	61	16
V and K sulphates with 0.4 mole of $(NH_4)_2SO_3$*	but-1-ene	680	0.1	2.4	79	89	43
Ni + ceramic with 0.097 mole of NH_4I *	but-2-ene	602	0.8	14.6	87	99	42
Bismuth molybdate	n-butenes	500	0.8	4	66	88	2
Basic Fe bromides	n-butenes	450	0.5	5.5	67	86	27
Bi and Fe phosphates	n-butenes	350			66	83	12
Mixed Sb and Sn oxides	n-butenes	370	1	8	65	88	25
Mixed Group VIII and IV oxides **	n-butenes	430	0.8	2.3	47	76	48,49
Quartz	n-butenes	550	0.5	5	48	48	50
Silica gel	n-butenes	550	0.5	5	44	45	50
V and K sulphates with 0.4 mole of $(NH_4)_2SO_3$ *	isopentenes	680	0.1	2.4	64	74	43
Vanadium pentoxide with 0.0275 mole of 1-iodo-3-methylbutane *	2-methylbut-2-ene	500	0.8	12	91	94	36
Bi and Fe phosphates	2-methylbut-2-ene				47	64	12
Mixed Sb and Sn oxides	2-methylbut-2-ene	380	2	17	40		25
Bi phosphomolybdate	isopentenes	510	1	24	36	63	51
Bi phosphotungstate	isopentenes	510	1,4	26	33	66	51
Bismuth molybdate	3-methylbut-1-ene	500	3	6	45	70	52
Bismuth molybdate	2-methylbut-1-ene	500	3	6	36	60	52
Bismuth molybdate	2-methylbut-2-ene	520	3	6	39	60	52
Cobalt molybdate	isopentenes	510	1.4	36	30	54	51
Phosphoric acid on Al_2O_3	2-methylbut-2-ene	450	1.1	9	56		10
Bismuth molybdate	ethylbenzene	550	0.3	1.2	23***		7

* The iodine- and sulphur-containing compounds were introduced into the reaction together with the initial hydrocarbon. The table indicates the number of moles of the additive per mole of the hydrocarbon.

** Composition of the catalyst not published.

*** Yield of styrene.

According to the data of other workers [55,56], the optimum composition of the molybdenum–bismuth catalyst is in the range Mo : Bi = 1–2 and probably depends on the nature of the carrier and the method of preparation of the catalyst. The extent of formation of carbon dioxide increases with the bismuth content in the specimen. Therefore the highest selectivity is attained in the presence of an excess of molybdenum in the catalyst (Mo : Bi = 2–4).

Kolobikhin and coworkers [57] investigated the effect of the pore structure in the carrier for the bismuth–molybdenum catalyst. They tested four silica gels of various brands with specific surfaces between 680 and 64 $m^2 g^{-1}$. As the specific surface of the silica gel increased, there was a corresponding increase in the conversion of n-butene but the selectivity with respect to divinyl fell. The decrease of the selectivity can probably be explained by the diffusion-dependent inhibition of the reactions on finely porous specimens [58], the divinyl formed undergoing secondary reactions.

2. KINETICS

a. Reaction Temperature

Depending on the properties of the catalyst and the reaction conditions, the maximum yields of divinyl and isoprene in the oxidative dehydrogenation of the corresponding mono-olefins were observed at 370–570°C. [1,18,59–62] With increase of temperature above the optimum value, the yields of the secondary reaction products, mainly carbon dioxide and also furan and carbonyl compounds [62], also rise.

According to the data of Tsailingol'd et al. [63], in the temperature range 410–490°C the temperature dependence of the rate constants for the overall conversion of n-butenes on the bismuth–molybdenum catalyst is defined by the expression

$$\lg k = -\frac{13900}{4.545T} + 3.18 \qquad (8)$$

Thus the apparent activation energy is 13.9 kcal $mole^{-1}$. According to the data of other workers, this quantity is much higher. Thus, according to Adams [1], it is 26 kcal $mole^{-1}$ for but-1-ene at 345–500°C. The apparent activation energies for the oxidative dehydrogenation and combustion of isopentenes at 475–525°C are approximately 21 kcal $mole^{-1}$. [64] At 340–390°C about 40 kcal $mole^{-1}$ was obtained for the oxidative dehydrogenation of but-1-ene [56]. As the temperature is increased above 390°C, the activation energy falls appreciably, probably because of the diffusion-dependent inhibition of the reaction [58].

b. Duration of Contact

Examination of data on the reaction of n-butenes on bismuth molybdate deposited on silica gel as a function of space velocity [53] shows that, other conditions being equal, the maximum yield of divinyl depends on the composition of the catalyst. On a specimen containing 35% of the active substance the same conversion is attained for a shorter contact time than on a specimen containing 13% of bismuth molybdate. With increase in contact time, the difference between the yields of divinyl and the selectivities of all the specimens decrease.

When the time of contact is increased above the optimum value, the yields of divinyl decrease due to secondary reactions, as happens on raising the temperature.

c. Concentrations of the Starting Materials

When the molar ratio oxygen : hydrocarbon is raised from 0.1 to 1, the yields of divinyl and isoprene in the dehydrogenation of the corresponding mono-olefins increase, but there is also an increase in the amount of oxygen-containing side-products formed: carbon dioxide, furan, and carbonyl and carboxy-compounds [53,54,62,65]. A necessary condition for the maximum yield of divinyl is the presence of oxygen in the effluent gases. The lower the oxygen to butenes ratio the greater is the decrease of the activity of the catalyst with time [53].

According to the data of Mel'nik and Tyuryaev [66], the initial "instantaneous" activity of the catalyst is independent of the concentration of oxygen, which determines only the extent of the subsequent fall of activity with time. The decrease of the yields of divinyl with time can be accounted for mainly by the change in the phase composition of the bismuth–molybdenum catalyst and not only by the deposition of carbonaceous substances. Indeed at low oxygen to butenes ratios the amount of divinyl and carbon dioxide formed in the first minutes of the reaction is greater than the amount which could form if all the oxygen supplied were utilised [66]. The decreased activity of the molybdenum–bismuth catalyst on reducing its oxygen content was demonstrated also by direct experiments with partial reduction of the catalyst [63]. On partial reduction, the higher oxides of bismuth and molybdenum are converted into lower oxides, as a result of which the activity of the catalyst decreases. According to the results of another investigation [67], the lattice oxygen is consumed during the reaction even when oxygen is present in a large excess in the reaction mixture.

Thus the oxygen of the catalyst itself participates in reactions involving the formation of divinyl and carbon dioxide. The oxygen in the gas phase has a dual function in the oxidative dehydrogenation process: to maintain the active oxidised form of the catalyst and to prevent coke formation. In order to ensure the presence of oxygen in the effluent gases in the usual flow-type reactor with a stationary catalyst bed, it is necessary to supply a considerable excess of oxygen at the inlet, but this leads to a decrease of selectivity due to formation of oxygen-containing compounds. Therefore reaction systems with internal mixing are preferred [68] for the oxidative dehydrogenation of olefins. Indeed, in a reactor with a suspended catalyst layer, more effective oxidative dehydrogenation of butenes was achieved than in a reactor with a stationary catalyst bed [68].

All that has been said so far about the effect of the concentration of oxygen applies to the region of low oxygen concentrations, up to the ratio oxygen : butenes = 0.8–1.0. When the oxygen : butenes ratio is increased to values in excess of unity, a change of oxygen concentration no longer has an appreciable effect on the yields of divinyl on the bismuth–molybdenum catalyst.

Tsailingol'd and coworkers [63] investigated the kinetics of dehydrogenation on the bismuth–molybdenum catalyst by a flow-circulation method at 410–490°C. The concentration of oxygen was varied in the range between 0.30 and 6.7 mole % and that of n-butenes between 2.55 and 18.60 mole %. An increase of the concentration of oxygen above 1–2% (at n-butene concentrations in the range 4–5 mole %) did not have an appreciable effect on the rate of the reactions, i.e. in this concentration range the reaction

was of zero order with respect to oxygen. The order of the reaction with respect to oxygen at lower contents of the latter in the system was not established. When the oxygen concentrations are not too low, the rate ω_1 of the overall conversion of n-butenes is given by the expression:

$$\omega_1 = \frac{k_1 P_{C_4H_8}}{1 + aP_{C_4H_8}}, \quad (9)$$

where k_1 is the rate constant for the overall conversion and a a constant which varies with temperature.

Adams and coworkers [1] investigated the kinetics of the dehydrogenation of individual n-butene isomers on the bismuth–molybdenum catalyst in a flow-type reactor. The overall conversion of each n-butene is described by a first-order equation with respect to the butenes. The rate of reaction of but-1-ene at 460°C is several times higher than those of but-2-enes, of which the *cis*-isomer is more reactive than the *trans*-isomer.

The kinetics of the oxidative dehydrogenation of mono-olefins with a carbon chain of more than four atoms is described by equations more complex than Eqn. (9).. The principal differences are the dependence of the reaction rate on the concentration of oxygen and inhibition by products. Thus, according to Adams [69], we have for pent-1-ene

$$\omega_1 = \frac{aP_{\text{hydrocarb}} P_{O_2}^{1/2}}{1 + bP_{O_2}^{1/2} + dP_{\text{diene}}}, \quad (10)$$

where a, b, and d are constants.

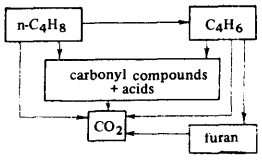
d. Effect of Reaction Products and Diluents

Dilution of butenes with water in proportions of 1 : 10 leads to increase yields of divinyl on the bismuth–molybdenum catalyst. The selectivity then changes much less [54]. Dilution with water in order to optimise the process is recommended also for other catalysts [13,25,70].

