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Dimerisation of Alkenes

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This review discusses published work on catalysts, reaction conditions, composition of products, and mechanism, relating to the dimerisation of alkenes. It is shown that dimerisation is a very important practical method of synthesis of higher alkenes of various structures. The relationship between the type of catalyst activity and the course of the reaction is demonstrated in the specific case of the dimerisation of propene. An analysis of the activity and selectivity of catalysts is given, and the effectiveness of various methods of dimerisation is assessed from the point of view of their industrial exploitation. The most detailed discussion is given to the literature on the dimerisation of alkenes under the influence of complex organometallic catalysts, which have a very high activity. The major areas of application of dimers as intermediates in petrochemical and general organic synthesis are indicated. 139 references.

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1. INTRODUCTION

Dimerisation of alkenes, unlike polymerisation, is a relatively new area of industrial organic synthesis, developed during the past decade. Previously, liquid polymers of ethylene, propene, and butenes were of relatively limited interest in the production of motor fuel constituents, lubricants, and some synthetic detergents (for example, dodecylbenzenesulphonates). The impetus for the deployment of effort in this direction was provided by Ziegler's discovery in 1952 of the selective dimerisation of alkenes by organoaluminium compounds, which demonstrated the possibility of synthesising individual higher alkenes of known structure. Ziegler's method was quickly adopted in three areas of practical importance: the preparation of but-1-ene by the dimerisation of ethylene, the synthesis of isoprene from propene, and the production of higher alkenes and primary alcohols with a linear carbon chain. The search for new dimerisation catalysts for alkenes was stimulated by a large number of papers on the use of C_4–C_6 alkenes as the starting products in dehydrogenation, oxidation, polymerisation, hydration, and other reactions. Progress in this area would obviously have been impossible but for the development of gas–liquid chromatography, infrared spectroscopy, and nuclear magnetic resonance as standard methods of analysis and identification of alkenes.

Many patents on the dimerisation of alkenes have appeared in recent years, as well as many papers on the mechanism of this reaction under the influence of various catalysts. However, a systematic review of the literature in this area has not yet been attempted: to the best of our knowledge, the present article is the first review of this subject. We shall not attempt to deal exhaustively with the existing literature, but we shall examine instead the correlation between the course of the reaction and the type of activity of the catalysts. The analysis will be made in the specific case of the dimerisation of propene, mainly because of the great practical importance of this reaction at the present time.

2. DIMERISATION CATALYSTS FOR ALKENES

A large number of dimerisation catalysts for alkenes, differing in the composition of the products and in the reaction conditions, has been described. In particular, the use of acidic catalysts for the preparation of liquid polymers (including dimers) of propene and isobutene[1,2] for use as motor fuel constituents and in the synthesis of detergents is well known. Ethylene does not dimerise under the influence of acidic catalysts. With propene, the primary dimerisation products undergo side reactions (polymerisation, isomerisation, disproportionation, etc.[3]). Hence the yield of the dimer of propene is small, and its isomeric composition is quite complex; we are therefore justified in concluding that acidic catalysts are unsatisfactory for the selective dimerisation of propene[4]. However, work on improving the selectivity of acidic catalysts is continuing, and will be discussed below.

Selective dimerisation of ethylene was first achieved with a cobalt catalyst[5]. Schultz and coworkers[6,7] have recently made a detailed study of the dimerisation of various alkenes on catalysts of this type. The main disadvantage of catalysts based on cobalt oxide is their relatively low activity, which limits the prospects of their industrial application.

The dimerisation of propene by finely dispersed potassium in a hydrocarbon medium[8] was reported in 1961. In spite of the low activity of the catalyst and of the stringent conditions of the reaction, the process has undergone considerable development in connection with the production of 4-methylpent-1-ene, an important monomer and intermediate in industrial organic synthesis.

The dimerisation of alkenes by Ziegler's method with alkylaluminium catalysts[9] offers the greatest practical interest at present. Thus, the dimerisation of propene in the presence of tripropylaluminium is the basis of an industrial method of preparation of isoprene from propene [10,11]. A process for the codimerisation of ethylene and propene to give 2-methylbut-1-ene, followed by dehydrogenation to

isoprene, has been developed[12]. The dimerisation of ethylene in the presence of triethylaluminium gives very pure but-1-ene, used in the production of high-quality polymeric products[13].

The dimerisation of alkenes under the influence of complex organometallic catalysts proceeds under mild conditions and with high yields of product. In 1961 a method of oligomerisation of ethylene with homogeneous catalytic systems of the Ziegler type was proposed in the U.S.A., based on alkylaluminium halides and nickel compounds[14], and in 1963 a method of dimerisation of propene was proposed in the U.S.S.R. using catalysts of very similar composition, as well as a method for the production of dienes by means of these catalysts[15-17]. The dimerisation of propene by alkylaluminium halides in conjunction with organic nickel salts has also been patented by the Shell Company[18].

The first reports of the dimerisation of alkenes by complex Ziegler catalysts were published almost simultaneously in West Germany[19,20], France[21], and the U.S.S.R.[22-24]. Ewers[19] used a highly active homogeneous catalyst prepared by treating nickel acetylacetonate, bis-(π-allyl)nickel, or π-allylnickel chloride with a dialkylaluminium chloride in a toluene medium. A paper by Wilke and coworkers[20] describes the dimerisation of ethylene and propene under the influence of π-allylnickel chloride in conjunction with Lewis acids and tertiary phosphines. Chauvin and coworkers[21] used the catalytic system nickel acetylacetonate–ethylaluminium dichloride. Complex dimerisation catalysts for alkenes based on various π-complexes of nickel have been proposed[25].

