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Catalytic Disproportionation of Unsaturated Hydrocarbons

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The review considers the data at present available on the disproportionation reaction† of olefins. The practical value of this versatile reaction, which opens up new pathways for synthesis of a wide variety of unsaturated hydrocarbons, is noted. The applications of the reaction to dienes and acetylenes are also considered.
Studies using various heterogeneous disproportionation catalysts have been described, together with simple process parameters (catalyst activity, temperature, pressure, etc).
Much attention has been devoted to the applications of homogeneous catalytic systems in the disproportionation of olefins and to the characteristics which distinguish them from heterogeneous catalysts. Problems concerned with the reaction mechanism and its stereochemical features are discussed.
The bibliography includes 92 references.

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I. INTRODUCTION

The most important and interesting reactions in organic chemistry discovered in the last decade undoubtedly include the disproportionation of olefins. This reaction apparently constitutes a new field in the chemistry of unsaturated compounds.

According to the first patent data [1-4] and more detailed subsequent studies [5,6], acyclic olefins can be converted in the presence of catalysts into higher and lower homologues:

$$\underset{50\%}{2\,RCH{=}CHR'} \rightleftarrows \underset{25\%}{RCH{=}CHR} + \underset{25\%}{R'CH{=}CHR'}.$$

The olefins with a smaller and larger number of carbon atoms (compared with the initial substance) are formed in almost equal molar amounts. The degree of conversion is limited by the thermodynamic equilibrium.

The new catalytic reaction immediately attracted attention, which led initially to the publication (starting in 1964) of numerous patents dealing with the search for the best disproportionation catalysts, the development of suitable conditions for the process, and its practical applications.

The considerable interest in the disproportionation of olefins is due to the versatility of this reaction and the consequent increase in the number of methods for the chemical processing of unsaturated hydrocarbons.

Some of these possibilities will be mentioned here. The disproportionation reaction constitutes an extremely effective means for the preparation of olefins with various structures, many of which serve as the starting material in many manufacturing processes. For example, the disproportionation of propene leads to the preparation of very pure ethylene and straight-chain butenes—olefins which are used in the large-scale manufacture of various valuable products (polyethylene, vinyl chloride, styrene, ethylene oxide, butadiene, butyl alcohols, and others).

The disproportionation of straight-chain butenes yields straight-chain pentenes—the starting material for the synthesis of isoprene. For the synthesis of olefinic hydrocarbons, disproportionation is particularly promising because many types of the initial olefinic raw material can be provided by the petrochemical industry.

An unusual feature of the reaction is the mutual disproportionation of two molecules of different olefins. In particular, if one of the olefins is ethylene, the reaction (the so called ethenolysis) makes it possible to convert olefins with an inner multiple bond into α-olefins [6-8].

The application of disproportionation to cyclo-olefins merits particular attention, since it provides a new synthesis of macrocycles [9-11]. Mutual disproportionation of cyclic and alicyclic mono-olefins leads to the formation of diolefins [12,13].

It is noteworthy that the disproportionation reaction is not characteristic solely of mono-olefins. Recently the disproportionation of dienes [14] and alkynes [15] was discovered. It is also likely that olefins with other than alkyl substituents can also be disproportionated, as shown by the disproportionation of stilbene [16]. All these findings suggest that the disproportionation process has general applicability and is characteristic of all unsaturated compounds.

An important feature of the reaction is the high purity of the products obtained, which could hardly be achieved by any other method of synthesis (especially with higher olefins).

A fundamentally new stage in the development of the disproportionation reaction has been the use of homogeneous catalytic systems [17-24], which exhibit an unusually high selectivity and stereospecificity. An industrial application of the disproportionation reaction has been achieved comparatively rapidly, particularly in the conversion of propene into ethylene and straight-chain butenes [25-27]. The first industrial apparatus for this process, which also included a system for the further conversion of straight-chain butenes into butadiene, was first used in Canada in 1966‡. The annual production

†In addition to the term "disproportionation", the terms "dismutation" and "metathesis" are also employed.

‡The process was patented by the Phillips Petroleum Co. under the name "Triolefin Process". [28]

from the apparatus with respect to the raw material (obtained from pyrolitic gas) was 31500 tonnes, the output of ethylene being 9000 tonnes and that of straight-chain butenes 22 700 tonnes[27]. Thus the problem of the utilisation of propene (the principal side product in the manufacture of ethylene), the demand for which lags behind its supply in the world markets[29], can be partially solved.

One can also point to other applications of the reaction which show promise for industry. For example, mixtures of ethylene and but-2-ene (disproportionation products of propene) can be usefully alkylated with isobutane[30,31]. The alkylated products thus obtained have a higher octane number than the alkylation products based on propene.

A combination of the cracking of petroleum raw material with olefin disproportionation and dehydrogenation processes and also with the isomerisation and polymerisation of olefins has been proposed in a number of studies[3, 32-35].

Thus the disproportionation of unsaturated hydrocarbons opens up new and interesting possibilities not only for preparative chemistry but also for chemical industry.

At the present time there are no publications in the USSR literature giving a systematic and general account of the advances in the disproportionation of olefinic compounds§. The aim of the present review is to fill this gap.

II. HETEROGENEOUS CATALYSTS FOR THE DISPROPORTIONATION OF OLEFINS

The range of metals whose compounds provide the basis of heterogeneous catalysts for the disproportionation of olefins was comparatively small until recently: these were mainly molybdenum, tungsten, and rhenium; the list has been appreciably expanded only in recent years, the following metals having been introduced: rhodium, iridium, osmium, ruthenium, niobium, tantalum, tellurium, lanthanum, thorium, vanadium, and tin.