With constant concentrations of butenes and oxygen, an increase of the concentration of water from 0 to 40 mole % at 410–470°C does not have an appreciable effect on the rate of reaction on the bismuth–molybdenum catalyst [63]. The same results are obtained when the concentration of carbon dioxide is changed approximately by a factor of 20 and that of divinyl by a factor of six. The dehydrogenation of mono-olefins with a large number of carbon atoms in the chain is inhibited by the products—diolefins [see Eqn. (10)]. According to Alkhazov and coworkers [71], the addition of isobutene also has an inhibiting effect in the dehydrogenation of isopentenes.

The rate of oxidation of divinyl to carbon dioxide on bismuth molybdate is described by a first-order equation with respect to divinyl and a zero-order equation with respect to oxygen [63], amounting under conditions of oxidative dehydrogenation to approximately one-twentieth of the rate of conversion of but-1-ene into divinyl [1], and is thus comparable to the rate of conversion of butenes into carbon monoxide and carbon dioxide. Therefore the carbon dioxide obtained in oxidative dehydrogenation must be regarded as formed partly from divinyl.

The formation of side-products in oxidative dehydrogenation on the bismuth–molybdenum catalyst can be represented by a parallel-consecutive reaction scheme [62]:



Depending on the nature of the catalyst, one or other side-product predominates. Thus, on the iron–zinc catalyst [72], cracking is the principal side-reaction.

e. Isomerisation

The oxidative dehydrogenation of butenes on the bismuth–molybdenum catalyst is accompanied by a change in isomeric composition: the amount of but-1-ene decreases and that of but-2-enes either increases or changes little, while the *cis*-but-2-ene : *trans*-but-2-ene ratio decreases [73]. This is due to the different reactivities of the individual isomers, which decrease in the series but-1-ene > *cis*-but-2-ene > *trans*-but-2-ene. The rate of oxidative dehydrogenation of isopentenes decreases in the series 3-methylbut-1-ene > 2-methylbut-1-ene > 2-methylbut-2-ene [52].

The change in the isomeric composition of mono-olfeins can also be attributed to isomerisation reactions which occur on many catalysts. The rate of the isomerisation reactions depends on the nature of the catalyst. According to Roginskii and coworkers [74,75], the degree of isomerisation of but-1-ene to but-2-ene on the bismuth–molybdenum catalyst without carrier is very low, while for bismuth phosphomolybdate on a carrier the isomerisation is fairly extensive under the conditions of oxidative dehydrogenation.

Studies of the dependence of the isomerising capacity of bismuth–molybdenum catalysts on the Mo : Bi ratio have shown that the rate of isomerisation is highest on molybdenum oxide [55,56]. Isomerisation is not observed under the conditions of oxidative dehydrogenation on a catalyst comprising Group VIII oxides [76].

Table 2. Relative reactivities of olefins in their oxidation on bismuth molybdate at 460°C.

Initial olefin	Main product	Reactivity with respect to the main product referred to	
		one molecule	one hydrogen atom in the allyl position
Propene	acrolein	0.11	0.037
cis-But-2-ene	butadiene	0.26	0.043
trans-But-2-ene	butadiene	0.19	0.032
Isobutene	methacrolein	0.50	0.08
But-1-ene	butadiene	1.00	0.5
2-Methylbut-2-ene	isoprene	2.7	0.3
Pent-1-ene	pentadiene	1.38	0.69
4-Methylpent-1-ene	methylpentadiene	1.6	0.8
Pent-2-ene	pentadiene	0.43	0.086
2-Ethylhex-1-ene	C_8H_{14}	2.8	0.7
3-Methylbut-1-ene	isoprene	2.7	2.7
3-Methylpent-1-ene	methylpentadiene	1.9	1.9
3-Ethylpent-1-ene	C_7H_{12}	1.4	1.4

f. Effect of the Structure of the Hydrocarbons

The unequal reactivities of the individual isomers in oxidative dehydrogenation were pointed out above. Table 2 presents the results of Adams [69] obtained in a study of the comparative reactivities of individual C_3–C_8 hydrocarbons. The reactivities are expressed in relative units with respect to but-1-ene. The reactivity of the allyl C–H bonds increases in the series primary < secondary < tertiary.

Substitution at any vinyl carbon atom increases the reactivity of the olefin. An increase of chain length increases the reactivity of the secondary allyl hydrogen atom (but-1-ene < pent-1-ene < 4-methylpent-1-ene), but reduces the reactivity of the tertiary allyl hydrogen atom (3-methylbut-1-ene > 3-methylpent-1-ene > 3-ethylpent-1-ene).

In the oxidation on bismuth molybdate of molecules which contain less than four carbon atoms in the chain (propene, isobutene) unsaturated aldehydes are formed instead of diolefins. In the reaction of mono-olefins which are readily dehydrogenated to diolefins, carbonyl compounds are formed as side-products. Considerable amounts of mono-unsaturated aldehydes are obtained in the oxidation of mono-subtituted isobutenes.

Certain deviations from the above behaviour can be quite naturally explained. For example, cyclopentene is converted only into total-oxidation products, probably due to the exceptionally high reactivity of cyclopentadiene. Conjugated diolefins are formed from the same molecule at a much higher rate than conjugated olefinic aldehydes.

As the number of carbon atoms in the molecule increases, the degree of inhibition by reaction products (diolefins and aldehydes) also becomes more pronounced. Inhibition by products is shown mainly in a reduction of activity without a significant change in the selectivity of the catalyst.

3. THE MECHANISM OF OXIDATIVE DEHYDROGENATION

a. Similarity of the Oxidative Dehydrogenation of n-Butenes to the Oxidation of Propene to Acrolein and Oxidative Ammonolysis

There exists a profound analogy between the oxidative dehydrogenation of butenes,

$$C_4H_8 + {}^1/_2O_2 \rightleftarrows C_4H_6 + H_2O\,, \qquad (7)$$

the oxidation of propene to the unsaturated aldehyde acrolein,

$$C_3H_6 + O_2 \rightleftarrows C_3H_4O + H_2O\,, \qquad (11)$$

and oxidative ammonolysis of propene with formation of acrylonitrile:

$$C_3H_6 + 1.5O_2 + NH_3 \rightleftarrows C_3H_3N + 3\,H_2O\,. \qquad (12)$$

All the above reactions take place readily on bismuth molybdate. Over a considerable concentration range their rates on this catalyst are described by a first-order equation with respect to the initial mono-olefin and a zero-order equation with respect to oxygen[77,78]. In all the reactions the activity of the catalyst falls in the presence of a deficiency of oxygen, the temperature variation of the yields of acrolein and divinyl in reactions (7) and (11) is approximately the same, the apparent activation energies for these reactions are similar[1], and the kinetic isotope effects in the conversion of deuteriated propene into acrolein and acrylonitrile are also equal[77].

Reactions (7), (11), and (12) have common features: (a) the initial hydrocarbon molecule contains at least one C=C double bond which is not dissociated during the reaction; (b) at least one of the aliphatic C–H bonds dissociated in the reaction is allylic. Transition-metal oxides catalyse these reactions which are sometimes referred to as allyl oxidative reactions.

By the time extensive studies on the oxidative dehydrogenation of olefins began, the oxidation of propene to acrolein had been largely investigated and this plays a definite role in the elucidation of the mechanism of oxidative dehydrogenation. The similarity of the kinetics of reactions (7), (11), and (12) shows that they have a common rate-limiting stage. The first order with respect to the olefin and the zero order with respect to oxygen when $P_{O_2} > (P_{O_2})_{min}$ are evidence that the olefin must take part in the rate-limiting stage.

b. The Mechanism of the Oxidation of Propene to Acrolein

Adsorption of the reactants. According to modern data, the reaction between propene and oxygen takes place on the surface of the catalyst. Both reactants are fairly readily adsorbed on the surface of catalysts such as molybdenum or bismuth oxides. The adsorption of oxygen is at least partially accompanied by dissociation by the active surface centres L:

$$O_2 + 2L \rightleftarrows 2L-\dot{O} \qquad (13)$$

The adsorption of propene on the bismuth–molybdenum catalyst is accompanied by dissociation and probably takes place on two surface adsorption centres.

It may be supposed, for example[78], that the transition state preceding dissociation is produced on interaction between a propene molecule and two active centres in which a surface π-complex between one active catalyst centre and the double bond of the propene, on the one hand, and a hydrogen of the methyl group and a second catalyst active centre, on the other, is formed:

$$H_2C{=}CH{-}CH_3 + L_1 + L_2 \rightleftarrows \left\{\begin{matrix} H_2C{=}CH-CH_2 \cdots H \\ \vdots \qquad\qquad \vdots \\ L_1 \qquad\qquad L_2 \end{matrix}\right\} \qquad (14)$$

The transition structure produced as a result of the weakening of the C–H bond in the methyl group is capable of dissociation:

$$\left\{\begin{matrix} H_2C{=}CH-CH_2 \cdots H \\ \vdots \qquad\qquad \vdots \\ L_1 \qquad\qquad L_2 \end{matrix}\right\} \rightarrow \underbrace{H_2C \cdots CH \cdots CH_2}_{L_1} + \underset{L_2}{H} \qquad (15)$$

Experimental confirmation. The above picture is in broad outline confirmed by the experimental data obtained in the study of the chemisorption of propene and the oxidation and oxidative ammonolysis of propene labelled with radioactive carbon and deuterium. It is virtually no longer possible to investigate the adsorption of propene at 300°C due to its decomposition on the surface of the bismuth–molybdenum catalyst[79]. Sachtler and De Boer[80] studied the oxidation on the bismuth–molybdenum catalyst of [1-^{14}C]-, [2-^{14}C]-, and [3-^{14}C]-propenes to acrolein. The product was decomposed photochemically into ethylene and carbon monoxide:

$$H_2C{=}CH{-}CHO \rightarrow H_2C{=}CH_2 + CO\,. \qquad (16)$$

The results obtained suggest that the carbon atom of the aldehyde group originates with equal probability both from the methyl and methylene groups of the initial propene. The studies on the oxidation of [1-^{13}C]-propenes on a deuteriated bismuth phosphomolybdate catalyst[81] and of [1-D]-propene and [3-D]propene on bismuth molybdate[77] also led to the conclusion that both terminal carbon atoms are equivalent.