The dimerisation of ethylene and propene and the codimerisation of these alkenes under the influence of catalytic systems based on alkylaluminium halides and organic nickel salts[22-24], similar to the stereospecific polymerisation catalysts for butadiene[26], is characterised by very mild conditions (room temperature and normal pressure). There is a marked difference between these catalysts and alkylaluminium catalysts containing "colloidal" nickel: the latter also are dimerisation catalysts for alkenes[27], but they require more stringent reaction conditions leading to the formation of dimers of different structure.

Thus, the dimerisation of alkenes can be achieved with catalysts of quite different type. Accordingly, a variety of dimerisation mechanisms and of structures of the resulting product are observed. The specific features of the dimerisation of various alkenes are discussed in detail below.

3. DIMERISATION OF ETHYLENE

According to Cheney and coworkers[28], ethylene dimerises on a cobalt catalyst at 40°C and 50 atm pressure with a conversion of ~ 50%, and 80% selectivity with respect to butenes. The conversion of the monomer and the composition of the dimer depend on the contact time: with an input of ethylene of 72 g per 1 litre of catalyst per hour the conversion is 74% and the main product of the reaction is but-2-ene (91%); if the input is raised to 360 g litre^{-1} h^{-1} the conversion drops to 37% and the dimer contains up to 70% of but-1-ene. Treating the carrier (activated carbon) with aqueous ammonia increases the activity of the cobalt catalyst but degrades its selectivity towards dimerisation[6,7]: the yield consists of ~ 20% butenes, 60% hexenes, and 20% high-boiling hydrocarbons. The hexene fraction consists mainly of linear alkenes. A great deal of work has been published on the dimerisation of ethylene on nickel catalysts[29-35]. The above solid dimerisation catalysts have not been exploited industrially so far because they are difficult to prepare, they have low activity and stability, and for a number of other reasons.

At the present time, the dimerisation of ethylene by homogeneous catalysis (and in particular using triethylaluminium as the catalyst) is attracting most attention. By this method[9], pure but-1-ene can be obtained with high yield by withdrawing it from the reactor as soon as it is formed or by carrying out the reaction in the presence of "colloidal" nickel[27]. The dimerisation of ethylene by Ziegler's method has been studied at the Scientific Research Institute of Synthetic Alcohols and Organic Products (NIISS)[36] and at the All-Union Scientific Research Institute of Olefins (VNIIOlefin)[37]. The purest but-1-ene is obtained at low conversions of the ethylene. Thus, it is convenient to prepare a mixture of ethylene and butene (containing up to 10% of butene) and to use it as the raw material for the production of a copolymer having good mechanical properties[37]. At higher conversions of the ethylene (20%), appreciable amounts of C_6 and C_8 alkenes are produced as well as but-1-ene.[38] Chernikova[13] studied the influence of various nickel compounds (as additives to the triethylaluminium) on the rate and selectivity of the dimerisation of ethylene. She suggests that the ethylene is activated on the surface of freshly reduced nickel, and this assists its further penetration along the aluminium–carbon bond.

Various catalytic systems for the dimerisation of alkenes based on aluminium alkyls and transition metal alkoxides have been proposed. Their activity is higher than that of the aluminium alkyls[39-42]: for example, ethylene dimerises at 50–100°C and 1–10 atm in the presence of triethylaluminium and tetrabutoxytitanium with up to 65% yield of but-1-ene[41]. The dimerisation of ethylene to but-2-ene at 0°C in the presence of the triethylaluminium–cobalt acetylacetonate catalytic system has also been reported[43].

Unlike the aluminium alkyls, alkylaluminium halides by themselves dimerise alkenes only in very low yields, even under drastic conditions[44]. However, they yield active dimerisation catalysts for ethylene in conjunction with dialkyldihalogenostannanes[45].

The most active dimerisation catalysts are prepared by treating alkylaluminium halides with nickel compounds. The use of these catalysts for the production of high-molecular-weight polyethylene was patented by Ziegler[46]. The dimerisation of ethylene under the influence of catalysts of this type has also been described in a patent[14]. The reaction was carried out in the presence of the complex of nickel carbonyl with triphenylphosphine, in conjunction with ethylaluminium sesquichloride, at 100°C and 30 atm. Subsequently, more active catalytic systems were disclosed, in which the nickel compounds were salts of organic acids, phenols, enols, or sulphonic acids, which are fairly readily soluble in hydrocarbon solvents[18]. An even more active catalyst was prepared from nickel acetylacetonate, ethylaluminium sesquichloride, and triphenylphosphine[19]: in this system, 18×10^5 moles of ethylene are dimerised in 15 min at 60°C per g-atom of nickel. The yield of butenes can be as high as 94%, with a 95% content of but-2-ene. As well as butenes, catalysis by systems of this type produces hexenes, the relative yield of ethylene dimers and trimers depending on the rate at which ethylene is passed through the catalyst solution[22].