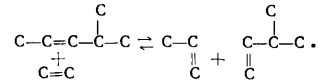
The most common catalysts are molybdenum, tungsten, and rhenium oxides deposited on alumina or silica gel. Among these the cobalt–molybdenum catalysts are outstanding because of their effectiveness, availability, and relative cheapness[1-8,37-57]. Their molybdenum oxide content is usually 1–15% (mainly 12–14%) and that of cobalt oxide is 1–5% (the optimum content is 2.5–3.5%). These catalysts are active over a very wide range of temperatures: from 20° to 400°C (the optimum range is 90 to 260°C); the pressure can vary from atmospheric to 140 atm. An industrial cobalt–molybdenum catalyst (11% MoO_3, 3.4% CoO, and 85.6% Al_2O_3)[5] showed a very high efficiency: for example at 205°C and a pressure of 32 atm, the conversion of propene supplied at a weight rate of 3.5–4.4 kg h^{-1} reached 42.4%, the selectivity being greater than 94%.

A chromium–molybdenum catalyst on alumina with somewhat better properties than the cobalt–molybdenum catalysts was proposed quite recently[52].

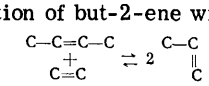
Tungsten oxide (usually 3% WO_3) also exhibits a high disproportionating activity[4,37,43-50,53-55]; however, this catalyst is effective at higher temperatures than the molybdenum catalyst (250–550°). Thus the maximum degree of conversion of propene (44.8%) in the presence of tungsten oxide is attained only at 427°C.[44,53] The use of tungsten oxide on silica gel for the synthesis of 2-methylbut-2-ene (the starting material in the synthesis of isoprene) by the disproportionation of a mixture of isobutene with but-2-ene or propene has been described[55]. For an isobutene conversion of 35%, the isopentene content in the C_5 fraction was 92–97% (450°C and 21 atm).

After the molybdenum and tungsten oxides, catalysts based on rhenium oxide (1–20% Re_2O_7) began to be employed[8,47-51,56-66]. They rapidly gained recognition owing to their activity, high selectivity, and resistance to catalytic poisons. Moreover, with rhenium catalysts it proved possible to carry out the reaction under milder conditions than on MoO_3 and WO_3: 20–100°C and atmospheric pressure. But-1-ene is converted into ethylene and hex-3-ene with a selectivity of 95.5% at a temperature as low as 25°C, the conversion being 38%.[64]

Rhenium catalysts yielded excellent results in ethenolysis[8,64]; in particular, 3-methylbut-1-ene and propene were obtained from 4-methylpent-2-ene and ethylene in 93% yield for a 94% conversion of the initial higher olefin (25–140°C and atmospheric pressure)[64]:



The disproportionation of but-2-ene with ethylene,



under the same conditions gives a 100% yield of propene (the conversion with respect to but-2-ene is 55%).

The disproportionation of readily polymerised secondary and tertiary olefins with alkyl and aryl substituents has been achieved in the presence of Re_2O_7/Al_2O_3.[65,66]

Apart from the molybdenum, tungsten, and rhenium oxides mentioned above, the carbonyls of these metals deposited in an amount of 5–10% on alumina are also employed as catalysts for the disproportionation of olefins[5,35,45,67]. The carbonyl catalysts are active at fairly low temperatures (100–150°C) and are particularly effective in the disproportionation of higher olefins. The dependence of the activity on the nature of the metal is the same as for the oxides, i.e. $Mo(CO)_6$ and $Re(CO)_{10}$ show the highest activity. For example, whereas the conversion of but-1-ene in the presence of $Mo(CO)_6/Al_2O_3$ (120°C and 35 atm) is 10% and that of pent-1-ene 60%, in the presence of $W(CO)_6/Al_2O_3$ the conversions of these olefins are 7 and 44% respectively[5].

Attempts were made to use alumina, silica gel, and aluminosilicates promoted with molybdenum and tungsten sulphides (2–10%) for the disproportionation of C_3–C_{20} olefins[49,68]. However, these catalysts proved to be relatively inactive over a fairly wide temperature range (65–535°C) (for example, the conversion of propene did not exceed 1.3%).[68]

Among catalysts including other metals in their composition, those with lanthanum, rhodium, iridium, osmium, and tin oxides on alumina are known[69]. They all exhibit very low disproportionating activity (for example, the maximum conversion of propene at 350°C was achieved in the presence of RhO_3 but amounted to only 6%). According to patent data[70-73], the disproportionation catalysts are also promoted by tantalum, tellurium, niobium, ruthenium, vanadium, and thorium (mainly as the oxides). Niobium, tantalum, and tellurium oxides proved to be the most effective among these. However, a quantitative comparison of the activities of these catalysts is difficult because of the differences in the test conditions.

§During the preparation of this paper, Bailey's review was published[36].

Recently it was discovered [74,75] that olefins are appreciably disproportionated on alumina alone. The conversion of propene in this process was 0.1–8.5% depending on temperature; a higher conversion was achieved at 400°C and atmospheric pressure, the selectivity being 12% with respect to ethylene and 58% with respect to straight-chain butenes.

The disproportionation reaction is probably very common in catalysis and accompanies many processes involving the formation or conversion of olefins in the presence of alumina. In particular, it has been shown [75] that disproportionation takes place in the dehydration of isopropyl alcohol [76] and also probably under the conditions of ethylene hydropolymerisation [77].

The principal parameters which determine the course of the olefin disproportionation reaction are catalyst activity, temperature, and contact time. Pressure apparently does not play a significant role (the reaction takes place without a change in volume); it has an effect only in consequence of a change in the density of the gases. The effect of these factors on the conversion and selectivity has been investigated in greatest detail for the disproportionation of propene [5,25,31,52,53,67,78,79] in connection with the development of the optimum conditions for the industrial process.

The kinetics of the disproportionation of propene on WO_3/Al_2O_3 (in a pilot plant) were examined [80] and it was shown that the reaction is between an adsorbed propene molecule and one from the gas phase (or physically adsorbed—Rideal's model). The rate of the process is limited by the rate of collision between the molecule and the catalyst surface. The apparent propene disproportionation energy is 21.6 kcal $mole^{-1}$.