Further reactions. The surface hydrocarbon complex $L_1(CH_2 \cdots CH \cdots CH_2)$ is capable of further reactions, in particular of losing another hydrogen atom or of

combining with oxygen. The formation of acrolein can occur as a result of the following reactions, for example:

$$L_1(CH_2 \cdots CH \cdots CH_2) + L-\dot{O} \rightarrow L_1(CH_2 \cdots CH \cdots CH) + L-OH, \quad (17)$$

$$L_1(CH_2 \cdots CH \cdots CH) + L-\dot{O} \rightarrow L_1(CH_2{=}CH{-}CHO) + L, \quad (18)$$

$$L_1(CH_2{=}CH{-}CHO) \leftrightarrows CH_2{=}CH{-}CHO + L_1, \quad (19)$$

or the surface unsaturated-hydrocarbon complex passes through intermediate stages involving isomerisation to surface radicals, for example:

$$L_1(CH_2 \cdots CH \cdots CH) \rightarrow L_1-\dot{C}H-CH=\dot{C}H_2 \xrightarrow{+L-\dot{O}} CH_2{=}CH{-}CHO. \quad (20)$$

The above hypotheses concerning the possible mechanism of the conversion of the adsorbed allyl radical into acrolein are consistent with the measurements of the kinetic isotope effects in the oxidation with oxygen of propenes deuteriated at the terminal carbon atoms[77]. The observed isotope effects proved to be greater than they should have been if the oxygen atom attacked directly the terminal carbon atom of the allyl radical, since in the latter case the question whether or not the attacked carbon atom contains H or D would have been insignificant.

The rate-limiting stage. On the basis of the kinetic data and the analogy between reactions (7), (11), and (12), it is assumed that dissociative adsorption of the olefinic hydrocarbons constitutes the slowest stage in these reactions. The zero order of reactions (7), (11), and (12) with respect to oxygen means that the rate of adsorption of oxygen at $P_{O_2} > (P_{O_2})_{min}$ is sufficiently high to compensate the time required for the conversion of the oxygen of the catalyst surface.

Thus in order to catalyse the allyl oxidation reaction, the catalyst must be capable of dissociating the C–H bond in the methyl group, while protecting at the same time the double bond in the initial olefin from oxidation. If the adsorption of the latter is so strong that it results in the dissociation of the double bond, degradative oxidation products are formed: acetaldehyde, formaldehyde, carbon dioxide, and others.

c. The Mechanism of the Oxidative Ammonolysis of Propenes

As stated above, the first stages of the oxidative ammonolysis and oxidation of propene to acrolein may be regarded as identical. According to Adams[77], the mechanism becomes different after the removal of the second hydrogen atom from the adsorbed hydrocarbon radical. In the presence of ammonium the unsaturated surface radical $L-\dot{C}H-CH=CH_2$ loses yet another hydrogen atom from the same carbon atom instead of combining with oxygen [reaction (20)]:

$$L_1-\dot{C}H-CH=CH_2 \xrightarrow{+L\dot{O}} L_1-\ddot{C}-CH=CH_2. \quad (21)$$

In turn the ammonia adsorbed in the presence of oxygen also undergoes oxidative dehydrogenation:

$$L_3(NH_3) + L-\dot{O} \rightarrow L_3(NH_2) + L-OH, \quad (22)$$

etc., until the formation of chemisorbed NH and N radicals, which is followed by the addition reaction, whose product is acrylonitrile:

$$L_1-\ddot{C}-CH=CH_2 + L_3-\ddot{N} \rightarrow CH_2-CH-CN + L_1 + L_3. \quad (23)$$

According to the views of Gel'bshtein and coworkers[78], acrylonitrile is formed consecutively via an intermediate stage in which acrolein is formed:

$$L_1(CH_2{=}CH{-}CHO) + L_3(NH) \rightarrow L_1(H_2C{=}CH{-}CN) + L_3(H_2O), \quad (24)$$

with subsequent desorption:

$$L_1(H_2C{=}CH{-}CN) \rightarrow L_1 + H_2C{=}CH{-}CN. \quad (25)$$

The kinetic equation derived on the hypothesis of the consecutive formation of acrylonitrile via acrolein as an intermediate[78] is qualitatively confirmed by experimental data. The formation of degradative reaction products (acetaldehyde, formaldehyde, hydrogen cyanide, acetonitrile, carbon dioxide, and others) may take place on catalytic centres where the adsorption of propene is stronger and is accompanied by the dissociation of the double bond.

d. The Mechanism of the Oxidative Dehydrogenation of Mono-olefins

In order to be capable of oxidative dehydrogenation to a diolefin, the initial olefin molecule must contain not less than four carbon atoms. By analogy with propene, the adsorption of n-butenes can be represented in the following manner:

$$\begin{matrix} CH_2{=}CH{-}CH_2{-}CH_3 \\ (\text{or } CH_3{-}CH{=}CH{-}CH_3) \end{matrix} \nearrow \underbrace{H_2C \cdots CH \cdots CH}_{L_1}-CH_2 + \underset{L_2}{H} \quad (26)$$

The C–H bonds at the secondary allyl carbon atom are more readily dissociated than those at the primary carbon atom, and therefore the dissociative adsorption of but-1-ene is faster than that of but-2-ene. In the oxidative dehydrogenation of n-butenes the second hydrogen atom is removed from the methyl group of the adsorbed hydrocarbon molecule and not from the allyl group as in the oxidation of propene to acrolein [Eqn. (17)][77]:

$$\underbrace{H_2C \cdots CH \cdots CH}_{L_1}-CH_3 + \underset{L}{\dot{O}} \rightarrow \underbrace{H_2C \cdots CH \cdots CH}_{L_1}-\dot{C}H_2 + \underset{L}{OH}, \quad (27)$$

and further

$$\underbrace{H_2C \cdots CH \cdots CH}_{L_1}-\dot{C}H_2 \rightarrow L_1(H_2C{=}CH{-}CH{=}CH_2) \rightarrow L_1 + H_2C{=}CH{-}CH{=}CH_2. \quad (28)$$

The removal of a hydrogen atom from the methyl group probably takes place much more readily than its removal from the allyl group, i.e. the possibility of the formation of a conjugated diolefin is much greater than that of the formation of the corresponding aldehyde. Considerable amounts of aldehydes are formed only from olefins branched at the vinyl atom[69].

Apart from the formation of a diolefin or an aldehyde, there is also a possibility of the recombination of the allyl radical with a hydrogen atom initially removed from the mono-olefin molecule. In this case the initial olefin or one of its isomers (with respect to the double bond) is formed [Eqn. (26)]. However, isomerisation on catalysts such as bismuth molybdate takes place much more slowly than oxidative dehydrogenation.

As in the formation of unsaturated aldehydes and oxidative ammonolysis, the dissociative adsorption of the initial olefin must be adopted as the slowest stage in the oxidative dehydrogenation of mono-olefins to diolefins. Apart from the similarity of the kinetics of these three reactions, further evidence in favour of the above view comes also from the unequal reactivities of the individual n-butene isomers. The rate of oxidative dehydrogenation increases in the series *trans*-but-2-ene < *cis*-but-2-ene < but-1-ene, but, starting with the stage in which the adsorbed allyl radical is present, the individual n-butene isomers are no longer distinguishable [Eqn. (26)].

The rate of dissociative adsorption is determined by the stability of the C–H bond dissociated on formation of the allyl radical from the initial olefin molecule. In agreement with the energies required for the removal of the allyl hydrogen atom by radicals, the rate of oxidative dehydrogenation increases in the series primary > secondary > tertiary allyl hydrogen atoms in the mono-olefin molecule. An increase in rate in the above series is also observed in the formation of the allyl carbonium ion, in conformity with the available data[82], according to which the hydrocarbon radicals adsorbed on the surface of oxidation catalysts are positively charged.

e. Effect of the Nature of the Catalyst

At the present time differences in the catalytic activity of oxides due to their chemical nature are still little understood. The available literature data on the variation of the activity and selectivity of certain catalysts for oxidative dehydrogenation of olefins with the chemical composition were examined in section II, subsection 1. The relation between catalytic activity and catalyst composition in other oxidative reactions, in particular in the oxidation of propene to acrolein and oxidative ammonolysis, is described in Refs. 82–85, for example. Certain new results will be examined here.

Belen'kii and coworkers[86] compared the effects of the molybdenum : bismuth ratio on the catalytic activity in the oxidation of propene to acrolein and in the oxidative dehydrogenation of butenes and isopentenes. The optimum composition of the catalyst proved to be the same for all three reactions and corresponded to the atomic ratio Mo : Bi = 2. These results provide yet another confirmation of the validity of the hypotheses concerning the identity of the active centres of the catalysts in these reactions.

According to other data, the Mo : Bi atomic ratio in the most active catalysts varies between 1 and 2 and apparently depends on the method of preparation of the catalyst and the presence of other substances, in particular a carrier.