Obviously, the chlorides of the platinum group metals and their complexes with alkenes[47-50] cannot find extensive practical application as dimerisation catalysts for alkenes because they are too expensive as well as being insuffici-

ently active. Palladium chloride dimerises ethylene with up to 90% selectivity at 20–70°C and 1–40 atm.[50] The yield of butenes is found to be very sensitive to the nature of the solvent[50]. A Dutch patent[48] recommends the use of a nitro-compound as the medium for this reaction. It has been suggested[50] that palladium chloride initiates the dimerisation in the presence of hydrogen chloride by a mechanism analogous to that of the Friedel–Crafts catalysts:

$$CH_2{=}CH_2 \xrightarrow[HCl]{PdCl_2} CH_3CH_2^+ PdCl_3^- \xrightarrow{CH_2=CH_2}$$

$$\rightarrow (CH_3CH_2CH_2CH_2)^+ PdCl_3^- \rightarrow (CH_3CH_2\overset{+}{C}HCH_3)\, PdCl_3^- \rightarrow CH_3CH{=}CHCH_3 + PdCl_2 + HCl$$

Rhodium chloride is active in the dimerisation of ethylene at 30–50°C, whereas ruthenium chloride requires a higher temperature[51].

Cramer[52] made a detailed study of the dimerisation of ethylene under the influence of rhodium chloride in alcoholic HCl solutions, and proposed the following mechanism for the reaction:

$$\begin{array}{ccc} Rh^{III}Cl_3 \cdot 3H_2O & & C_2H_4 + [C_2H_5Rh^{III}Cl_3S]^{2-} \quad (B) \\ +C_2H_4 \downarrow (1) & & +S \uparrow\downarrow -S\ (3) \\ (A)\ [Cl_2Rh^{I}(C_2H_4)_2]^- & \xrightarrow[(2)]{+H^+,\,Cl^-} & [C_2H_5Rh^{III}Cl_3(C_2H_4)S]^- \quad (C) \\ +C_2H_4 \uparrow -C_4H_8\ (6) & & +S \downarrow (4) \\ (E)\ [Cl_2Rh^{I}S(CH_3CH_2CH{=}CH_2)]^- & \xleftarrow[(5)]{-H^+,\,Cl^-} & [CH_3CH_2CH_2CH_2Rh^{III}Cl_3S_2]^- \quad (D) \end{array}$$

($S = Cl^-, H_2O$ or solvent).

Activation of the catalyst (*1*) occurs by the reaction between $RhCl_3$ and ethylene with formation of a complex anion of univalent rhodium with two ethylene ligands. This is followed by fast protonation (*2*) of the complex (A) to give the ethyl derivative (B), and by addition (*4*) of a coordinated molecule of ethylene at the rhodium–carbon σ-bond (limiting step), with formation of the butyl derivative (D). The latter is rapidly converted into the complex (E) containing a butene ligand, which is rapidly replaced by ethylene, reaction (*6*). Thus, the starting complex (A) is regenerated. The author[52] introduces the ligands *S* into the formulae in order to satisfy the coordination numbers of Rh^{I} and Rh^{III} (4 and 6 respectively).

4. DIMERISATION OF PROPENE

a. Cationic Dimerisation

Catalysts of the acidic type have not gained wide acceptance in practice for the selective dimerisation of propene because of the low yields and complex composition of the dimer, due to the possibility of side reactions under the conditions of dimerisation. The reactivity of low-molecular-weight alkenes towards dimerisation under the influence of acidic catalysts increases very significantly in the series ethylene–propene–isobutene, as a result of the electronic σ,π conjugation effect. A proton (or cation) attacks the propene molecule in accordance with Markovnikov's rule:

$$CH_3{-}CH{=}CH_2 \xrightarrow{+H^+} CH_3{-}\overset{+}{C}H{-}CH_3$$

$$CH_3{-}CH{=}CH_2 + CH_3{-}\overset{+}{C}H{-}CH_3 \rightarrow CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightarrow$$

$$\xrightarrow{-H^+} CH_3{-}\underset{CH_3}{CH}{-}CH{=}CH{-}CH_3\ .$$

The resulting intermediate isohexyl carbonium ion usually interacts rapidly with the next propene molecule to give the trimer, and so on. Also, the secondary carbonium ion is not stable[53], and easily rearranges according to the scheme

$$CH_3\overset{+}{C}HCH_2CH_3 \xrightarrow{-H^+} \text{4-methylpent-1-ene, 4methylpent-2-ene}$$

$$CH_2\overset{+}{C}HCH_2CH_3 \;(CH_3 \text{ on } CH_2) \rightarrow CH_3\overset{+}{C}(CH_3){-}CH_2CH_2CH_3 \xrightarrow{-H^+} \text{2-methylpent-1-ene, 2-methylpent-2-ene}$$

$$CH_2\overset{+}{C}HCH_2CH_3 \;(CH_3 \text{ on } CH_2) \rightarrow CH_3\overset{+}{C}H{-}CH(CH_3){-}CH_2CH_3 \rightarrow \text{3-methylpent-2-ene, 3-methylpent-1-ene.}$$

As a result of these reactions the propene dimer has a complex isomeric composition in which 2- and 3-methylpentenes predominate, being thermodynamically the most stable. The same is true also for catalysts such as alumina–silica, boron trifluoride, aluminium halides, zinc chloride, etc.

