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The Reactions of Mono-olefins in the Presence of Alkali Metals and Their Derivatives

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Studies devoted to reactions of mono-olefins in the presence of alkali metals and their derivatives—mainly metallation, dimerisation, codimerisation, and isomerisation reactions—are reviewed. The catalysts, the reaction conditions, the product composition, and the problems of the reaction mechanisms are considered. It is shown that the specificity of the action of alkali metal catalysts is associated with the common features of the formation and reactions of organic derivatives of the alkali metals and that the reactions in the presence of such catalysts may serve as a basis for the development of promising procedures for the processing of mono-olefins.
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I. INTRODUCTION

Mono-olefins are the main raw material in modern petrochemical industry; their world-wide manufacture runs into many millions of tonnes per year. For this reason, studies on the reactions of these hydrocarbons are as a rule of great practical importance.

Mono-olefins are known to have a dual nature: they are regarded as weak acids and bases, since they are capable of exchanging hydrogen for a metal, of combining with a proton, or of behaving as an electron donor. The dimerisation, codimerisation, metallation, alkylation, and isomerisation reactions of mono-olefins in the presence of basic catalysts give rise to extensive possibilities for the synthesis of individual hydrocarbon monomers and intermediates in petrochemical synthesis. The high selectivity of these reactions makes it possible to obtain in useful amounts such relatively thermodynamically unstable olefins as 4-methylpent-1-ene, 3-methylpent-1-ene, 3-ethylpent-1-ene, etc. The content of these α-alkenes in the petroleum processing products (cracking or pyrolysis products) is negligible and their isolation is hindered by the similarity of the physicochemical properties of the isomers.

The isomerisation of mono-olefins and certain diolefins in the presence of alkali metal catalysts makes it possible to shift the double bond to the required position under mild conditions without affecting the carbon skeleton. The alkylation of alkylbenzenes [by olefins] in the presence of these catalysts results in the selective addition of the olefins to the side chain only, so that subsequent dealkylation can yield also chain olefins with a specific structure, for example isopentenes.

The first attempt at a broad survey of the reactions catalysed by bases was made in 1962 by Pines and Schaap [1]. Pis'man's monograph was devoted to the industrial synthesis of 4-methylpent-1-ene [2]. Two reviews [3,4] dealt mainly with the dimerisation and codimerisation of olefins in the presence of transition metal complexes, the problems of the reactions on basic catalysts being only partly considered.

The present review is concerned with the extensive data published in recent years and also with certain early studies on the reactions of unsaturated compounds, mainly mono-olefins, in the presence of alkali metals and their derivatives in the light of modern ideas about the nature and mechanism of acid–base catalysis.

II. REACTIONS OF OLEFINS WITH ALKALI METALS AND THEIR COMPOUNDS

The hydrogen in many hydrocarbons can be replaced by an alkali metal, which is characteristic of acids, and an organometallic compound may be obtained. The substitution can occur both on direct treatment with the metal and on treatment with another organometallic compound containing the alkali metal. With increase of the atomic weight of the alkali metal, the rate of metallation as a rule increases. The rate can also increase when the metal in the fused or finally comminuted state, solutions in liquid ammonia, and the sodium–potassium eutectic mixture are used [5]. The rate of metallation depends on the mobility of the hydrogen in the molecule of the organic compound too. Olefins exhibit a comparatively weak acidity and are only slowly metallated directly by alkali metals [6]. The transmetallation reaction, described for the first time by Shorygin [7], proceeds much more readily:

$$HR + R' - M \rightleftarrows R - M + R'H ,$$

where M = Li, Na, K, Cs, or Rb and R and R' are hydrocarbon groups.

Kocheskov and Talalaeva [8] formulated the rules for metallation: (a) the yield of the organometallic compound increases with acidity when the same metallating agent acts on different hydrocarbons; (b) under identical conditions, the hydrocarbon with greater acidity is metallated faster; (c) in the presence of a deficiency of the metallating agent, the compound which is a stronger acid is also metallated preferentially.