Several chemical compounds are formed in the system molybdenum–bismuth. The phase $Bi_2O_3.2MoO_3$, which corresponds to the atomic ratio Mo : Bi = 1, shows the highest activity, among the mixed oxides of molybdenum and bismuth, in the oxidation of propene to acrolein and oxidative ammonolysis to acrylonitrile[79,87,88] Bleijenberg et al.[89] did not observe the formation of the phase with the composition Mo : Bi = 1, and yet specimens with precisely this component ratio proved to be the most active in oxidative dehydrogenation[56]. The 1 : 1 atomic ratio corresponds also to the optimum composition of bismuth–tungsten catalysts[90], while in the best antimony–tin catalysts the atomic ratio is Sn : Sb = 1 : 8. The catalytic activities of various bismuth tungstates differ from one another less than those of bismuth molybdates. The most active form of the tungstate is in fact less active than that of bismuth molybdate.

There are as yet very few data concerning the nature of the active centres responsible for chemisorption and catalysis in the oxidative dehydrogenation of olefins. According to the views of Sachtler and De Boer[80], a bond between one of the carbon atoms and a surface oxygen atom forms in the dissociative adsorption of olefins on oxides. According to Trapnell[91], dissociative adsorption of hydrocarbons takes place on metal ions with an unfilled *d* shell. In the latter case two-point dissociative adsorption of the olefins can occur, for example at a doublet consisting of molybdenum and bismuth atoms. This hypothesis appears justified if it is remembered that catalysts with the atomic ratio Mo : Bi = 1 are active. The centre responsible for the dissociation of the double bond and degradative oxidation can have the same composition (a molybdenum or bismuth atom) but differs by the higher energy of the donor–acceptor interaction with the olefin molecule.

Stroeva and coworkers[92] investigated the relation between the composition of bismuth–molybdenum, cobalt–molybdenum, and antimony–tin catalysts and their electrical properties, on the one hand, and their activity in the oxidative oxidation of the C–H bond, on the other. If follows from the results that, for all three binary systems, the physicochemical nature of the promoting effect of the second oxide is different. In the system MoO_3–Bi_2O_3 the promoting effect is accompanied by the formation of a chemical compound with the atomic ratio Mo : Bi = 1. According to the above authors' views, the active centre is a doublet consisting of molybdenum and bismuth atoms. In the system MoO_3–Co_3O_4 the promoting effect of cobalt is associated with an increase of the specific surface: cobalt molybdate has no catalytic properties and behaves as a carrier. The active centre can consist of two molybdenum atoms. In the system Sb_2O_4–SnO_2 the possible role of tin consists in an increase of the concentration of antimony cations in the most oxidised state and also in an increase of the internal surface of the catalyst. The active centre can consist of two antimony atoms.

Batist et al.[56] suggest that the formation of the intermediate allyl structure on the surface of the bismuth–molybdenum catalyst occurs at the vacant anionic site which is produced as a result of the removal from the surface of the hydroxyls formed in selective oxidation reactions [reactions (17), (21), and others]:

$$2\,OH^- \rightarrow H_2O + \square_d + O^{-2}, \qquad (29)$$

where $\square_d$ is a vacant anionic site. The adsorbed allyl radical is bound to a molybdenum ion via a π-bond. According to Batist et al.[56], the promoting effect of bismuth is associated with an increase in the susceptibility of the catalyst to dehydroxylation and reduction.

In a number of studies attempts were made to establish correlations between the catalytic and other physicochemical properties of the catalysts associated with the mobility of their ions and electrons. Sachtler and De Boer[80] compared the activities, selectivities, and capacities for reduction of the catalysts, and Gel'bshtein, Margolis, and coworkers[78,87,80] compared the catalytic properties and electron work functions.

According to the data of Kolchin et al.[87], the maximum electron work function of mixed bismuth and molybdenum oxides is observed at an atomic ratio of 6 : 4, i.e. corresponds approximately to the highest activity of the catalyst. However, according to other data[78], there is no parallel variation of the electron work function and catalytic activity of the oxidation of propene to acrolein and oxidative ammonolysis. Kolchin et al.[90] arrived at the same conclusion in a similar study of bismuth–tungsten catalysts.

According to the data of Sachtler and De Boer[80], the conversion of propene and the selectivity with respect to acrolein are roughly correlated with the susceptibility of the catalysts to reduction. The susceptibility to reduction (Table 3) was defined as the reciprocal of the absolute temperature at which a rate of reduction of 7.4×10^{-3} moles of hydrogen per gramme of catalyst per hour ($T_{7.4}$) is attained. Under the conditions of the experiments, the principal oxidation products were acrolein, carbon monoxide, and carbon dioxide. With increase in the susceptibility of the catalysts to reduction, the overall degree of conversion of

propene increases and the selectivity with respect to acrolein falls.

The existence of a relation between catalytic activity and the susceptibility of the catalyst to reduction may be attributed to the fact that the susceptibility of the oxide to reduction reflects the mobility of its constituent oxygen, which participates in the catalytic steps in the oxidation of propene. Low mobility is the reason for low activity of the catalyst. On the other hand, if the mobility of oxygen is too high, the formation of the products of the total oxidation of the hydrocarbon is facilitated: for selective oxidation of the C–H bond, the mobility of oxygen should have a definite optimum value.

Table 3. Dependence of the degree of oxidation of propene on the susceptibility of the catalyst to reduction.

Metal of the oxide	Susceptibility to reduction $10^3/T_{7.4}$, deg^{-1}	Yields of propene oxidation products at 520°C, %		
		overall conversion	acrolein	selectivity with respect to acrolein
Mo deposited at 98°C	1.17	2	2	70
Mo deposited at 20°C	1.29	16	9	59
Mo–Bi	1.51	66	55	84
W–Bi	1.52	55	32	58
Mo–Co	1.54	28	9	32
Sn–Sb–Mo	1.70	29	13	46
Mo–Cu	1.73	55	28	50
Mn	2.02	~100	~0	~0

Sachtler and De Boer[80] obtained a kinetic equation based on the theory of absolute reaction rates with the following main assumptions: (a) carbon and oxygen compete in the adsorption process; (b) the rate of adsorption of oxygen greatly exceeds the rate of its consumption by reaction (11); (c) carbon dioxide and carbon monoxide are formed from acrolein. This kinetic equation is qualitatively consistent with the experimental observation that the activity and the selectivity vary with the susceptibility of the catalyst to reduction.

III. OXIDATIVE DEHYDROGENATION OF SATURATED HYDROCARBONS

In contrast to mono-olefins, the oxidation of saturated hydrocarbons with oxygen gives low yields of dehydrogenation products. Therefore much attention has been given to oxidative dehydrogenation under the action of reagents more effective than oxygen, in the first place iodine. When iodine was applied, fairly high yields were obtained and fairly high selectivity with respect to the dehydrogenation products was achieved.

We shall examine initially oxidative dehydrogenation with oxygen.

1. DEHYDROGENATION IN THE PRESENCE OF OXYGEN

The dehydrogenation of saturated hydrocarbons in the presence of oxygen, like that of olefins, in an oxidative, and not a dehydrogenation, reaction accompanied by subsequent oxidation of hydrogen. Depending on the experimental conditions, different proportions of oxygen-containing compounds and cracking products are formed together with the dehydrogenation products. Oxidation reactions are of the radical-chain type and take place mainly in the bulk-phase of the reaction system. In contrast to olefins, solid catalysts which have an effective selective dehydrogenating effect in the oxidative dehydrogenation of saturated hydrocarbons are unknown. The catalysts used were capable only of a comparatively slight increase in the yield of the dehydrogenation products.

a. Low- and High-Temperature Oxidation of Hydrocarbons

Most hydrocarbons are oxidised at about 300°C and below, and in many respects the mechanism of this oxidation is radically different from the mechanism of oxidation at higher temperatures. The products of the low-temperature oxidation of hydrocarbons are mainly aldehydes, ketones, alcohols, carbon monoxide, and carbon dioxide; in the high-temperature oxidation the principal reactions are cracking and dehydrogenation. Under the conditions usually employed, the transition from the low- to the high-temperature mechanism usually occurs in the range 350–500°C. This range depends relatively little on the individual hydrocarbon, so that the oxidations of many saturated hydrocarbons probably occur by similar mechanisms. In the temperature range for the transition from one mechanism to the other the temperature coefficient of the rate of oxidation is anomalous: with increase in temperature, the rate of reaction passes through a minimum in the transition region.

There are numerous data[93–107] concerning the amounts of unsaturated hydrocarbons formed as a function of the experimental conditions. Some of these are quoted in Table 4. With increase in the butane oxidation temperature from 300° to 700°C, the yield of oxygen-containing compounds decreases, that of ethylene and propene increases, and that of butenes passes through a maximum[107]. The extent of formation of oxygen-containing organic products also falls markedly as the oxygen : carbon ratio decreases. For example, with the ratio oxygen : butane ≤ 0.1, at 500°C virtually the only oxygen-containing compound is water[103]. In the homogeneous oxidation of saturated hydrocarbons small amounts of diolefins sometimes form in addition to mono-olefins[104] and in the high-temperature oxidation of ethane small amounts of acetylene are produced[98].