Attempts have been made to increase the selectivity of the dimerisation of propene under the influence of acidic catalysts, mainly by the addition of various modifiers. For example, the propene dimer obtained in the presence of 0.5% phosphoric acid containing metallic copper consists of ~ 64% methylpentenes and can be used for the production of isoprene[54]. The firm "Scientific Design Co." has patented a process for the dimerisation of propene having up to 95% selectivity, using an alumina–silica catalyst treated with a 10% solution of sodium carbonate. However, the conversion of propene under these conditions does not exceed 5%, which detracts very significantly from the value of the method[55]. Enhanced selectivity for the dimerisation of propene has been reported by using the following catalysts: phosphoric acid containing propan-2-ol,[56] alumina–silica modified by transition metal oxides[57] and sulphides[58], and magnesium silicate[59].

b. Anionic Dimerisation

Numerous patents have been filed on the dimerisation of propene under the influence of alkali metals in the form of dispersions in hydrocarbon media[8,60–64], or supported on carriers (graphite, active carbon, alumina, talc, etc.)[65–70]. Catalysts of this type are attracting considerable interest because they allow 4-methylpent-1-ene, an important monomer, to be prepared from propene. The stereoregular polymers which can be prepared from 4-methylpent-1-ene are superior to other thermoplastics in their overall properties[71]. They have a very low density, and a higher melting point than polyethylene or polypropene, as well as being good electrical insulators. Moulded articles and fibres of poly-(4-methylpent-1-ene) have a high tensile strength[72]. The dimerisation reaction requires drastic conditions (150–200°C, 50–70 atm) and long contact times. In order to shorten the induction period, alkylphenols[73,74], ethers[75], or alkyl halides[76] are often added to the catalyst as promoters. The catalyst for use on a solid carrier is prepared[77] by blending the molten alkali metal with particles of the carrier at 225–500°C.

The yield of the propene dimer varies between 70 and 95% of the propene used. The primary dimerisation product is 4-methylpent-1-ene. However, dimerisation can be accompanied by migration of the double bond of the alkenes by the scheme

4-methylpent-1-ene ⇌ 4-methylpent-2-ene ⇌ 2-methylpent-2-ene

and therefore the composition of the dimerisation product depends on the exact form of the catalyst and on the reaction conditions. The choice of carrier plays an important role: in particular, its porosity should not be too high[71]. A proposed dimerisation catalyst consists of sodium or lithium, dispersed on an anhydrous potassium salt[78-81]. The dimerisation of propene by a continuous method[65] at 140°C and 100 atm, and a volume velocity of 0.7 h^{-1}, on a Na/K_2CO_3 catalyst, gives a dimer of the following composition: 4-methylpent-1-ene (85%), 4-methylpent-2-ene (7%), 2-methylpent-2-ene (0.5%), 2-methylpent-1-ene (0.5%), and n-hexenes (7%). Separation of 4-methylpent-1-ene and 4-methylpent-2-ene is difficult because the boiling points are very similar. Hence, the use of a mixture of the two isomers in the polymerisation has been suggested[71]. In a Belgian patent[65], the dimer was fractionated on a column with an efficiency of 100 theoretical plates, with a 60% take off, giving a distillate containing 99.9% of 4-methylpent-1-ene.

Using potassium on granulated magnesia as the dimerisation catalyst, the product contains 55% of 4-methylpent-1-ene, 38% of 4-methylpent-2-ene, and 7% of other hexenes[82]. Polymerisation of a mixture of alkenes of approximately this composition in the presence of $AlBr_3$ has been suggested for the preparation of a liquid polymer useful for electrical insulation and as a lubricating oil additive[83]. Alkali metals on graphite[84], active carbon[85], carbon black[86], alumina[87], magnesium silicate[88], and metal hydrides[89] catalyse the dimerisation of propene mixed with methylpentenes of various compositions. These catalysts can be regenerated by being heated to 200–300°C in a stream of hydrogen[85,86].

The dimerisation mechanism of propene in the presence of alkali metals has been investigated by Shaw and coworkers[90], who suggest that the reaction involves the formation of an organometallic compound with a strongly polar M–C bond on the catalyst surface. Partial dissociation with formation of carbanions as kinetically independent particles is possible:

$$CH_3{=}CH{-}CH_3 \xrightarrow{M} [CH_3 \cdots CH \cdots CH_3]^- M^+ .$$

The allyl carbanion attacks a propene molecule. The resulting isohexyl carbanion, unlike the allyl carbanion, is not stabilised by interaction of an unshared electron pair with the double bond. It is very reactive, and extracts a proton from the next propene molecule. The end result of these transformations is the production of 4-methylpent-1-ene and simultaneous regeneration of an allyl carbanion:

$$[CH_2{=}CH{=}CH_2]^- M^+ + \overset{\delta^-}{CH_2}{=}\overset{\delta^+}{CH}{-}CH_3 \longrightarrow CH_2{=}CHCH_2\underset{CH_3}{\underset{|}{C}}HCH_2\ M^+ \longrightarrow$$
$$\xrightarrow{+C_3H_6} CH_2{=}CHCH_2\underset{CH_3}{\underset{|}{C}}HCH_3 + [CH_2{=}CH{=}CH_2]^- M^+ .$$

Isomerisation of 4-methylpent-1-ene occurs through the formation of a carbanion with migration of an allyl proton:

$$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH{=}CH_2 + R^-M^+ \xrightarrow{-RH} \left[CH_3\underset{CH_3}{\underset{|}{C}}HCH \cdots CH \cdots CH_2\right]^- M^+ \xrightarrow{+RH}$$
$$\rightarrow CH_3\underset{CH_3}{\underset{|}{C}}HCH{=}CHCH_3 + R^-M^+ .$$

The following alkali metal derivatives as well as the alkali metals themselves are used as dimerisation catalysts: hydrides[91-93], amides[94,95], and carbides[96]. The reaction conditions and the composition of the products obtained in the presence of these catalysts are about the same as when alkali metals are used. The dimerisation of propene under the influence of carbon complexes of the alkali metals has been proposed as the first stage in the synthesis of isoprene from propene[97]. A dimer containing ~ 65% of 4-methylpent-2-ene is isomerised into a mixture of 2-methylpent-2-ene and 3-methylpent-2-ene on an alumina-silica catalyst at 290°C, followed by pyrolysis at 670°C with a contact time of 0.5 s and dilution with water vapour in the molar ratio of 1 : 5.