However, the results obtained in a recent study [81] for the initial rate of the disproportionation of propene (in the presence of the cobalt–molybdenum catalyst) support another mechanism: the reaction takes place between two propene molecules adsorbed on the surface of the catalyst (the Langmuir–Hinshelwood model).

A thermodynamic calculation has been carried out on the disproportionation of propene and the equilibrium constants have been determined in the range 50–300°C. [82]

The activity of disproportionation catalysts, like that of catalysts in other processes, is determined mainly by the nature of the metal and the type of carrier; in addition, promoting additives, the method of preparation of the catalyst, and catalytic poisons have a considerable influence.

As already mentioned, transition metal (tungsten, molybdenum, and rhenium) compounds are best catalysts for the disproportionation of olefins. Cobalt [5,78], alkali and alkaline earth metals [6,41–44,49] and also compounds of Group VIII metals [49] have been recommended as promoting additives to oxide catalysts. Side reactions (isomerisation, coke formation, etc.) are mainly suppressed in their presence.

A general method for enhancing the activity of disproportionation catalysts consists in their preliminary activation by gases at 300–900°C (nitrogen, hydrogen, oxygen, carbon dioxide, carbon monoxide, helium, and dry air) followed by treatment with an inert gas (mainly nitrogen). Thus the conversion of straight-chain pentene after treatment of WO_3/SiO_2 with carbon monoxide increased by 36.5%. [43] The effect of preliminary treatment on the activity of disproportionation catalysts has been confirmed by infrared spectroscopy [79] [for $Mo(CO_6)/Al_2O_3$]. The effectiveness of the catalysts, in particular a rhenium catalyst, depends to some extent on the polarity of the solvent in which the oxide is dissolved for subsequent impregnation of the carrier [60]. When dioxan, methanol, and water were used, the degree of disproportionation of but-1-ene was 31.5, 29, and 24.6% respectively with molar selectivities in relation to $C_2 + C_6$ olefins of 95, 93, and 78.2%.

To improve the activity of the solid oxide catalysts, it is recommended that [72] they be treated in a hydrocarbon solution by the hydrides of organic derivatives of Group I, II, or III metals (for example with triethylaluminium).

Alumina, silica gel, and aluminosilicates were mainly employed as carriers, and less frequently aluminium, magnesium, titanium, zirconium, and calcium phosphates [31,70] and magnesium [4], thorium, and zirconium oxides [70]. The oxides of Group IV elements were employed for rhenium catalysts [58,59,62] and it was found that in the presence of Re_2O_7/SnO_2 the conversion of but-2-ene was higher by a factor of 10 compared with Re_2O_7/Al_2O_3 (other conditions being equal) [62]. One cannot rule out the possibility that carriers comprising the oxides of Group IV elements themselves catalyse the disproportionation reaction.

The conversion of olefins increases by 5–10% and the period of constant activity of the catalyst is doubled when the alumina carrier is first treated with a 0.001–10 N solution of an organic or inorganic acid (mainly hydrochloric and acetic acids) [45,48,51,63,67,69].

The problem of the effect of catalytic poisons on the activity of heterogeneous disproportionation catalysts is very important. The majority of different types of olefinic starting materials are obtained by pyrolysis or thermal cracking and contain numerous admixtures which deactivate the catalysts (water, hydrogen sulphide, oxygen and its compounds, and also alkynes and alkadienes). The presence of water or sulphur compounds in the starting material rapidly reduces the conversion of the olefins. For example, when propene is saturated with water, its conversion in the presence of WO_3/SiO_2 is reduced in 1 h to 10% and in the presence of sulphur dioxide to 16%, while hydrogen sulphide completely deactivates the catalyst [53]. The elimination of water and sulphur compounds under industrial conditions can be successfully achieved using molecular sieves [25].

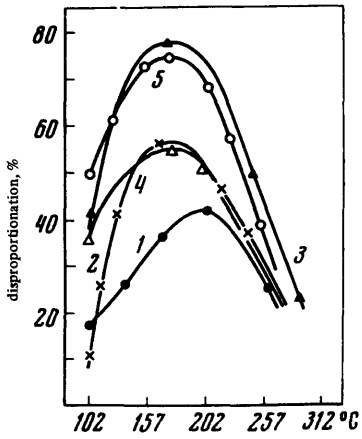
Alkynes and alkadienes, which form coke and polymer deposits on the catalysts, are also powerful catalytic poisons [43]. In this case the activity of the catalyst can be restored only by regeneration. The yield of coke is reduced by the addition of 2–4% of cobalt oxide to molybdenum oxide [5]. In addition, the olefinic starting materials may be subjected to preliminary purification, designed to remove acetylenes and dienes, by selective hydrogenation on industrial palladised catalysts [25].

Disproportionation in the presence of 10–60% of hydrogen is recommended as a method which eliminates the necessity for a careful preliminary removal of alkadienes from alkenes; at the same time the activity and the useful life of the catalyst increase appreciably [49].

The resistance of the catalyst to poisons increases with process temperature; however, as will be shown below, high-temperature conditions are undesirable for many reasons.

The presence in the olefinic starting material of paraffinic and cycloparaffinic hydrocarbons does not affect the reaction and therefore they can be used as inert diluents [5,43,48,53,69]. Thus a change in the concentration of propene in the starting material from 60 to 99% (the residue was propane) did not affect its conversion. This is very important, since there is then no need to concentrate the olefins before their disproportionation.

The effect of process temperature on the degree of conversion of olefins was investigated in the disproportionation of propene [5,25,52,53,82], straight-chain butenes [5,6], straight-chain pentenes [5], hex-1-ene [5], oct-1-ene [5] and other olefins [48,51,68]. In all cases the temperature dependence of their conversion is described by a curve with a maximum, which is typical of reactions the rate of which is limited by an equilibrium (see Figure).



Effect of temperature on the degree of disproportionation of olefins: 1) propene; 2) but-1-ene; 3) pent-1-ene; 3) hex-1-ene; 5) oct-1-ene.