The yields of diolefins obtained were not limited by the equilibrium: the equilibrium yields of diolefins in the oxidation of saturated hydrocarbon by oxygen at about 500°C, at atmospheric pressure, and with the equivalent composition of the initial mixture can reach 100%.[108]

b. The Mechanism of the High-Temperature Oxidation

The mechanism of the formation of olefins under the conditions of the homogeneous oxidation of saturated hydrocarbons has been the subject of discussion for a long time. The mechanism proposed by Shtern[95] for the oxidation of propane may be regarded as one of the most successful mechanisms for the oxidation of saturated hydrocarbons available at present. According to this mechanism, propene forms as a result of the removal by an oxygen molecule of a hydrogen atom from the propane and the subsequent breakdown of the resulting propyl radical into propene and a hydrogen atom:

$$C_3H_8 + O_2 \rightarrow \text{iso-}\dot{C}_3H_7 + H\dot{O}_2, \qquad (30)$$

$$\text{iso-}\dot{C}_3H_7 \rightarrow C_3H_6 + \dot{H}. \quad (31)$$

Nevertheless this reaction path appears unlikely because of the high activation energy (about 40 kcal mole^{-1}) of stage (31). Therefore Semenov [109] suggested the following mechanism for the conversion of propane into propene:

$$C_3H_8 + O_2 \rightarrow \text{iso-}C_3H_7 + H\dot{O}_2, \quad (32)$$

$$\text{iso-}\dot{C}_3H_7 + O_2 \rightarrow CH_3{-}\underset{\dot{O}{-}\dot{O}}{CH}{-}CH_3. \quad (33)$$

After isomerisation the peroxy-radical formed breaks down with formation of propene:

$$CH_3{-}\underset{\dot{O}{-}\dot{O}}{CH}{-}CH_3 \rightarrow CH_3{-}\underset{\dot{O}{-}OH}{CH}{-}\dot{C}H_2, \quad (34)$$

$$CH_3{-}\underset{\dot{O}{-}OH}{CH}{-}\dot{C}H_2 \rightarrow C_3H_6 + H\dot{O}_2. \quad (35)$$

However this mechanism too met with objections [95], since it leads to a no less serious inconsistency with experiment. In particular the ratio of the rates of formation of organic products with and without oxygen should have been much greater than is found experimentally [95].

Table 4. Formation of olefins in the oxidation of certain saturated hydrocarbons.

Initial hydrocarbon	Moles of oxygen per mole of hydrocarbon in the starting material	Temperature, °C	Pressure, atm	Dehydrogenation to mono-olefins, %: with respect to starting material	Dehydrogenation to mono-olefins, %: with respect to product	References
Ethane	0.3	680	1	50	62	101
Propane	0.23	700	1	15	25	101
Propane	0.17	540	1	16	56	102
Propane	0.5	465	0.4	20	49	95
Propane	1	350	0.4	13	25	95
n-Butane	0.1	500	0.55	7	35	103
n-Pentane	1	500	1	10	25	104
Isopentane	0.5	400	1	9	30	105
Cyclohexane	2.7	400	1	15*		106

* Yield of cyclohexene

The majority of present day investigators assume that the second stage of the reaction involves the removal by an oxygen molecule of a hydrogen atom from the alkyl radical [103-105,110-112]:

$$\dot{C}_nH_{2n+1} + O_2 \rightarrow C_nH_{2n} + H\dot{O}_2. \quad (36)$$

Appleby and coworkers [103] obtained the following equation for the reaction of n-butane at low oxygen : butane ratios:

$$-\frac{d[C_4H_{10}]}{d\tau} = k[C_4H_{10}]^{3/2}[O_2]^{1/2}. \quad (37)$$

The kinetic data were obtained by a flow method at 485–525°C (τ is the contact time): Eqn. (37) was derived by the stationary-state method using the following mechanism:

$$C_4H_{10} + O_2 \rightarrow C_4H_9 + HO_2, \quad (38)$$

$$C_4H_9 + O_2 \rightarrow C_4H_8 + HO_2, \quad (39)$$

$$HO_2 + C_4H_{10} \rightarrow H_2O_2 + C_4H_9, \quad (40)$$

$$2HO_2 \rightarrow H_2O_2 + O_2, \quad (41)$$

$$H_2O_2 \xrightarrow{\text{wall}} H_2O + 1/2\,O_2, \quad (42)$$

$$2HO_2 \xrightarrow{\text{wall}} H_2O + 1\,1/2\,O_2, \quad (43)$$

$$C_4H_9 \rightarrow CH_3 + C_3H_6, \quad (44)$$

$$CH_3 + C_4H_{10} \rightarrow CH_4 + C_4H_9, \quad (45)$$

$$C_4H_9 \rightarrow C_2H_5 + C_2H_4, \quad (46)$$

$$C_2H_5 + C_4H_{10} \rightarrow C_2H_6 + C_4H_9. \quad (47)$$

c. Effect of the Solid Surface

Eqns. (38)–(47) show that the above mechanism of oxidative dehydrogenation and cracking presupposes chain termination on the walls. In actual fact, however, in hydrocarbon oxidation reactions both chain initiation and chain termination probably occur on the walls of the reactor. The available experimental literature data on the effect of the wall on the reaction of saturated hydrocarbons in the presence of oxygen are extremely few and non-systematic. However, it is possible to arrive at the reliable conclusion, on their basis, that the surface of the wall does indeed influence the reaction and that, depending on the experimental conditions and the nature of the wall, the latter can both slow down and accelerate the reaction. The initiating effect of the surface can be associated, for example, with the fact that it facilitates the removal of a hydrogen atom from the hydrocarbon molecule as a result of the chemisorption of oxygen:

$$L - \dot{O}_2 + C_4H_{10} \rightarrow L{-}O_2H + \dot{C}_4H_9. \quad (48)$$

$$L - \dot{O}_2 + \dot{C}_4H_9 \rightarrow L - O_2H + C_4H_8, \quad (49)$$

The possible mechanism of the further conversion of the mono-olefin into the diolefin was examined in section II, subsection 3d.

Martin and Niclause [113,114] investigated the effect of the reactor walls on the pyrolysis of propane and isopentane in the presence of added oxygen (up to 2%). The experiments were performed in a static reactor at initial hydrocarbon pressures of 25–50 mmHg at 480–550°C. The pyrolysis of propane takes place with formation of the following main products: propene, ethylene, methane, and hydrogen. In the pyrolysis of isopentane cracking products are mainly formed. When the surface : volume ratio ($S:V$) for the reactor is increased, the rate of reaction falls, which suggests that the walls of the Pyrex reactor have an inhibiting effect. The pyrolysis was accelerated by washing the reactor with the chromic acid mixture and by preliminary treatment with steam but was retarded when the walls were covered with potassium chloride or lead oxide (PbO).

Selwitz and Stanmyer [105] compared the conversion of isopentane into isopentenes at 400°C in reactors made of quartz, stainless steel, and quartz covered by a thin layer of silver. The smallest yield of isopentene was observed in the reactor whose walls had been covered by a layer of silver, and, what is more, the latter was markedly corroded during the reaction.

According to the data of Sultanova and Nagiev [115], quartz packing somewhat accelerates the dehydrogenation of diethylbenzenes to divinylbenzenes in the presence of hydrogen peroxide, which is decomposed under the conditions of the reaction with formation of oxygen. The favourable effect of the quartz surface on the dehydrogenation is also stated in a patent [116], where it is recommended that n-butene be brought into contact with alternating layers of activated charcoal and quartz. Although only about 8% of the hydrocarbon is then converted into n-butenes, fairly high selectivity (64%) is attained.

Various investigators attempted to increase the yields of the products of oxidative dehydrogenation by using other solid catalysts. Vanadium oxide "or its mixtures with oxides of tin, cobalt, chromium, manganese, uranium, tungsten, lead, bismuth, or zinc" have been suggested as catalysts in certain patents [117,118]. Under optimum conditions (temperature 400°C, n-butane : O_2 : diluent = 1 : 1 : 9) about 10% of butenes and only 1.9% of divinyl is obtained. However, the selectivity with respect to olefins is about 85%. Some patents [119,120] recommend calcium and nickel phosphates, on which yields of 6% of divinyl and 2% of butenes were attained. Ferric, manganic, or germanium oxides and calcium or lithium chlorides have been recommended as catalysts for the oxidative dehydrogenation of saturated hydrocarbons in the presence of oxygen [121].

The authors of some patents [122,123] assert that 17% of the initial n-butane is converted into divinyl in the course of 100 min on a fluidised bed of sodium phosphomolybdate with discontinuous contact. The formation of such large amounts of diolefins is probably related less to the nature of the catalyst than to reactor design or other factors which influence the process.

It follows from the data examined that in most cases the yields of olefins obtained on solid catalysts are close to those in an empty reactor (Table 4), but the selectivity in the presence of a solid catalyst is much higher. This suggests that the role of the solid catalyst may consist in the suppression of side-reactions. This may apply primarily to cracking reactions.

d. Effect of Radical-Forming Additives

The oxidative dehydrogenation of saturated paraffins, like that of olefins, can be greatly accelerated under the influence of small amounts of certain additives, which readily give rise to free radicals. Thus, on addition of iodine to a reaction mixture containing a saturated hydrocarbon and oxygen, the yields of dehydrogenation products increase sharply [108,124-126]. Apart from iodine, oxidative dehydrogenation by oxygen is activated also by other halogens or substances which decompose with formation of halogens: hydrogen and ammonium halides [127] and alkyl halides [128]; or the reaction can be activated by passing the reaction mixture through fused halides, for example lithium, lead, cadmium, etc. iodides [129-131].

The addition of ozone at temperatures in excess of 400°C also accelerates the yields of saturated hydrocarbon dehydrogenation products [105]; on the other hand, at lower temperatures ozone retards the dehydrogenation. Added butenes also have an inhibiting effect on the dehydrogenation of butane [76,103]. The oxidative dehydrogenation of saturated hydrocarbons in the presence of oxygen and small amounts of radical-generating substances will be examined in detail in subsection 3.