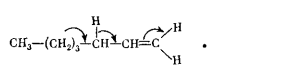
The presence of multiple bonds or rings in the molecule of the organic substance greatly alters the energy required to abstract a proton. Thus it amounts to 95

kcal mole^{-1} in propane and 98 kcal mole^{-1} in ethane, while in toluene it is only 77.5 kcal mole^{-1} and the abstraction of the allyl hydrogen atom in propene requires 77 kcal mole^{-1}.[9] Alkylbenzenes are alkylated at a high rate at the α-carbon atom of the aliphatic substituent[10-12]. The substitution of hydrogen in naphthalene by a metal is much faster than in benzene[13-15]. The acidity of alkynes is still higher, increasing in the sequence[14] $HC{\equiv}CH < HC{\equiv}C-C_5H_{11} < {\equiv}C-C_6H_5$.

Ethylene is a much weaker acid than acetylene; it is metallated only by strong bases, for example by pentylsodium[11]. The substitution of protons in ethylene by alkyl groups increases the acidity of the olefin, because the vinyl group activates the hydrogen atoms at the carbon atom nearest to it. For this reason, propene is metallated more readily than ethylene, the hydrogen in the methyl group being preferentially substituted by the metal[5,6,17,18]. Its dimetallation leads to the formation of $NaCH_2-CH{=}CHNa$.[19] Mono- and di-substituted products were also obtained in the metallation of isobutene[17]: $CH_2{=}C(CH_3)CH_2Na$ and $CH_2{=}C(CH_2Na)_2$.

The metallation of but-1-ene by pentylsodium and subsequent carbonation yield mainly $CH_2{=}CHCH(CH_3)COOH$ and smaller amounts of $CH_3CH{=}CHCH_2COOH$, $CH_3CH_2CH{=}CHCOOH$, and dimetallation products[17]. Pent-1-ene is metallated[17] mainly with formation of $CH_2{=}CHCHNaCH_2CH_3$ and $NaCH{=}CH(CH_2)_2CH_3$. Under the influence of pentylsodium, hex-1-ene also gives rise to two compounds[16]: the first corresponds to the metallation of the methylene group in the α-position relative to the multiple bond and the second is formed, as in the case of but-1-ene, as a result of the migration of the double bond: $CH_3(CH_2)_2CH{=}CHCH_2Na$. Such isomerisation with migration of the double bond to the centre of the chain has been described for reactions with phenyl-, benzyl-, and pentylsodium[20]. The metallation of hexenes with a branched chain also involves mainly the substitution of the allyl hydrogen atom; for example 2,3-dimethylbut-1-ene is converted, after metallation and carbonation, into $CH_2{=}C(i\text{-}C_3H_7)CH_2.COOH$. When there is no allyl hydrogen atom, as in 3,3-dimethylbut-1-ene, the terminal carbon atom in the vinyl group is metallated[16].

Studies on the metallation of C_7 and higher α-olefins[21-28] have shown that, with increase of the carbon chain length in olefins, their acidic properties are weakened[5] and the nature of their reactions changes somewhat. For example, it has been established experimentally[25,26] that already in the case of hept-1-ene vinyl substitution products predominate in the reaction mixture at the beginning of the reaction. It appears that in α-olefins with more than six carbon atoms the double bond not only withdraws electrons from the C–H bond in the allyl position but is also responsible for the successively decreasing inductive shift of electron pairs in the same direction[26]:



This shift compensates to some extent the decrease of electron density in the C–H allyl bond, which leads to the predominance of vinyl substitution products. This phenomenon has not been observed in low-molecular-weight α- and β-olefins and their acidity changes in the following sequence[5]: $(CH_3)_2C{=}CH_2 > CH_3-CH{=}CH_2 > CH_3CH{=}CHCH_3 > CH_3CH_2CH{=}CH_2 > (CH_3)_2C{=}CHCH_3 > (CH_3)_2C{=}C(CH_3)_2$.