Optimum temperatures correspond to the majority of the most favourable combinations of degree of conversion and selectivity, since after the attainment of the temperature of the onset of isomerisation and cracking, the efficiency begins to decrease rapidly. Thus, when the temperature is increased from 95° to 205°C ($CoO.MoO_3.Al_2O_3$ catalyst, pressure 32 atm), the conversion of propene increases from 17.9 to 42.6%. According to a thermodynamic calculation [82], a further increase of temperature should lead to increased conversion. Nevertheless, above 200°C the conversion fell to 14.6% (at 300°C), in all probability due to side processes and deactivation of the catalyst. The best combination of degree of conversion and selectivity for propene is achieved at 163°C.

Thermodynamically the disproportionation process is independent of pressure. [82] However, experimental data [5,43,52,53] show that an increase of pressure favours the process to some extent. Probably this effect may be explained by an increase of the concentration of the olefin on the catalyst surface, which in turn leads to an increase of the rate of reaction. It has also been noted that [43] a decrease of pressure (below 10 atm) in the disproportionation of higher olefins promotes the formation of products with a more branched chain than in the initial substances. In certain cases (particularly in the presence of MoO_3) an increase of pressure was accompanied by an increase in coke formation [43]. A pressure below 40 atm is usually optimum (for example, in the disproportion of propene it is 32 atm).

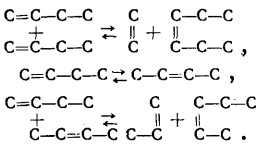
The space velocity at which the stream of starting material is supplied varies within wide limits probably only in the case of propene (between 10 and 130 kg h^{-1}) and does not influence appreciably the degree of conversion [25]. However, a further increase of space velocity (> 180 h^{-1}) leads to some decrease of the conversion of propene [52]. In the disproportionation of higher olefins, the rate of supply of the olefinic starting material plays an important role in determining the possibility of isomerisation, which usually becomes very appreciable at low flow rates of the starting material and almost disappears at high flow rates.

The contact time is related to pressure and space velocity and also depends on temperature and the activity of the catalyst. It can vary from 0.1 s to 120 min, the optimum time recommended being 0.1–60 s.

The main factor which precludes a 100% yield of the required products in the disproportionation of olefins is undesirable side reactions (isomerisation, cracking, polymerisation, condensation, and others), which inevitably occur to some extent on heterogeneous catalysts. However, by careful choice of conditions, the majority of side processes may be suppressed to an extremely insignificant level ensuring thereby a higher selectivity and conversion. The only reaction which cannot be completely eliminated is isomerisation.

It is noteworthy that the isomerising activity of the catalyst decreases more rapidly than its disproportionating activity [6]. Probably this is evidence that both reactions occur at different catalyst active centres. On this basis, isomerisation may be to a large extent suppressed by poisoning the acid regions of the catalyst (which are responsible for its isomerising capacity) by adding small amounts of alkali and alkaline earth metals [6,7,41–49], the effectiveness of the alkali metal ions increasing in the sequence sodium < potassium < rubidium < caesium [41]. When the catalyst is cautiously poisoned and appropriate conditions are chosen, it is possible to control the isomerisation reaction and to obtain pure olefins with a high degree of selectivity.

With this idea in mind, a detailed study was made of the disproportionation of straight-chain butenes [6], which can lead both to ethylene and hex-3-ene (from but-1-ene) and to propene and straight-chain pentenes (from but-2-ene):



By varying the reaction temperature, the rate of supply of but-1-ene, and the amount of sodium in the catalyst, it was possible to find the optimum conditions for both the disproportionation reaction (the formation of $C_2 + C_6$ olefins) and for isomerisation (the formation of $C_3 + C_5$ olefins). The highest selectivity with respect to $C_2 + C_6$ olefins (90.7%) was achieved in the presence of a cobalt–molybdenum catalyst treated with a 0.2 *N* solution of $NaHCO_3$ (140°C). An increase of temperature and a decrease of the rate of supply of but-1-ene promote its isomerisation to but-2-ene and hence an increase in the yield of $C_3 + C_5$ products.

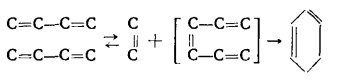
One of the important advantages of the olefins disproportionation process is the purity of the products. If one starts with a pure starting material, then theoretically pure alkenes should be obtained. However, in practice the reaction products are usually contaminated by impurities from various sources (the starting material and the regenerating gas), which are retained on the catalyst and are liberated in the subsequent working period. Moreover, another source of impurities is side reactions accompanying the disproportionation (isomerisation, cracking, hydrogenation, hydrogen transfer).

Nevertheless, the experience gained on an industrial apparatus for the disproportionation of propene has convincingly demonstrated that the majority of the sources of impurities can be controlled to some extent, so that the propene conversion products (ethylene and straight-chain butenes) do not require additional purification (the purity of of commerical ethylene, for example, can be easily raised to 99.9%).[25]

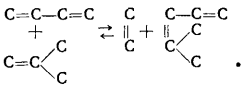
Not only mono-olefins but also dienes undergo the disproportionation reaction[14]. So far only heterogeneous catalysts for the process are known. In particular tungsten oxide deposited on silica gel (7% WO_3) with a small amount of sodium (0.19% Na_2O) catalyses at 538°C and atmospheric pressure the disproportionation of buta-1,3-diene, penta-1,3-diene, and also mixtures of these dienes with mono-olefins (propene, butenes).

The conversion of dienes (the cleavage of butadiene by *trans*-but-2-ene) in the presence of this catalyst reached 39% in the best case, but mostly did not exceed 10%. The selectivity in relation to the desired products was 46–100%. The reaction is complicated by the oligomerisation of the dienes in the presence of a tungsten catalyst (the amount of dimers in individual experiments reached 32%).