The alkyl derivatives of alkali metals also catalyse the dimerisation of propene at temperatures between 40 and 225°C and pressures up to 250 atm.[98] Complexes of the general formula AMR_3 can also be classified with this type of catalyst, where A is an alkali metal, M is zinc, cadmium, tin, or lead, and R is hydrogen or a hydrocarbon radical[99]. Because of the low activity of these catalysts, contact times of up to 20 h are needed[99], which argues against their practical exploitation.

Thus, catalysts based on the alkali metals and their derivatives can dimerise propene, with a high yield of the desired product, but they require the application of high temperatures and pressures, and long contact times, and they are also very sensitive to impurities in the feed material. According to patent specifications[65,97], the water content of the starting propene should not exceed 0.001%, that of methylacetylene and allene 0.02%, and the oxygen content should not exceed 0.0005 wt.%†.

c. Organometallic Synthesis

The dimerisation of propene by Ziegler's method[9] in the presence of aluminium alkyl catalysts leads to the formation of pure 2-methylpent-1-ene. Due to the absence of isomerisation reactions, 2-methylpent-1-ene is obtained in up to 95% yield[27]:

$$\overset{\delta^+\ \delta^-}{al{-}CH_2CH_2CH_3} + \overset{\curvearrowright}{CH_2}{=}CH{-}CH_3 \longrightarrow al{-}CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

$$al{-}CH_2\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3 \longrightarrow al{-}H + CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2CH_2CH_3$$

$$\overset{\delta^+\ \delta^-}{al{-}H} + \overset{\curvearrowright}{CH_2}{=}CH{-}CH_3 \longrightarrow al{-}CH_2CH_2CH_3 \quad \text{etc.}$$

$(al = \frac{1}{3}\,Al)$

In addition to the main reaction, "anomalous" addition of propene occurs to a minor extent, giving 5–6% of n-hexenes. The selectivity for dimerisation is strongly dependent on temperature[10,11], pressure, and contact time[10]. Studies of the dimerisation kinetics[100,101] have shown that the reaction order with respect to propene is close to unity. Activation energies of 11.7[100] and 14 kcal $mole^{-1}$ [101] have been reported.

Many modifications of the Ziegler method are known. For example, additions of boron alkyls have been made to the catalyst[102] in order to increase the rate of dimerisation. For the same purpose, various metal additions have been suggested, in particular aluminium, copper, or silver[103], and also salts such as iron(III) chloride[104]. To increase the yield of the propene dimer, the reaction has

† It has recently been announced[139] that the British Petroleum Company has established the production of 4-methylpent-1-ene on a semi-industrial scale (output 2000 tonnes per annum). The bulk of this product is delivered to I.C.I. for the production of polymers. Among the possible uses of 4-methylpent-1-ene we note the dimerisation to 2-isobutyl-6-methylhept-1-ene (in the presence of aluminium alkyls), oxidation to isobutyl methyl ketone in the presence of palladium chloride, autoxidation to epoxyalcohols, isomerisation to 2-methylpent-2-ene, and halogenation[139].

been carried out in a high-boiling organic solvent[105], and the linear velocity of the reactant stream through the reactor has been controlled[106]. Aluminium alkyls containing nickel or platinum compounds[107,108] have also been used as catalysts. An interesting method of dimerisation of alkenes with an internal double bond uses an alkylaluminium containing 1–20 wt. % of alumina–silica, zeolite, silica gel, activated alumina, or other cocatalyst[109].

The Ziegler dimerisation of propene is used as the first stage in the production of isoprene from propene[10,11]. The Goodyear Company, which produces 2-methylpent-1-ene on an industrial scale, has carried out research on the use of the propene dimer as a starting material in industrial organic synthesis[110]. In the Soviet Union, work in this direction is proceeding at the Yaroslavl' Technological Institute[111].

d. Coordination Dimerisation

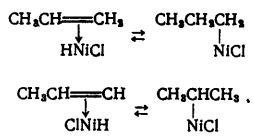
In this Section we shall discuss the dimerisation of propene under the influence of complex organometallic catalysts. The special feature of the mechanism of action of these catalysts is the formation of intermediates consisting of mixed transition metal complexes with alkene ligands. Thus, it is convenient to refer to this type of dimerisation as coordination dimerisation.