Conant and Wheland[30] estimated the acidity by a calorimetric method and by carboxylating organosodium or organopotassium compounds; McEwen[31] and Shatenshtein[32] used in addition the polarimetric method. Streitwieser and coworkers[33,34] measured the equilibrium constant in the reactions of lithium or caesium cyclohexylamide with C–H acids. Cram[35] attempted to establish a universal acidity scale for all classes of hydrocarbons using the above data and the results obtained in other studies[36-38]. In an extensive review, Reutov et al.[39] examined the available methods for the determination of the equilibrium acidity and concluded that it is so far possible to determine the acidity of hydrocarbons in aprotic solvents only up to $pK_a \simeq 30$. The acidity of weaker acids (alkenes, arenes, alkanes, etc.), which is estimated by indirect methods, is lower than the value predicted by Cram's scale. This somewhat limited information about the relative acidities and basicities of hydrocarbons, enabled Shatenshtein[5,40,41] and Cram[35] to correlate the above properties of organic compounds with their behaviour in different chemical reactions.

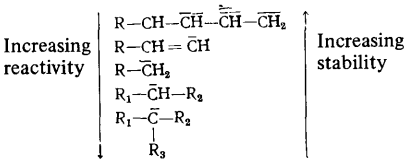
Isotope exchange of hydrogen with strong bases[40] makes it possible not only to estimate the acidities of individual C–H bonds but also to characterise simultaneously the base functioning as the nucleophile[42]. For example, examination of the rate of exchange of hydrogen in propene showed that at 25 °C three hydrogen atoms are already exchanged after 15 min. The exchange of five atoms takes place comparatively rapidly (up to 1.5 h), while the last hydrogen atom exchanges at a much lower rate[32]. The rate of exchange of six hydrogen atoms in the two methyl groups of isobutene is approximately an order of magnitude lower than in the CH_3 group of propene but an order of magnitude higher than the rate of exchange of the last two atoms. When isobutene is compared with tetramethylethylene (whose molecule has the same group of atoms but its structure is symmetrical and for this reason it has no dipole moment), the rate of reaction is seen to decrease by almost two orders of magnitude[5].

Thus the acidity of individual hydrogen atoms varies significantly as a function of the structure of the olefin molecule and in metallation one must expect the formation of an organometallic compound in which the most acidic hydrogen atom has been replaced by the metal. However, according to Morton and Holden's data[17], the structure and proportions of straight-chain butene metallation product are independent of the position of the double bond in the initial olefin. It has been shown for crotyl-lithium[43] that the ratio of different forms of organometallic compounds of the allyl type is determined by the reaction conditions, in particular by the temperature and the nature of the solvent. It has been established by NMR methods[44] that the first and third hydrogen atoms are equivalent in allyllithium $CH_2{=}CH-CH_2Li$, which indicates either the possibility of a rapid reversible migration of lithium between these atoms or the formation of a compound in which the lithium atom is delocalised[45]. It has been shown similarly[46] that the following species coexist in ethereal solutions of crotyl-lithium: $CH_3-CH{=}CH-CH_2Li$ and $CH_3-CH(Li)-CH{=}CH_2$.

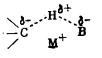
A number of workers[42,47-49] explained the nature of such organometallic compounds in terms of the concept of "polar" quantum-mechanical resonance, for the description of which the ground state of the anionic component is represented by a set of classical structural formulae for all possible electronic isomers, each of which is characterised by a definite contribution to this state[42]. The delocalisation of bonds, lone electron pairs, charges, and spins is energetically favourable and leads to resonance stabilisation of the molecule[42]. Delocalisation of the

negative charge facilitates the formation of a carbanion, but lowers the reactivity of the given compound[50].