An interesting observation of the formation of cyclohexadiene (instead of the expected hexatriene) was made in the disproportionation of buta-1,3-diene:

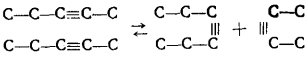


The disproportionation of dienes together with mono-olefins (a process similar to ethenolysis) makes it possible to obtain with a high degree of selectivity a new mono-olefin and a diene. For example, ethylene and 4-methylpenta-1,3-diene was obtained with 100% selectivity from buta-1,3-diene and isobutene:



Thus the disproportionation of dienes opens up vast possibilities both for preparative synthesis and for the industrial manufacture of valuable diene hydrocarbons of different structures.

The wide variety of disproportionation reactions of unsaturated hydrocarbons is also shown by the fact that these reactions are undergone by alkynes[15]. The formation of homologues was noted in many catalytic and thermal reactions of alkynes¶, but the experimental proof of disproportionation was obtained only recently for pent-2-yne[15]. The catalyst was tungsten oxide on silica gel. When the reaction was performed in a stream of cyclohexane at 350°C and at atmospheric pressure, pent-2-yne was converted with an overall yield of 44% into but-2-yne and hex-3-yne (molar ratio 1–1.2) and also a polymer. The selectivity with respect to the alkynes is 53%.



The first experiments on the disproportionation of alkynes left no doubt that this reaction, like that in the series of alkenes, constitutes a new means for the synthesis of a wide variety of acetylene homologues.

Summarising the applications of heterogeneous disproportionation catalysts, one must emphasise some of their advantages, such as relatively ready availability, the possibility of employment for a wide range of olefins (C_3–C_{40}, regardless of the position of the multiple bond and the degree of chain branching), and also a very favourable olefin: catalyst ratio (between 1000 : 1 and 1 : 1).

At the same time mention must be made of some important disadvantages of heterogeneous disproportionation. These include in the first place inadequate process selectivity. This applies in particular to higher olefins, the disproportionation products of which must be regarded as the result of two competing processes: double bond migration, and disproportionation. The reaction is apparently sufficiently selective only for the special case of the disproportionation of propene to ethylene and straight-chain butenes.

In addition, in the presence of heterogeneous catalysts the disproportionation usually takes place at elevated temperatures and pressures, which gives rise to certain disadvantages in the technological formulation of the process. Finally, another negative feature is the lack of continuity in the disproportionation process using heterogeneous catalysts owing to the comparatively extensive coke deposition on them during operation (up to 20%).

III. HOMOGENEOUS DISPROPORTIONATION OF OLEFINS

The disproportionation of olefinic hydrocarbons is one of the catalytic processes for which homogeneous catalysis by complex compounds has only just begun to be employed. Nevertheless, the few available data[17–24] on this problem indicate a wide scope of homogeneous disproportionations, primarily in the solution of applied problems involving the synthesis of various olefins. At the same time, the use of homogeneous catalysts makes it possible to obtain more profound information about the reaction mechanism.

The homogeneous catalysts at present available, which are capable of catalysing the disproportionation of olefins, are largely based on tungsten and molybdenum complexes.

The study of homogeneous disproportionation was begun by Calderon and coworkers[17–19], who reported the disproportionation of olefins in the presence of a new catalytic system (for this reaction), consisting of tungsten hexachloride, ethylaluminium dichloride and ethyl alcohol, using benzene as the solvent. A much less active catalyst was obtained without ethyl alcohol. None of the systems component alone is an active catalyst of the disproportionation or migration of the C=C bond (under the process conditions). The aluminium : tungsten ratio can be varied within wide limits, but best results were obtained for a 4 : 1 ratio. The $WCl_6 + C_2H_5AlCl_2 + C_2H_5OH$ catalytic system proved very effective in the disproportionation of C_4 and higher olefins with a non-terminal double bond. The reaction was achieved at room temperature and atmospheric pressure; equilibrium was established extremely rapidly (in seconds).

The selectivity of the homogeneous disproportionation proved to be very high. Thus in the case of pent-2-ene, but-2-ene, and hex-3-ene, it reached 99.6%.

A relative disadvantage of the $WCl_6 + C_2H_5AlCl_2 + C_2H_5OH$ catalytic system is slight oligomerisation of olefins, which was found to depend on the position of the double bond in the alkene and decreased in the sequence but-2-ene > alk-2-ene > alk-3-ene > alk-6-ene. The solvent (benzene) was alkylated to a very slight extent. There was also some loss of activity of the catalyst with time.

¶The disproportionation of acetylene has been postulated in its photolysis[83].

The binary catalytic system comprising tungsten hexachloride and n-butyl-lithium is free from all these disadvantages [20], the second component playing the role of a reducing and alkylating agent for WCl_6. Neither tungsten hexachloride nor n-butyl-lithium gives rise separately to olefin reactions, i.e. any anionic (due to C_4H_9Li) or cationic (due to WCl_6) processes can be completely ruled out. The new homogeneous catalyst proved to more be selective. For example, pent-2-ene was converted with 100% selectivity into but-2-ene and hex-3-ene regardless of the degree of conversion.

However, in contrast to the preceding homogeneous system, where the olefin : WCl_6 ratio could reach 10 000, the catalyst with n-butyl-lithium was sufficiently effective only for olefin : WCl_6 ratios not exceeding 100 (the optimum ratio was 50).

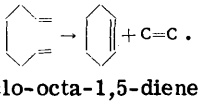
The dependence of catalyst activity on the Li/W ratio has not so far been explained. It was found that the system catalyses effectively the disproportionation of pent-2-ene only for a 2 : 1 ratio of these metals.

The attempts to replace the n-butyl group by isomeric groups were unsuccessful. The conversion of pent-2-ene decreased in the series n-butyl > s-butyl > t-butyl and after 15 min of reaction, amounted to 15, 4, and 0% respectively.

Recently reports have been published [21-24] about yet another type of homogeneous catalytic system for the disproportionation of olefins—the nitrosyl complexes $L_2Cl_2(NO)_2M$ (where M = Mo or W and L = Ph_3P, C_5H_5N, PH_3PO, and others) treated with alkylaluminium chlorides in chlorobenzene. Like the previous homogeneous catalysts, these systems are effective at a low temperature (0–50°C).