The complex catalysts of the Ziegler type, based on alkylaluminium halides and nickel compounds, are extremely active towards the dimerisation of propene under quite mild reaction conditions, and in this respect they are distinctly superior to the catalysts of the types discussed above. For example, a catalyst prepared by mixing 1 mmole of nickel acetylacetonate, 45 mmole of ethylaluminium sesquichloride, and 16 mmole of triphenylphosphine gives 2.6×10^5 moles of the propene dimer (90% yield) in 2 h at 60°C and 10 atm in a toluene medium[19]. The dimer contains 4-methylpent-2-ene (37.0%), 2-methylpent-2-ene (26.5%), 2-methylpent-1-ene (17.4%), 4-methylpent-1-ene (1.6%), 2,3-dimethylbut-1-ene (6%), 2,3-dimethylbut-2-ene (0.5%), hex-2-ene (5.6%), and hex-3-ene (5.6%).[19] A propene dimer containing 75% of methylpentenes and 20% of n-hexenes is formed in the presence of a catalytic system based on π-allylnickel iodide, aluminium bromide, and triphenylphosphine[25]. Replacing the triphenylphosphine by tricyclohexylphosphine yields a dimer containing 67% of dimethylbutenes and 31% of methylpentenes[25]. Catalysts based on π-allylnickel chloride are reported to be used for the dimerisation of propene on a laboratory scale at the Max Planck Institute (Mülheim, W.Germany).[20,112] Trialkylphosphines are added to the catalyst to increase its activity and to obtain products of desired structure[20]. At 30–50°C and 15 atm pressure the conversion of propene is 95%, and the selectivity with respect to the dimer is 88%. The Lurgi–Ruhrgas company has planned an industrial plant for the dimerisation of propene having a capacity of 80 000 tonnes per annum[112]. Its main product is expected to be 2,3-dimethylbut-2-ene, which is intended to be used for the production of 2,3-dimethylbuta-1,3-diene and motor fuel constituents[112]. Dimerisation of ethylene can be achieved in the presence of bis(cyclopentadienyl)nickel[113], and dimerisation of propene by using phosphine complexes of nickel in conjunction with Lewis acids[114].

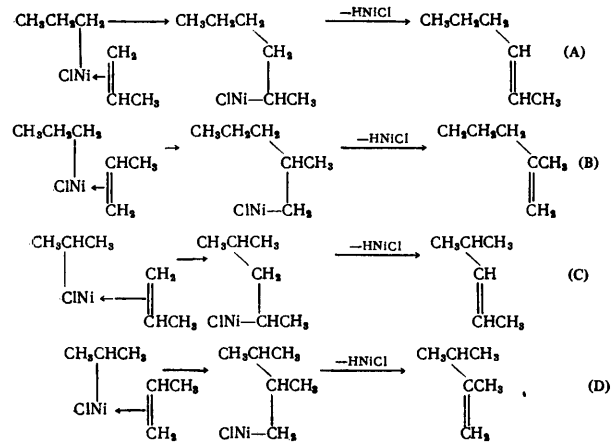
It has been suggested that the activity of complex Ziegler catalysts towards the dimerisation of alkenes[23] and similar reactions[115] arises from the formation of complex hydrides and alkyl derivatives of the transition metal, for example, HNiCl, coordinated to the alkylaluminium halide. The initiation of the dimerisation and the regeneration of the catalyst after each reaction cycle can thus be explained[115]:

$$C_3H_4 + HNiCl \rightarrow C_3H_5NiCl$$
$$C_3H_5NiCl + C_3H_4 \rightarrow C_6H_9NiCl$$
$$C_6H_9NiCl \rightarrow C_6H_8 + HNiCl \text{ etc.}$$

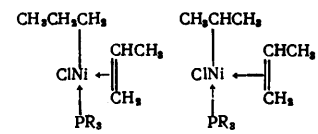
A later, more detailed mechanism for the dimerisation accounts for the structure of the propene dimer and for the influence of tertiary phosphines on the course of the reaction[116]. Two configurations of the alkene ligands are possible in the intermediate π-complexes, leading to the formation of different alkyl derivatives of the transition metal:



The subsequent coordination of a second molecule of alkene can give four types of π-complexes, leading to dimers of different structure:



Paths (B) and (D) are least likely, because of steric hindrance to the formation of the starting π-complexes. But these can be stabilised by the addition of trialkylphosphines to the system[117]:

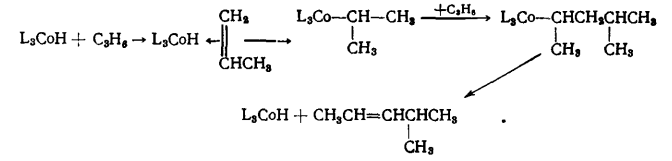


leading to the formation of 2-methylpent-1-ene and 2,3-dimethylbut-1-ene as the primary dimerisation products, which then isomerise to 2-methylpent-2-ene and 2,3-dimethylbut-2-ene respectively.

Complex catalysts based on alkylaluminium halides and nickel salts are active in the isomerisation of alkenes, which occurs under the conditions of the dimerisation reaction and determines the final composition of the reaction products[22,118]. Impurities in the starting alkene can drastically affect the rate of dimerisation of propene[24].

The dimerisation of propene under the influence of cobalt oxide deposited on active carbon can also be classified as coordination dimerisation, because the mechanism proposed by Schultz and coworkers[6] for this reaction includes the formation on the catalyst surface of π-complexes and complex alkyl derivatives of cobalt. This catalyst is peculiar in that large amounts (50–55%) of n-hexenes are formed in its presence. The catalyst is thermally unstable, and

therefore the yield of dimer decreases on raising the temperature (the conversion is 72.7% at the optimum temperature of 85°C). Diene hydrocarbon impurities poison the catalyst irreversibly. The authors suggest that the entity responsible for catalysis is a complex hydride of cobalt having at least one coordination position free to form a π-complex with the alkene[6]:



5. DIMERISATION OF BUTENES AND HIGHER ALKENES

Most of the dimerisation catalysts for ethylene and propene should be suitable, in principle, for the dimerisation of C_4 and higher alkenes. However, practically all the published data relate exclusively to acidic catalysts and organoaluminium compounds, because they offer acceptable yields of the dimers.