2. DEHYDROGENATION IN THE PRESENCE OF IODINE

The method of oxidative dehydrogenation with iodine was proposed in a number of patents, mainly in 1958–1959. [30,132]

a. Dehydrogenation Without an Acceptor and Oxygen

Raley and coworkers [133] investigated the reaction of iodine with saturated hydrocarbons ranging from C_2 to C_5, cyclopentane, and methylcyclopentane at temperatures between 495° and 685°C, iodine : hydrocarbon molar ratios between 0.4 and 4.6, and various contact times. Under these conditions the principal reactions involved dehydrogenation:

$$C_nH_{2n+2} + 2I_2 \rightleftarrows C_nH_{2n-2} + 4HI, \quad (3)$$

$$C_nH_{2n+2} + I_2 \rightleftarrows C_nH_{2n} + 2HI, \quad (50)$$

and

$$C_nH_{2n} + I_2 \rightleftarrows C_nH_{2n-2} + 2HI. \quad (51)$$

Hydrogen iodide is formed in an amount which is almost equivalent to the iodine which has reacted. Organic iodides and polymers were observed as side-products.

The equilibrium yields of propane and isobutane dehydrogenation products in the reaction with iodine are quoted by Benson and coworkers [134,135] and those for n-butane by Kozorezov [136] and Basner et al. [137]. When the temperature is raised above approximately 450°C, the diolefins : mono-olefins ratio increases appreciably, but below 600°C mono-olefins predominate. As the contact time is increased until equilibrium is attained, the yields of dehydrogenation products also increase, while the diolefins to mono-olefins ratio falls (Table 5). [133]

Table 5. Effect of the duration of contact at 550°C.

Reactants	Iodine : n-butane = 1.3			Iodine : isopentane = 1.6		
Duration of contact, s	0.7	1.3	equilibrium	1.3	2.6	equilibrium
Degree of conversion of C_nH_{2n+2}, %	51	76	82	69	90	92
C_nH_{2n-2}/C_nH_{2n}	0.38	0.28	0.24	0.42	0.28	0.27
Yield of C_nH_{2n-2}, %	14	16	16	19	18	20

If the initial saturated hydrocarbon contains six and more carbon atoms in its chain, aromatic hydrocarbons are formed together with olefins [138-140]:

$$C_nH_{2n-2} + I_2 \rightleftarrows C_nH_{2n-4} + 2HI \quad (52)$$

and

$$C_nH_{2n-4} + I_2 \rightleftarrows C_nH_{2n-6} + 2HI \quad (53)$$

(for $n \geqslant 6$). With increase of the iodine : hexane ratio from 0 to 2 at 500°C the degree of conversion into dehydrocyclisation products increases [138]. At low iodine : hexane ratios (up to 0.1–0.15) the dominant products are hydrocarbons with five or less carbon atoms. The same dehydrogenation products as in the reaction of saturated hydrocarbons with iodine (mono- and di-olefins, aromatic compounds, and others) can be obtained when iodine is replaced by bromine [141].

b. Kinetics of the Dehydrogenation Reaction

Teranishi and Benson [142] investigated the kinetics of the dehydrogenation of isobutane with iodine in a static reactor at 250–310°C. No induction period was observed. The reaction kinetics are described by the equation

$$\frac{[\text{iso-}C_4H_{10}](1-B)}{2S} = a_1 + a_2\frac{[HI]}{[I_2]^{1/2}} + b\frac{[HI]}{[I_2]}, \quad (54)$$

where $B = [\text{iso-}C_4H_8][HI]^2/K[\text{iso-}C_4H_{10}][I_2]$ and K is the equilibrium constant for the overall reaction

$$\text{iso-}C_4H_{10} + I_2 \rightleftarrows \text{iso-}C_4H_8 + 2HI, \quad (55)$$

$S = -d[I_2]^{1/2}/dt$ and a_1, a_2, and b are constants. An equation similar to Eqn. (54) also describes the kinetics of the dehydrogenation of propane with iodine [143].

c. The Mechanism of the Dehydrogenation Reaction

The dissociation energy of the iodine molecule is low (36 kcal mole^{-1}) and at high temperatures iodine breaks down partially into atoms:

$$I_2 + M \rightleftarrows 2\dot{I} + M. \quad (56)$$

In the reaction with a saturated hydrocarbon molecule the iodine atom abstracts a hydrogen atom, yielding an alkyl radical:

$$n\text{-}C_4H_{10} + \dot{I} \rightleftarrows HI + n\text{-}\dot{C}_4H_9. \quad (57)$$

Depending on the conditions, the alkyl radical undergoes different further reactions. At temperatures up to 500°C and above cracking occurs predominantly in the presence of low iodine concentrations:

$$n\text{-}\dot{C}_4H_9 \rightarrow \dot{C}_2H_5 + C_2H_4, \quad (58)$$

while at higher iodine concentrations butenes are mainly formed:

$$\dot{C}_4H_9 + \dot{I} \rightarrow C_4H_8 + HI. \quad (59)$$

At temperatures much lower than 500°C the amount of dissociated iodine is small and butenes can be produced via the intermediate formation of iodides, for example [133]:

$$\dot{C}_4H_9 + I_2 \rightarrow C_4H_9I + \dot{I}, \quad (60)$$

$$C_4H_9I + \dot{I} \rightarrow \dot{C}_4H_8I + HI, \quad (61)$$

$$\dot{C}_4H_8I \rightleftarrows C_4H_8 + \dot{I}. \quad (62)$$

The kinetic data of Benson and coworkers [142,143] are consistent with the hypothesis that the slowest stage of the reaction is the removal of a hydrogen atom from the saturated hydrocarbon molecule:

$$\dot{I} + RH \rightleftarrows \dot{R} + HI. \quad (63)$$

Eqn. (54), which describes satisfactorily the experimental data for the dehydrogenation of propane and isobutane by iodine, was obtained on the assumption of a steady state for the alkyl radical and alkyl iodide.

According to Raley et al. [133], the conversion of mono-olefins into diolefins is similar to the conversion of saturated hydrocarbons into mono-olefins. The rate of the mono-olefins → diolefins reaction is much higher than that of the saturated hydrocarbons → mono-olefins reaction and the equilibrium yields of diolefins at temperatures of the order of 500°C are lower than those of mono-olefins. This can explain the experimental finding that the diolefins to mono-olefins ratio decreases as the system approaches equilibrium (Table 5).

According to the data of Back and Cvetanovich [144] the conversion of but-1-ene into divinyl at 65°C in the presence of iodine can occur with intermediate formation of iodides and iodine-containing radicals:

$$\dot{I} + C_4H_8 \rightarrow C_4H_8I. \quad (64)$$

C_4H_8I is a radical or π-complex from which a hydrogen atom is removed:

$$C_4H_8I + \dot{I} \rightarrow C_4H_7I + HI. \quad (65)$$

Then follows the rapid stage

$$C_4H_7I + \dot{I} \rightarrow \dot{C}_4H_7I_2, \quad (66)$$

and subsequently

$$\dot{C}_4H_7I_2 + \dot{I} \rightarrow C_4H_6I_2 + HI, \quad (67)$$

$$C_4H_6I_2 \rightarrow C_4H_6 + I_2. \quad (68)$$

Thus according to modern theories, the high-temperature conversion of saturated hydrocarbons into diolefins in the presence of iodine involves a chain mechanism with intermediate formation of hydrocarbon radicals and mono-olefins. The rate of conversion of mono-olefins into di-olefins is much higher than that of saturated hydrocarbons into mono-olefins. At lower temperatures there is also the possibility of the intermediate formation of iodides and iodide radicals.

d. Dehydrogenation in the Presence of Acceptors and Solid Catalysts

The iodine which has reacted can be regenerated by means of solid acceptors in accordance with Eqns. (5) and (6). If an acceptor is introduced into the reaction zone, then, as a result of the adsorption of hydrogen iodide, the equilibria of reactions (3) and (51) are displaced towards the formation of diolefins which leads to an appreciable increase in their yields.

The dehydrogenation of n-butane by iodine in a flow reactor at 520–524°C using butane diluted with nitrogen in the proportions butane : nitrogen = 1, in the presence of manganese dioxide as an acceptor, was investigated by Kolobikhin and coworkers [145]. Apart from divinyl and n-butene, cracking products, organoiodine compounds, and resinous and solid products were observed. Hydrogen and isomerisation products do not form in appreciable amounts. As the iodine : butane ratio is increased from zero to 1.43, the yields of divinyl likewise increase and those of butenes and cracking products pass through a maximum. On further dilution with nitrogen from 1 : 1 to 1 : 4, the yields of divinyl change slightly but those of butenes decrease appreciably [146].

The productivity of apparatus for oxidative dehydrogenation with iodine can be enhanced by using reactors with a fluidised acceptor bed [147]. Here the spent acceptor is continuously removed from the reaction zone. On raising the temperature from 480° to 580°C in apparatus with a fluidised acceptor bed the degree of conversion of n-butane increased and the maximum selectivity with respect to dehydrogenation products was observed at 550°C. An increase of the contact time above the optimum value favours cracking and complete oxidation of hydrocarbons by the oxygen of the acceptor.

The dehydrogenation of isopentane in the presence of iodine and manganese oxides shows approximately the same features as the dehydrogenation of n-butane [148].

An increase in the yields of the dehydrogenation products in the presence of iodine can also be achieved by the introduction of solid catalysts which do not behave as acceptors of hydrogen iodide (platinum, palladium, ferrous iodide, cupric iodide, and others) [138,149], whose activity is attributed to their capacity to catalyse the decomposition of hydrogen iodide:

$$HI \rightarrow H_2 + I_2, \quad (69)$$

e. Dehydrogenation in the Presence of Oxygen

Introduction of oxygen into a reaction system containing a saturated hydrocarbon and iodine leads to an appreciable

increase of the yield of diolefins [133,145,148,150,151]. Oxygen-containing organic products are then formed only in small amounts. If oxygen is present in the system, a smaller amount of iodine is required for the attainment of the same yield of divinyl.