The activity of the nitrosyl catalytic complex depends on the nature of the metal and the ligand [21,23]. Tungsten-containing catalysts are less active than the analogous molybdenum compounds. The $(C_5H_5N)_2Cl_2(NO)_2Mo$ complexes showed the highest selectivity. In addition to the disproportionation reaction the systems including ethylaluminium dichloride as a co-catalyst catalyse also the isomerisation reaction, which greatly reduces the process selectivity. The most active catalyst was obtained with methylaluminium sesquichloride.

It should be noted that the effectiveness of the homogeneous disproportionation in the presence of nitrosyl complexes is as a whole much lower than in the presence of the systems with tungsten hexachloride indicated above. However, nitrosyl-containing catalysts are very effective in the disproportionation of $\alpha\omega$-dienes and cyclic olefins with ethylene [23]. Thus octa-1,7-diene undergoes intramolecular disproportionation with formation of cyclohexene as the main product:



The ethenolysis of cyclo-octa-1,5-diene leads to the formation of deca-1,5,9-triene.

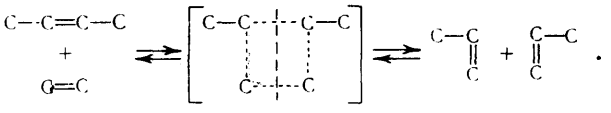
The kinetics of the homogeneous disproportionation of pent-2-ene were investigated, using the nitrosyl complexes described above [24]. The order of the reaction, which is unity with respect to the catalyst and variable with respect to the olefin, was determined: at a low olefin concentration the order is closer to 2, while at very high concentrations it approaches unity. The activation energy was found to be 6.6 kcal $mole^{-1}$.

Comparison of the results of applying catalytic systems of various types in the disproportionation of olefins makes it possible to define clearly the advantages of homogeneous over heterogeneous catalysts. The most important of these are milder process conditions combined with a high efficiency, selectivity, and stereospecificity (this feature is discussed in the last section of the review) and relative simplicity of action, which makes it possible to establish the most significant features of the kinetics and mechanism of the reaction.

Hence the urgent necessity to continue the search for complex catalytic systems for homogeneous disproportionation of olefins is quite evident.

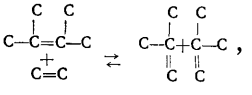
IV. MECHANISM OF DISPROPORTIONATION

The mechanism of both heterogeneous and homogeneous disproportionations of olefins is essentially based on the concept of the coordination of unsaturated ligands (olefins) with transition metals. The first considerations in relation to the mechanism of the reaction concern its occurrence in the presence of heterogeneous catalysts. Banks and Bailey [5] and then Bradshaw and coworkers [6] put forward the hypothesis that the intermediate stage in the disproportionation of olefins involves the formation of a four-membered ring—"quasicyclobutane". The reaction carried out by Bradshaw and coworkers [6], which is the reverse of the disproportionation of propene, i.e. the ethenolysis of but-2-ene ($CoO–MoO_3$ catalyst), may be regarded as confirming to some extent this hypothesis. They suggested, in accordance with the mechanism involving the formation of quasicyclobutane, that the only reaction product is propene:



A further development of the hypotheses concerning the disproportionation mechanism may be found in the work of Mol and coworkers [84,85], who suggested the formation of 1,2-dimethylcyclobutadiene (in the case of propene) as an intermediate. They also believe that the intermediate is formed as a result of the adsorption of two olefin molecules on the catalyst surface.

Quite recently Crain [7] questioned Mol's hypothesis of the formation of cyclobutadiene π-bonds by the transfer of four hydrogen atoms from two olefin molecules to the catalyst surface. He based his criticism on the ethenolysis of 2,3-dimethylbut-2-ene,

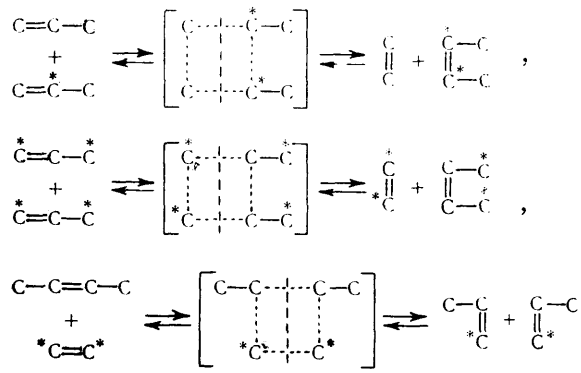


the product of which is isobutene, whereas according to Mol's hypothesis of the migration of hydrogen atoms to the catalyst the process should lead to methylbutenes, propene, and straight-chain butenes. Nevertheless, no traces of these substances were found in the ethenolysis products.

Important evidence in favour of the disproportionation mechanism involving the formation of an intermediate four-membered surface ring was provided by the study of the reaction using radioactive olefins [75,85-88].

In the disproportionation of [2-^{14}C] propene in the presence of Re_2O_7/Al_2O_3 [83] or in the presence of alumina alone [75], it was found that among the products only the straight-chain butenes exhibit specific radioactivity and that it is twice as high as for the initial propene. In the

case of propene with the extreme carbon atoms labelled, i.e. [1,3-^{14}C]propene, both reaction products, i.e. ethylene and straight-chain butenes, proved to be radioactive. Moreover, in the ethenolysis of but-2-ene using radioactive ethylene, propene containing radioactive carbon was isolated. The result described could have been obtained for the following disproportionation mechanism:

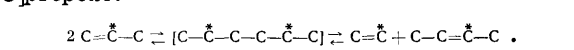


The mechanism of the disproportionation of propene in the presence of a cobalt–molybdenum catalyst was also investigated with the aid of radioactive carbon, attention being concentrated on the isomerisation reaction [87,88]. The results of these experiments confirmed the validity of the four-centre mechanism. Clark and Cook [88] note that at low temperatures (60°C) in the reaction involving [1-^{14}C]propene radioactivity was detected only in ethylene; [2-^{14}C]propene gave rise to radioactive butene. However, at an elevated temperature (100–160°C) the disproportionation of [1-^{14}C]propene yields two radioactive products —ethylene and butene, which the authors believe can be explained by the isomerisation of [1-^{14}C]propene to [3-^{14}C]propene. The apparent activation energy for disproportionation is 7.7 kcal mole^{-1} and for isomerisation 17.3 kcal mole^{-1}. On the other hand, the authors do not rule out the possibility of the formation at high temperatures of two adsorbed π-allyl complexes in the disproportionation of which the radioactive atom will enter ethylene and butene with equal probability.