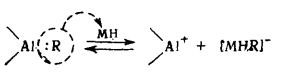
The preparation of the dimer of isobutene in the presence of acidic catalysts (aimed at producing motor fuel constituents) has been known for a long time and does not require special discussion. Higher asymmetrical dialkylethylenes, and also trialkylethylenes, undergo dimerisation similarly to isobutene. For example, 2-methylpent-1-ene in the presence of 70% H_2SO_4 at 50°C dimerises in 30 min with a yield of 80% (on the basis of the added monomer) and 95% (on the basis of the reacted monomer)[111]. High selectivity for the dimerisation of 2-methylpent-1-ene and 2-methylpent-2-ene has been reported for H_3PO_4 on kieselguhr[111] and on an alumina–silica catalyst[119]. It has been pointed out that the dimer of isohexenes boils over a very narrow range of temperatures[111]. The structure of the dimer has recently been investigated[120], and shown to include the following main components: 2,4,4-trimethyl-3-ethylhept-1-ene, 4,6,6-trimethylnon-3-ene, and 4,6,6-trimethylnon-4-ene. Polyanskii and coworkers[121] have investigated the dimerisation of isopentenes on a cation-exchange resin.

In the presence of aluminium alkyls, but-1-ene smoothly dimerises to 2-ethylhex-1-ene, and hex-1-ene to 2-butyloct-1-ene.[9] The dimerisation of butenes by this method has been studied at the Scientific Research Institute of Synthetic Alcohols and Organic Products[122,123].

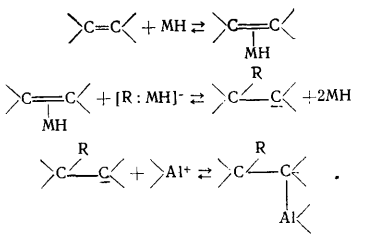
Sladkov and coworkers demonstrated that but-1-ene, but-2-ene, and their mixtures can be used to prepare 2-ethylhex-1-ene in the presence of triethylaluminium and cocatalysts[122]. They proposed a reaction mechanism which explains the role of the transition metal cocatalysts. It is assumed[123] that the interaction between triethylaluminium and the metal compounds (silver, cobalt, nickel, etc.) gives rise to "subcompounds" of the metals in a reduced state according to the scheme

$$M^{+n} \xrightarrow{+me} M^{+(n-m)}.$$

These exist as hydrides or halides (M^+H^- or M^+Cl^- respectively), which are highly electrophilic. The role of the subcompounds in substitution, isomerisation, and polymerisation reactions is discussed. Thus, polymerisation reactions are assisted by "sub-ions" through the formation of active ions from aluminium alkyls:



and they also interact with the double bond and enhance its electrophilic properties:



Alkenes with internal double bonds also dimerise in the presence of aluminium alkyls, but more slowly, and they undergo preliminary isomerisation to the corresponding α-alkenes. Thus, hept-1-ene and hept-3-ene form the same dimer[124]. Dimerisation of alkenes with 3–12 carbon atoms has been proposed[125] in the presence of aluminium alkyls containing trialkylboranes at 195–200°C. For example, hex-2-ene is converted into 2-butyloct-1-ene (in 20% yield) in 4 h under the influence of tri-isobutylaluminium and tributylboron. Similarly, 4-methylpent-1-ene and 2-methylpent-1-ene dimerise to 2-isobutyl-6-methylhept-1-ene. It is thought that trialkylborane promotes the isomerisation of the β-alkene to an α-alkene, which subsequently dimerises[125].

But-1-ene and but-2-ene dimerise at 20°C under the influence of the di-isobutylaluminium chloride–nickel oleate catalytic system (yield of dimer ~ 70%). Infrared and NMR spectral studies of the dimer have shown the presence of 3-methylheptenes, 3,4-dimethylhexenes, and n-octenes, with various positions of the double bond[126].

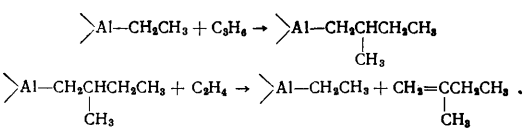
The dimerisation of butenes and hexenes over a cobalt oxide catalyst (13%) supported on carbon has been studied in detail by Schultz and coworkers[6]. After 6 h at 150°C, but-1-ene is converted (13.6% conversion) into a dimer containing 65.3% of n-octenes, 34.4% of 3-methylheptenes, and 0.3% of 3,4-dimethylhexenes. Hex-1-ene gives, after 12 h at 150°C, 18.6% of a product which after hydrogenation contains 82.8% of n-dodecane, 14.8% of 5-methylundecane, and 2.4% of 4-ethyldecane[6]. Alkenes with more than six carbon atoms are dimerised in the liquid phase at 30–40°C over alumina promoted by HF (1%) with 10–20 min contact times. The dimers are used in the production of lubricants and alcohols for the synthesis of plasticisers[127]. Dodecenes have been prepared by the dimerisation of the dimer of propene in the presence of the hydrate of boron trifluoride[128] or of the $BF_3.H_3PO_4$ complex[129].