The accelerating effect of oxygen on the formation of diolefins is associated primarily with the oxidation of hydrogen iodide by reaction (4), which leads to the regeneration of iodine. There are reasons to believe that the role of oxygen is not restricted to the oxidation of hydrogen iodide. This problem will be discussed in greater detail in subsection 3.

f. Chemical Composition and the Porous Structure of the Acceptor

Apart from manganese oxides, mixtures of iron oxide with potassium iodide [152] and of manganese and calcium oxides [153], nickel oxide [154], copper [155], etc. have been proposed as hydrogen iodide acceptors. The oxides, hydroxides, or carbonates of various metals can also serve as acceptors of hydrogen bromide if bromine is used instead of iodine in the oxidative dehydrogenation [156].

Tyuryaev and coworkers [157,158] made a comparative study of various acceptors. Among the acceptors tested—the oxides of calcium, barium, strontium, zinc, nickel, iron, cobalt, copper, and manganese—the highest yields of isoprene were obtained on barium, calcium, and manganese oxides. Among metal carbonates, the most effective absorbers of hydrogen iodide are sodium and barium carbonates. The manganese oxide giving the highest yield of isoprene is Mn_3O_4. However, on repeated use, all the oxides tested (Mn_2O_3, MnO_2, and Mn_3O_4) exhibit approximately the same properties in the dehydrogenation processes [148]. This is because the reaction of hydrogen iodide with the oxides results, regardless of the composition of the latter, in the formation of manganese(II) iodide, which yields Mn_3O_4 in the regeneration process under the influence of oxygen:

$$3\,MnI_2 + 2O_2 \rightarrow Mn_3O_4 + 3\,I_2. \qquad (70)$$

Calcium oxide is a more active acceptor than calcium carbonate [159]. When the experiments are repeated on any of the above acceptors, the composition of the latter changes to the steady-state composition corresponding to the ratio $CaO : CaCO_3 = 1 : 3-4$ (by weight).

There is a simple relation between the nature of the oxide and the acceptor capacity: the yields of isoprene vary in parallel with the decrease of the free energy of the reaction in which the acceptor combines with hydrogen iodide [157].

Metal oxide acceptors can be prepared by impregnating porous carriers [150,151,153,160]. Kolobikhin and coworkers [160] compared the following materials as carriers for manganese oxides: KSM and steam-treated silica gels, aluminosilicate, and γ-alumina. The yields of divinyl and the selectivity fall with decrease in pore size and with increase of the specific surface, and they depend on the nature of the carrier. Under the experimental conditions [160] the test specimens were regenerated at different rates and the degree of regeneration was not the same. Therefore the reduction of divinyl yields observed on decrease of acceptor pore size can be the result of the overall effect of two factors: incomplete regeneration of the acceptor and decrease of the rate of absorption of hydrogen iodide by the acceptor. Both phenomena may be associated with an increase of inhibition of the process by factors dependent on internal diffusion.

The present author [161] compared the effects of two acceptor specimens: one porous and one with low porosity. The first consisted of calcium oxide deposited on KSK silica gel and the second was obtained by mixing calcium oxide with a small amount of kaolin (Table 6). Whereas high yields of divinyl were obtained on both specimens, very little isoprene was produced in the presence of the porous specimen. It is difficult to explain by internal-diffusion-dependent factors such striking difference in the behaviour of n-butane and isopentane on changing the porous structure of the catalyst, in view of the slight difference in the dimensions of the n-butane and isopentane molecules compared with the dimensions of the pores of the coarsely porous silica gel. We shall return to this problem later.

Table 6. Effect of the porosity of the acceptor on the oxidative dehydrogenation of saturated hydrocarbons.

Catalyst	Specific surface, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Hydrocarbon	Yields under optimum conditions, %	
				of diolefins*	of monoolefins*
CaO with added kaolin	0.7	0.05	n-butane	69	<1
			isopentane	41	<1
CaO on KSK silica gel	100	0.4	n-butane	67	8
			isopentane	1	26

* With the same number of carbon atoms as the initial saturated hydrocarbon.

3. DEHYDROGENATION IN THE PRESENCE OF OXYGEN AND SMALL AMOUNTS OF IODINE

a. Some Experimental Data

The effect of oxygen on the oxidative dehydrogenation of saturated hydrocarbons in the presence of nearly equivalent amounts of iodine was examined in subsection 2e. Here we shall examine the features of the process in the presence of small amounts of iodine, sufficient only for the initiation or inhibition of reaction. As will be seen below, under these conditions the dehydrogenation reaction has certain specific features.

The variation of the degree of conversion of n-butane with temperature, duration of contact, and the concentrations of iodine and oxygen was investigated by Kuz'michev et al. [108]. The maximum yields of divinyl were obtained at 530°C. At higher temperatures the yields of cracking and combustion products increase and there is more coke formation. In the absence of iodine the main reaction is oxidative cracking†. On addition of small amounts of iodine, the cracking and overall conversion curves pass through a minimum. A sharp increase in the yield of divinyl is observed on raising the iodine : n-butane ratio to 0.05–0.06. On further increase of the concentration of iodine, the change in the yield of divinyl is less pronounced, while the yield of butenes continuously increases. The addition of small amounts of oxygen accelerates mainly the cracking reaction. A considerable increase in the yield of divinyl is observed only for oxygen : n-butane ratios in excess of 0.5.

† Cracking is the main reaction also at much lower temperatures [108].

Adel'son and Nikonov [162,163] did not observe a minimum on the curve relating the degree of conversion to the concentration of iodine in the dehydrogenation of isopentane. The present author investigated [164] the comparative effects of the addition of iodine and hydrogen iodide and bromide on the reaction of n-butane in the presence of oxygen. It was shown that, with the same amount of added halogen, the yields of divinyl decrease in the series HI > I_2 > HBr.

b. The Possible Mechanism of Dehydrogenation in the Presence of Added Halogen

When the hydrocarbon, iodine, and oxygen are present simultaneously, the reaction of the hydrocarbon with iodine takes place more readily than with oxygen. Therefore, according to the existing hypotheses [125,133,165], oxidative dehydrogenation in the presence of both oxygen and iodine has the same mechanism as without oxygen (see subsection 2c), the role of oxygen consisting in regeneration by reaction (4). However, it is quite likely that its role is not limited to interaction with hydrogen iodide but that oxygen participates actively in the intermediate stages of the formation of dehydrogenation products. Then in the presence of equivalent proportions of oxygen and the saturated hydrocarbon small amounts of added iodine can be regarded as reaction initiators. Iodine is known to initiate certain hydrocarbon oxidation reactions at high temperatures [95].

With equivalent proportions of the hydrocarbon and oxygen in the absence of iodine, the main reaction is cracking. The minimum in the degree of conversion at iodine : n-butane ratios between 0.01 and 0.02 can be accounted for by the dual function of iodine: inhibition of the cracking reaction and participation in oxidative dehydrogenation. If the role of iodine was restricted to the initiation of the reaction between the saturated hydrocarbon and oxygen, the addition of iodine would not significantly alter the relative yields of various products but the overall conversion would then certainly be increased. If the role of iodine consisted only in the inhibition of cracking, then, after a decrease in the rate of the latter to a minimum, further addition would not increase the yield of dehydrogenation products. Probably in oxidative cracking unstable intermediate compounds are formed, which are the first to be attacked by the added iodine. On increasing the amount of iodine, the latter acts in addition as a reactant in oxidative dehydrogenation.

At a low iodine concentration the variation of the yield of divinyl with the concentration of oxygen consists of two steps: a significant increase in the yield of divinyl is observed at oxygen : n-butane ratios ranging approximately from zero to 0.1 and from 0.55 to 0.8. It is difficult to explain the second rise in the divinyl yield curve (at high oxygen concentrations) from the standpoint that the role of oxygen is limited to oxidation of the hydrogen iodide produced, since oxygen is in considerable excess relative to the hydrogen iodide present. There are also other grounds to believe that the role of oxygen is not restricted to oxidation of hydrogen iodide. Thus, according to the data obtained by the present author, the introduction of oxygen favours the decomposition of iodine-containing hydrocarbon derivatives into unsaturated compounds. Therefore, apart from the cracking reaction, the role of oxygen consists also in participation in dehydrogenation by oxidising hydrogen iodide and probably in interaction with hydrocarbon molecules or intermediate iodine-containing species.

To investigate the kinetics of dehydrogenation in the presence of added iodine, the present author [166] used a reactor with internal stirring. The order of the divinyl formation reaction and of the overall reaction proved to be 0.4–0.55. This suggests that a hydrocarbon molecule or a hydrocarbon radical participates in the slowest stage and therefore the rate-limiting stage is not the dissociation of iodine [reaction (56)] or oxidation of hydrogen iodide [reaction (4)]. It was also shown that the oxidation of hydrogen iodide is faster than oxidative dehydrogenation [164].