Lefebvre and Chauvin[4] quote stability and reactivity series for carbanions:



In the metallation and isotope exchange reaction under consideration, which proceeds via the mechanism of an acid–base interaction, one must expect the formation in the limit of ions with a tervalent negatively charged carbon atom (free carbanions). In practice, polarised transition complexes with more or less stable hydrogen bonds are probably formed[5,32]. Their structure can be represented by the scheme[51,52]

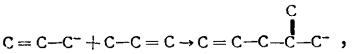


The organic derivatives of alkali metals, formed as a result of metallation, can be highly reactive intermediates in many chemical reactions which are discussed below. This is explained by the greater ionic character of the C–M bond in these compounds compared with other organoelement compounds[53]. Alkenylsodium compounds can also be used to synthesise various unsaturated derivatives with functional groups and also unsaturated carboxylic acids, unsaturated sulphonic acids, unsaturated alcohols, etc.[54]

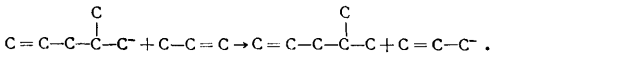
III. REACTIONS OF OLEFINS CATALYSED BY DISPERSED ALKALI METALS AND THEIR COMPOUNDS

The first reports about the catalytic reactions of olefins in the presence of alkali metals were published as early as 1936.[55] Thirteen years later Freed took out patents for the dimerisation and codimerisation of alkenes in the presence of these catalysts[56,57]. The liquid products of the codimerisation of ethylene and propene, catalysed by metallic sodium, contained hydrocarbons with less than 10 carbon atoms, mainly pentenes and heptenes. The process was carried out under fairly severe conditions at temperatures and pressures in the range 275–400°C and 250–1000 atm respectively[56]. Under the same conditions, mainly hexenes were obtained from ethylene and isobutene and heptenes from propene and isobutene. The use of promoting agents (anthracene and naphthalene) made it possible to reduce the reaction temperature to 125–250°C.[57] The individual compositions of the olefins obtained were not determined.

Having investigated the dimerisation and codimerisation reactions of olefins in the presence of the "sodium with anthracene" catalyst, Mark and Pines[58] concluded that this reaction proceeds via the intermediate formation of resonance-stabilised carbanions, which determine the position where the olefin molecule adds. In the dimerisation of propene via the mechanism



the resulting isohexenyl carbanion, which is not stabilised by resonance, is rapidly involved in an acid–base reaction with the excess olefin. This leads to the regeneration of the allyl carbanion and the formation of 4-methylpent-1-ene:



The codimerisation of cyclohexene with ethylene, propene, and isobutene yielded mainly the products of the addition of olefins to cyclohexenyl carbanion, which confirms the postulated mechanism. 2,4,4-Trimethylpent-1-ene was obtained on dimerisation of isobutene[58].

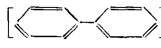
The low content of the thermodynamically least stable hexene, namely 4-methylpent-1-ene, in the products of the dimerisation of propene in the presence of the "sodium with anthracene" catalyst can be explained by its isomerisation with migration of the olefinic double bond to more stable methylpentenes with the double bond in the inner part of the molecule, in consequence of the high reaction temperature and the presence of the aromatic promoting agent. Indeed, subsequent studies[59–61] showed that propene can be successively dimerised to 4-methylpent-1-ene in the presence of dispersions of potassium, rubidium, and caesium in hydrocarbon solvents (such as alkanes, mineral oil, naphthenes, and aromatic hydrocarbons) as well as ethers and ammonia. The highest rates were achieved in benzene, but in this case a much greater amount of propane and solid condensation products is formed[61].

In the absence of aromatic promoting agents, dispersions of sodium and lithium are as a rule ineffective. However, their mixtures with "heavier" alkali metals (potassium and caesium) as well as mixtures of these metals are much more effective in the oligomerisation of olefins than potassium and caesium individually[62]. The dispersion of lithium obtained by the exchange reaction between an organolithium compound LiR (where R is an alkyl group) and a free alkali metal (as a rule potassium) is highly active[63–65]. Possibly in this case the high activity is associated with the fact that the catalytic complex incorporates a mixture of potassium and lithium. It has been shown[66] that preliminary heating of the catalyst to temperatures preceding codimerisation and its maintenance at these temperatures in the presence of olefins (for example, but-2-ene) greatly increases the rate of codimerisation of this olefin with ethylene and increases the yield of 3-methylpent-1-ene from 38 to 55 wt.%. It is suggested that the alkali metal catalyst be regenerated by heating it to 200–400°C in an inert solvent[67], but it has been stated[68] that such regeneration is ineffective.