Banks and Bailey [86] postulated that the four-centre mechanism is common to various reactions of olefins (disproportionation, isomerisation, polymerisation, etc.), the reaction pathway depending on the ability of the catalyst to promote the migration of hydrogen atoms. In particular, disproportionation takes place when olefin molecules are adsorbed with formation of a four-centre complex, the desorption involving the dissociation of two opposite bonds without the migration of hydrogen.

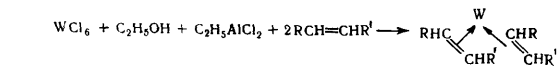
The results of numerous experiments on the disproportionation of mono-olefins with a wide variety of structures [6–8] and also diolefins [14] and acetylenes [15] agree satisfactorily with the hypothesis of the formation of an intermediate surface cyclobutane and constitute an additional argument in favour of the "quasicyclobutane" mechanism.

Thus it is possible to exclude the "linear" mechanism of the disproportionation of olefins [90] according to which radioactive ethylene and but-1-ene should be formed from [2-^{14}C]propene:



Homogeneous disproportionation yields much more complete information about the reaction mechanism. In their discussion of the mechanism of homogeneous disproportionation, Calderon and coworkers [17–19] also began with the hypothesis of an intermediate four-membered cyclic compound as the transition state and the possibility of its formation was considered wholly using the hypothesis of the coordination of olefins to transition metals. According to the concept of these authors, the disproportionation of olefins consists of three consecutive stages; the formation of a bisolefin–metal complex, transalkylidenation, and finally exchange of the olefins in the complex.

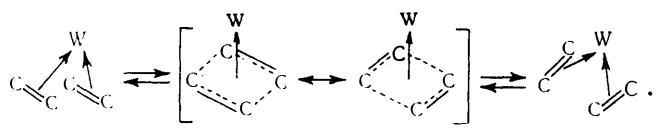
The first reaction stage, i.e. the formation of the bisolefin complex with tungsten, probably includes as an initial stage the reaction of tungsten(VI) with $C_2H_5AlCl_2$ in the presence of the free olefin, which leads to the reduction of tungsten(VI) to tungsten(IV):



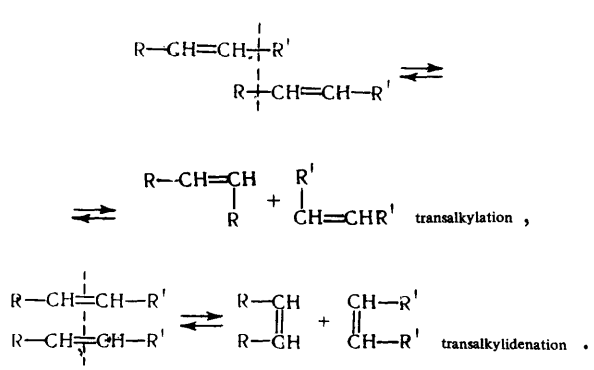
(The capacity of organoaluminium compounds to reduce transition metal halides is well known.)

Next tungsten(IV) is coordinated to two molecules of the olefinic ligand in the *cis*-configuration with formation of a bisolefin complex. The olefin bonds in the latter may be delocalised, as in the analogous structure of norbornadienetungsten tetracarbonyl. It is suggested that two olefin molecules form a four-membered ring—the square base of a tetragonal pyramid with the tungsten atom at the apex. The positions of the remaining ligands have not so far been determined. Nor is the role of ethanol in the catalytic reaction clear.

The next stage is transalkylidenation, consisting in the dissociation of the double bonds weakened by the coordination of the olefin to the metal [tungsten(IV)] and the formation of new multiple bonds:

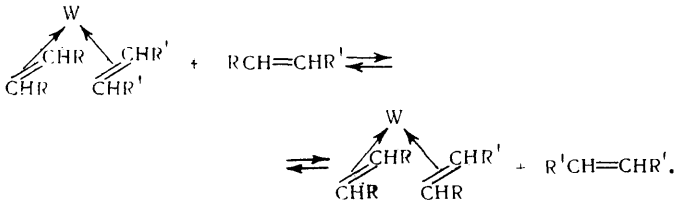


The transalkyledination mechanism, i.e. the exchange of alkylidene and not alkyl groups in disproportionation, was proved experimentally in experiments with deuterated olefins [18,19]:



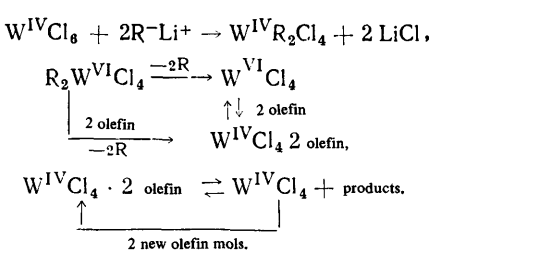
The isotope composition of the products agrees only with the four-centre mechanism.

Finally, the last reaction step—the exchange of the olefinic ligands in the coordination complex—alternates with the preceding stage—transalkylidenation:



The high rate of homogeneous disproportionation can be explained only by a very high rate of the last stage, i.e. the exchange of olefinic ligands. Examples of fast exchange reactions involving certain complexes of olefins with metals are known [91,92]. Thus the replacement of ethylene in Zeise's salt $K[(CH_2{=}CH_2)PICl_3].H_2O$ by other olefinic ligands is very rapid [91,93].