An interesting method for the dimerisation of higher branched alkenes in the liquid phase relies on brief exposure to high-intensity radiation. The radiation can be in the form of fast electrons, X-rays, gamma rays, or radiation from nuclear reactors[130]. The dimer of di-isobutene was prepared by this method in 74% yield. The mechanism of the radiation-induced dimerisation of higher alkenes has been the object of special investigations[131].

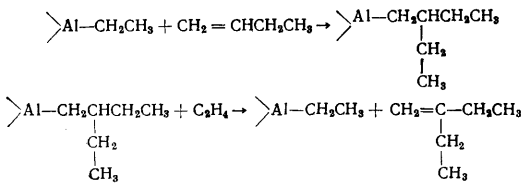
6. CODIMERISATION OF ALKENES

When a mixture of alkenes is used as the starting material, separate dimerisation of each of the alkenes can occur, or alternatively molecules of different alkenes can be combined. In the latter case the term "codimerisation" is appropriate. Most of the catalysts described above allow the codimerisation of ethylene with propene and other alkenes.

The most important application of codimerisation at present is the Ziegler[9] codimerisation of ethylene with propene (or but-1-ene) as a basis for the production of isoprene on an industrial scale[12]. The method depends on the addition of propene to triethylaluminium, followed by the replacement of 2-methylbut-1-ene by ethylene:



Similarly, 2-ethylbut-1-ene can be prepared from ethylene and but-1-ene:



The preparation of isoprene from ethylene and propene has been disclosed in a patent[132]. A mixture of 56.4 g of triethylaluminium and 12.6 g of propene was heated in an autoclave for 30–60 min at 130–140°C. After cooling, a small quantity of "colloidal" nickel was added (as a cocatalyst for the displacement step), 6.72 litres of ethylene were added, and the displacement reaction was carried out by heating the reaction mixture at 160–170°C for 2–3 h. A 20 g yield of 2-methylbut-1-ene was obtained, and subsequently dehydrogenated to isoprene at 700°C on a Fe_2O_3–MgO catalyst, using a 1 : 10 dilution of the vapour. According to another patent[133], 2-methylbut-1-ene can be obtained in ~ 90% yield by the codimerisation of ethylene and propene in a single stage, in the presence of tri-isopentylaluminium at 125–135°C, and with a 3 : 3 : 1 molar ratio of ethylene : propene : $(iso\text{-}C_5H_{11})_3Al$. An interesting method[134] for the simultaneous preparation of 2-methylbut-1-ene and 2-methylpent-1-ene relies on contacting an ethylene–propene mixture with triethylaluminium for 5–50 s at 220–300°C.

Garmonov and Chevychalova[135] prefer to carry out the addition of propene to triethylaluminium at 120–180°C and 40–50 atm, and the displacement reaction at 20°C and 15 atm in the presence of nickel (0.2% on the basis of the aluminium alkyl). Babaev[136] examined some special features of the codimerisation of alkenes in the presence of tri-isobutylaluminium. He attempted to codimerise ethylene with propene in a single stage, but the yield of isopentene did not exceed 30%. In the codimerisation of ethylene with but-1-ene at 225°C, a C_6 fraction containing up to 90% of 2-ethylbut-1-ene is formed in 30% yield[136]. It should be noted that 2-ethylbut-1-ene can be used for the preparation of isoprene by isomerisation to 3-methylpent-2-ene followed by pyrolysis[10].

Normal pentenes are the main product of the codimerisation of ethylene and propene in the presence of alkali metals on carriers[79,91,137]. For example, when potassium supported on talc is used as a catalyst at 115°C, the product obtained from ethylene and propene contains 70% of pent-1-ene, 26% of pent-2-ene, and 4% of hexenes[137]. Ethylene and isobutene undergo codimerisation on a Na/K_2CO_3 catalyst to give a mixture of 2-methylpent-1-ene and 2-methylpent-2-ene in various proportions. The codimer obtained from ethylene and but-1-ene under similar conditions contains 52% of 3-methylpent-1-ene, 21% of 3-methylpent-2-ene, and 27% of n-hexenes. Ethylene and but-2-ene give a product of the following composition: 3-methylpent-1-ene (47%), 3-methylpent-2-ene (16%), hex-2-ene (32%), and hex-3-ene (5%).[79] The product of the codimerisation of ethylene and but-2-ene has been suggested as a starting material for the production of isoprene[138].

Under the influence of complex organometallic catalysts, the alkenes undergo individual reactions as well as codimerisation[22]. When a mixture (1 : 1) of ethylene and propene is passed through a catalyst solution of di-isobutylaluminium chloride and nickel oleate (Al : Ni = 100) at 25°C and 1 atm pressure, the product contains 23% of butenes, 43% of pentenes, 22% of hexenes, and 12% of higher hydrocarbons. The pentene fraction contains 60.7% of pent-2-ene, 35.3% of 2-methylbut-2-ene, 2.6% of 2-methylbut-1-ene, and 1.4% of pent-1-ene.[22] A similar composition of the product is observed when cobalt oxide on carbon is used as the catalyst[7]. In this instance 40% of pentenes is formed, containing ~ 80% of pent-2-ene.

The codimerisation of ethylene with propene under the influence of rhodium chloride in alcoholic solution at 60°C and 1000 atm pressure for 16 h has been described[51]. The product is a mixture of pentenes and hexenes. Analytical hydrogenation of the C_5 alkenes yielded approximately equal amounts of n-pentane and 2-methylbutane.

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