A detailes study of the dimerisation of propene in the presence of dispersions of alkali metals[69] led to the conclusion that the yield of 4-methylpent-1-ene depends on the experimental conditions and the nature of the alkali metal used. A higher content of 4-methylpent-1-ene (up to 86 wt.%) in the reaction products was achieved in the presence of potassium dispersions without aromatic promoting agents at a reaction temperature not exceeding 150°C and an alkali metal concentration not exceeding 50 g litre^{-1};[70–72] admittedly, under these conditions the degree of conversion fell appreciably (to 10–15%). Simultaneous experiments on the isomerisation of 4-methylpent-1-ene and 4-methylpent-2-ene in the presence of a dispersion of sodium containing anthracene and a dispersion of potassium without aromatic additives[69] showed that, under the conditions of the dimerisation of propene, the double

bond of 4-methylpent-1-ene migrates. The use of dispersions of heavy alkali metals without aromatic promoting agents in inert alkane solvents complicates somewhat the formation of the organometallic initiator derived from the alkali metal. It is most likely that it proceeds via unstable intermediates, formed as a result of electron transfer from the alkali metal to the olefin π-bond (radical-anions)[69].

When the dimerisation and codimerisation reactions of olefins are carried out in the presence of alkali metals in aromatic hydrocarbons[60] or using aromatic promoting agents such as biphenyl, naphthalene, and anthracene[73,74], the induction period decreases and (under the conditions of periodic experiments) the degree of conversion rises owing to the high acidity of the aromatic hydrocarbons. The highest degree of conversion and selectivity were achieved in the presence of the "potassium with biphenyl" catalyst[73]. The authors state that this is due to the higher rate of metallation of this aromatic hydrocarbon with formation of the "complex"



The modification of alkali metal catalysts by aliphatic or aromatic ethers and ketones[75] did not lead to a significant increase of the rate of reaction and process selectivity. It is recommended that catalysts consisting of a mixture of alkali metals with their oxides, hydroxides, or fluorides be used[76-78]. Catalysts having the general formula $A(MR^1, R^2, R^3)$, where A is the alkali metal, M is zinc, mercury, cadmium, or tin, and R^1, R^2, and R^3 are hydrocarbon groups or hydrogen, have been described[79,80]. The selectivity of the formation of 4-methylpent-1-ene in the presence of these catalysts is not more than 80%.

Promotion of catalysts based on alkali metals by alkyl halides[81-83], alkylphenols[84,85], allyl or aryl ethers[86], alkylamines[87], and other organic compounds[88-92] did not increase significantly their activity and selectivity in the formation of α-olefins in the dimerisation and codimerisation reactions of low-molecular-weight alkenes.

The formation mainly of 3-ethyl-substituted products in the codimerisation of ethylene with but-2-ene and pent-2-ene[66,68] instead of the straight-chain olefins expected from the relative acidity, can be accounted for in terms of the characteristics of the metallation reaction. These results can probably be explained by the formation from both α- and β-olefins of the same organometallic compounds, the carbanionic component of which can be described by the resonance involving the following structures:

$$R-\bar{C}H-CH=CH_2 \longleftrightarrow R-CH=CH-\bar{C}H_2 .$$

The authors[68] represent the intermediate in combination with the alkali metal cation and not in the form of an individual kinetic species, as was suggested previously[58], but the influence of the cation on the reaction is not discussed.