The work of Wang and Menapace[20] on a catalytic system comprising tungsten hexachloride and n-butyl-lithium constitutes further confirmation of the role of coordination interaction in the olefin disproportionation mechanism. Their reaction mechanism includes the substitution of two chlorine atoms in tungsten hexachloride by two alkyl groups, the subsequent mono- or bi-molecular reduction of tungsten(VI) to tungsten(IV), and the coordination of the latter to two pent-2-ene molecules:



The formation of the reaction products from the intermediate coordination complex $W^{IV}Cl_4.2$olefin and the regeneration of the catalyst can be explained using the concepts of Calderon and coworkers [18,19].

Some information concerning the reaction mechanism can be obtained from the analysis of the results reported recently by Kotari and Tatsuma [92], who found that the WCl_6–ethylaluminium dichloride catalytic system can catalyse both alkylation and disproportionation reactions depending on the way in which the process is carried out. If the catalyst is prepared first (in toluene) and then the olefin (pent-2-ene) is added, toluene is rapidly alkylated. When pent-2-ene is added to toluene, then tungsten hexachloride, and finally ethylaluminium dichloride, disproportion mainly takes place. The authors suggested that the catalytically active complex contains reduced tungsten [tungsten(IV)] coordinated to the solvent and aluminium via chlorine bridges. The "quasicyclobutane–tungsten" complex can be converted into a catalytically inactive state by the action of toluene.

It is noteworthy that recently data have been published showing the possibility that homogeneous disproportionation can be interpreted in terms of a non-concerted mechanism including an oxidative addition stage. Thus in a study of the valence isomerisation of cubane catalysed by rhodium compounds, Cassar et al. [94] concluded that the reaction proceeds via a non-concerted oxidative addition mechanism and suggested that the mechanism for a number of reactions, including the disproportionation reaction, might be revised appropriately.

V. STEREOCHEMICAL CHARACTERISTICS OF THE REACTION

The stereochemistry of heterogeneous disproportionation has been hardly investigated; some observations concerning the relative amounts of the *trans*- and *cis*-forms of the reaction products were made only in the disproportionation of C_3–C_5 olefins in the presence of a molybdenum oxide catalyst [5]. Moreover, in a few studies the amounts of *cis*- and *trans*-isomers were fixed. It is therefore at present impossible to arrive at any conclusion concerning the stereoselectivity of heterogeneous disproportionation catalysts.

The stereospecificity of homogeneous catalytic systems is much more pronounced. The stereochemistry of homogeneous disproportionation was investigated using complex catalysts based on tungsten [19,20] and also nitrosyl complexes of molybdenum [22].

Initially, it was found [19] that in the disproportionation of pentene and hexenes (with an internal double bond) in the presence of the WCl_6–$C_2H_5AlCl_2$ + C_2H_5OH catalytic system *trans*-*cis*-products are formed in the proportions predicted by thermodynamics. The final proportions of the isomers are then independent of the *trans*/*cis* ratio in the initial olefins.

The stereochemistry of homogeneous disproportionation was investigated in greater detail [20] in the presence of the WCl_6 + C_4H_9Li complex catalyst, using pure *cis*- and *trans*-isomers of pent-2-ene and also their mixture as the initial olefins. The results of this investigation differ from those of the previous studies. It was found that the ratio of the isomers in the reaction products depends to some extent on the *trans*–*cis* distribution in the initial olefins. The latter factor also determines the degree of conversion of the olefins. The *trans*-isomer reacts much more slowly than the *cis*-isomer or the mixture of the two isomers.

The stereospecificity of the catalyst is fairly high; for example, in the disproportionation of a mixture consisting of 46% of *trans*- and 54% of *cis*-isomers of pent-2-ene the final *trans*/*cis* ratio for but-2-ene was 4.2, which corresponds to 81% of the *trans*-form.

All these findings were fairly convincingly explained on the hypothesis of the formation of an intermediate bisolefin complex [20]. Thus the lower reactivity of *trans*-pent-2-ene compared with the *cis*-isomer is evidently due to the steric hindrance arising in the coordination of *trans*-olefins to the metal.

The discrepancy between the results obtained in the presence of different catalysts for the dependence of the *trans*/*cis* ratio in the reaction products on the stereochemical composition of the initial olefin can probably be explained by additional stereoisomerisation, which may occur owing to cationic aluminium-containing fragments.

Among homogeneous catalysts, nitrosylmolybdenum complexes $(C_5H_5N)_2Mo(NO)_2Cl_2.C_2H_5AlCl_2$ showed the highest stereoselectivity, as demonstrated by the conversion of pent-2-ene into but-2-ene and hex-3-ene [22]. The ratios of the *trans*- and *cis*-isomers of all three olefins reached the equilibrium values regardless of the isomeric nature of the initial pent-2-ene. However, it was found that in the early stages of the reaction the ratio of the isomers is appreciably determined by that in the initial olefin.

Interesting correlations were established between the total concentration of *cis*-olefins in the reaction mixture and the degree of conversion. The rate of disproportionation and the rate of stereoisomerisation were found to

decrease simultaneously, which is apparently evidence of a close relation between these processes and of their occurrence in the presence of the same catalyst.

To account for the above finding, the bisolefin–metal model for the intermediate complex has been successfully employed[22].

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It is not difficult to predict that in the near future new homogeneous systems catalysing the disproportionation of unsaturated hydrocarbons will be found. One can also expect that homogeneous catalysis will make it possible to solve many problems of the practical application of the reaction. The elucidation of the mechanism of the action of homogeneous disproportionation catalysts will promote the application of theoretical concepts in the chemistry of complex compounds to catalytic problems.

At the same time one should expect further advances in the selection and modification of heterogeneous catalysts for the disproportionation of olefins.

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