Since reaction (4) is fast, when added iodine is replaced by hydrogen iodide, the reaction system contains almost the same quantity of molecular iodine as when the latter is added directly into the reactor. However, in the presence of hydrogen iodide there is the additional possibility [apart from the dissociation of iodine molecules by reaction (56)] that iodine atoms and also HO_2 radicals will enter the system:

$$HI + O_2 \rightarrow \dot{I} + H\dot{O}_2. \qquad (71)$$

Therefore the yields of divinyl in the presence of hydrogen iodide are higher than with the same amounts of iodine. When iodine is replaced by bromine, the rate of dehydrogenation decreases appreciably because of the higher dissociation energy of the Br–Br bond (46 kcal $mole^{-1}$) compared with the dissociation energy of the I–I bond (36 kcal $mole^{-1}$).

c. Effect of a Solid Surface on Dehydrogenation in the Presence of Oxygen and Added Iodine

When the walls of the quartz reactor are lined with sodium chloride or alumina or a steel reactor is used, the yields of divinyl are appreciably reduced [167]. In order to determine whether the observed effect is due to the inhibiting effect of alumina and sodium chloride or whether, on the other hand, it is caused by the activation of dehydrogenation by the quartz surface, the effect of the volume to surface ratio for the reactor on the degree of conversion of n-butane was investigated. The results show that the walls of the quartz (and also Pyrex) reactor appreciably accelerate the dehydrogenation. For example, when the volume : surface ratio of a quartz reactor was increased from 0.015 to 0.34 cm, the yield of divinyl decreased from 18 to 9%.

The comparative effects of certain solid catalysts on the yields of dehydrogenation products are shown in Table 7. [161,167] Depending on its nature and porous structure, the catalyst accelerates or inhibits the dehydrogenation reaction. The yields of divinyl on silica gel with a specific surface of 24 $m^2 g^{-1}$ are much higher than on quartz. However, on increasing the specific surface to 120 $m^2 g^{-1}$, the efficiency of the process is somewhat reduced. On alumina the yields of divinyl fall appreciably on increasing the specific surface of the catalyst. Other relations are observed for isopentane and n-hexane. The maximum yields of isoprene are obtained on non-porous catalysts, in agreement also with data on the effect of the porosity of the acceptors (Table 6). On the other hand, even alumina with the highest specific surface has a favourable effect on the dehydrocyclisation of n-hexane.

Apart from the substances listed in Table 7, other active catalysts have been proposed for the dehydrogenation of saturated hydrocarbons in the presence of added iodine: halides of alkali and transition metals and silver on silica gel or α-alumina [168–172], Fe_3O_4, and lithium hydroxide [173].

d. Possible Role of the Solid Catalyst

Since, as in the absence of iodine (subsection 1c), it is unlikely that the acceleration of dehydrogenation in the presence of solid catalysts is due to a major change in the reaction mechanism, as usually happens in heterogeneous catalysis, it follows that in the presence of the catalyst the rate of reaction does not change much relative to the rate in the empty reactor and that the selectivity of the process does not change appreciably (Table 7). For the latter reason, it is also difficult to suppose that the role of the catalyst consists in chain termination for the competing reaction. The more likely hypothesis is that the reaction mechanism remains largely unchanged; the reaction takes place in the bulk-phase but the active surface accelerates the slowest stages.

Table 7. Effects of solid catalysts on oxidative dehydrogenation (hydrocarbon : oxygen : nitrogen = 1 : 1 : 10, temperature 530–540°C).

Catalyst	Specific surface, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$	Yields, % of divinyl from n-butane $\varphi = 0.03$* w.r.t. starting material	Yields, % of divinyl from n-butane $\varphi = 0.03$* w.r.t. product	Yields, % of isoprene from isopentane $\varphi = 0.08$ w.r.t. starting material	Yields, % of isoprene from isopentane $\varphi = 0.08$ w.r.t. product	Yields, % of benzene from n-hexane $\varphi = 0.04$ w.r.t. starting material	Yields, % of benzene from n-hexane $\varphi = 0.04$ w.r.t. product
Empty reactor **	—	—	9	47	6	37	6	17
Quartz	0.01	—	8	66	13	60	7	20
Silica gel I	24	0.79	24	76	3	12	18	49
Silica gel II	120	0.83	23	67	—	—	—	—
Alumina	190	0.77	<1	<1	<1	<1	10	30
Alumina	56	0.67	3	8	—	—	—	—
5% KBr and 1% AgI on silica gel I	25	0.7	13	47	—	—	—	—
5% KBr and 1% AgI on quartz	20	0.72	33	73	5	20	16	51
	0.1	—	9	51	18	58	—	—

* φ is the iodine : hydrocarbon molar ratio.
** At the same flow rate as in the experiments with catalysts.

Kolobikhin et al.[172] believe that the accelerating effect of solid catalysts on the oxidative dehydrogenation of n-butane in the presence of oxygen and added iodine is associated with the catalysis of the oxidation [according to the overall Eqn. (4)] of the hydrogen iodide formed in the dehydrogenation. Indeed, solid materials such as broken quartz, silica gel, and other silicon-containing substances catalyse the oxidation of hydrogen iodide with oxygen[174–177]. However, this finding alone is insufficient to explain the activating effect of catalysts; one might expect the acceleration of the oxidative dehydrogenation by catalysts for the oxidation of hydrogen iodide only if the hydrogen iodide oxidation stage was the slowest in oxidative dehydrogenation, but this is not confirmed experimentally (see subsection 3b). Indeed the present author's data[164] show that there is no parallel variation of the activity of the catalyst in oxidative dehydrogenation and the acceleration of the oxidation of hydrogen iodide.

It follows from Tables 6 and 7 that the wide differences in the effect of the porous structure on the reactions of n-butane, isopentane, and n-hexane are associated mainly with the secondary reactions of unsaturated products[161]. The present author investigated[161] the reactions of divinyl and isoprene on quartz, silica gels, and alumina. Divinyl and isoprene are converted mainly into coke-like and tarry products. At 530°C, with the ratios divinyl : iodine : oxygen : nitrogen = 1 : 0.03 : 1 : 10 and a duration of contact of 0.6 s, 22% and 42% of divinyl react respectively in the empty reactor and in the presence of silica gel. Therefore the increased yield of divinyl in the dehydrogenation of n-butane in the presence of silica gel, relative to the empty reactor (Table 7), cannot be due to the inhibition of the decomposition of the divinyl formed. Under these conditions almost complete reaction of divinyl was observed on γ-alumina, which probably accounts for the absence of divinyl from the n-butane reaction products on this catalyst.

Isoprene enters into secondary reactions much more readily than divinyl and this probably explains the decrease of its yield with increasing porosity of the catalysts, this being observed both in experiments with small amounts of iodine (Table 7) and in the presence of acceptors (Table 6). Thus the effect of the solid catalyst on oxidative dehydrogenation in the presence of iodine and oxygen is complex and probably consists in the acceleration of the slow stage of the process and in the participation of the catalyst in secondary reactions of the products.

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In recent years significant advances have been achieved in the field of oxidative dehydrogenation of hydrocarbons. Conditions have been found under which the formation of dehydrogenation products in considerable yields is the dominant process in the reaction between the hydrocarbon and an oxidising agent. The oxidising agents may be oxygen or halogens and also substances which give rise to them on decomposition.

On interaction with oxygen, the dehydrogenation of mono-olefins to more unsaturated hydrocarbons takes place in the presence of heterogeneous catalysts. There are virtually no such catalysts for the dehydrogenation of saturated hydrocarbons. The use of iodine-containing substances even in small amounts makes it possible to dehydrogenate fairly readily not only olefins but also saturated hydrocarbons. An increase in the degree of unsaturation of the product is favoured by the introduction into the reaction zone of hydrogen iodide acceptors.

Solid catalysts which are not acceptors and which are capable of accelerating appreciably the oxidative dehydrogenation of saturated hydrocarbons are also known, but their effect on the process is radically different from that of the catalysts for the oxidative dehydrogenation of olefins. While the latter is a typical heterogeneous-catalytic reaction, the homogeneous chain-radical mechanism probably persists in the presence of catalysts suitable for oxidative dehydrogenation of saturated hydrocarbons and the role of the solid surface may consist in the acceleration of the slowest stages of the process.

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Condensation of Unsaturated Compounds with Formaldehyde (the Prins Reaction)

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In their review Arundale and Mikeska[1] made a thorough compilation of extensive data on the reaction of olefins with aldehydes and the use of the reaction products in organic synthesis. In recent years numerous papers have appeared in the scientific literature dealing with the mechanism and the chemistry of the Prins reaction and also the possibility of using ion-exchange resins as catalysts, first demonstrated in our laboratory[2].

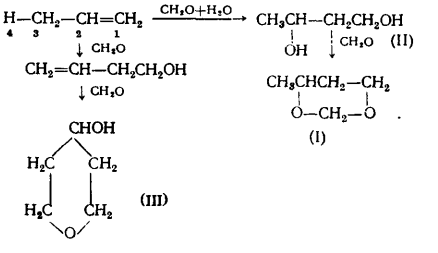
We attempted to review the literature for the period 1953–1965.

1. SYNTHESIS OF 1,3-DIOXANS FROM OLEFINS IN THE PRESENCE OF ACID CATALYSTS

a. Condensation of Olefins with Formaldehyde† in the Presence of Acid Catalysts

In the presence of acid catalysts the main products are 1,3-dioxan and 1,3-glycol. The highest rate of condensation is observed in the reaction of isobutene with formaldehyde. Tertiary olefins with high molecular weights, straight-chain olefins, and also higher aldehydes are less reactive. Apart from the acid catalysts used earlier for the reaction (sulphuric, acetic, hydrochloric, and hypochlorous acids), nitric acid[3] and KU-2 cation-exchange resin[2] have been employed.

In the reaction between propene and formaldehyde investigated by Farberov and coworkers[4,5] optimum conditions are attained at sulphuric acid concentrations of 1–5 wt. %. In the presence of acid of this concentration the main products are 4-methyl-1,3-dioxan (I) (85% yield), butane-1,3-diol (II) (3–5% yield), 1-hydroxytetrahydropyran (III) (7–8% yield), and traces of allylmethanol:



According to the hypotheses put forward by Nesmeyanov and Kabachnik[6], olefins of this type are characterised by

† In some cases formaldehyde is denoted by fa.