Wilkes[70,74,93-97] attempted to reproduce the laboratory data[56,57] on a larger scale in a pilot apparatus (reactor volume 38 litres) and to test the schemes for industrial processes developed by the authors of these investigations[62,67]. He concluded[74] that a dispersion of potassium is appreciably reactive only for a particle size in the range 1–10 μm. With increase of particle size, the access of the starting material to lower layers of the metal is hindered, which leads to reactions between organopotassium compounds with formation of condensation products which hinder access to the catalyst surface. Potassium is in the fused state at the reaction temperature (120–170°C) and the maintenance of suspensions with such fine particles is difficult, since they combine into larger aggregates on collision. In order to avoid the coagulation of the liquid metal particles, it is suggested[74] that oleic acid be added and that potassium be deposited on 50 μm talc particles. The use of such a stabilised dispersion, or the "precipitation catalyst" in Wilkes' terminology, ensures more satisfactory results. However, they are not quite as good[74] as in the gas-phase process in the presence of catalysts consisting of "alkali metals on inorganic carriers", which will be described below.

Analysis of studies on the codimerisation of olefins[68] led Wilkes to the conclusion that the reactivity of olefins with respect to metallic potassium decreases in the sequence ethylene > propene > isobutene and that a radical-anion is not formed as an intermediate. On the basis of these data as well as the results of the alcoholysis of the catalysts—metallic potassium and potassium hydride in a dispersed form and on a carrier (K_2CO_3), Wilkes suggested that the catalyst is formed on two centres, the hydride and a vinyl substitution product being generated[98]:

$$R-\overset{R_1'}{\overset{|}{C}}=CH_2 + 2K \rightleftarrows \underset{(I)}{\left[R-\overset{R'}{\overset{|}{C}}=CH\right]^-} K^+ + KH ,$$

where R, R′, and R_1' are hydrogen or alkyl groups.

In the subsequent reaction with propene, the vinyl carbanion (I) gives rise to the thermodynamically more stable allylpotassium and the initial olefin is regenerated. The reaction of potassium hydride with propene yields propane and allylpotassium.

This mechanism is inconsistent with later experimental data[68]. Preferential vinyl metallation would be expected to result in the formation of a product of the addition of propene to vinylsodium (3-methylbut-1-ene) in the codimerisation reactions between ethylene and propene and in vigorous dimerisation of ethylene with formation of but-1-ene. However, appreciable amounts of 3-methylbut-1-ene were not detected under these conditions[68,97], while the dimerisation of ethylene proceeds at a rate approximately two orders of magnitude lower than the dimerisation of butenes[100]. It is interesting to note that even insignificant amounts of but-1-ene, formed in the dimerisation of ethylene, rapidly combine with another ethylene molecule, and up to 27.0 wt.% of the ethylene trimer 3-methylpent-1-ene was detected in the reaction product[100].

All these findings permit the conclusion that the metallation of ethylene (vinyl metallation) proceeds, as shown previously[6,16,17], at a much lower rate than the allyl metallation (for example, the metallation of propene). The stage involving the formation of the catalyst, where the metallation takes place in the presence of a relatively inactive metallating agent (alkali metal), therefore proceeds via a stage in which a radical-anion is formed and not the product of the vinyl metallation of the olefin. The cause of the high rate of codimerisation of ethylene with propene or straight-chain butenes is probably the greater ease of addition of ethylene to anions compared with other olefins[58].

The dimerisation and codimerisation reactions of olefins are regarded not only as the addition of alkenes to carbanions but also as a specific instance of limited (degenerate) anionic homopolymerisation or copolymerisation of olefins[4,102]. This approach makes it possible to explain certain features of these reactions, for example the

dependence of the yield of oligomerisation products on the monomer ratio and the degree of conversion [102,103].

Having examined the possible pathways to the formation of dimerisation and codimerisation products of monoolefins in the presence of alkali metal catalysts, we shall now proceed to the prototropic shifts induced by the isomerisation of unsaturated hydrocarbons which is catalysed by bases as well as other substances. It has been established [104] that in an anhydrous medium KOH causes the stereospecific isomerisation of straight-chain butenes at 320°C to *cis*-but-2-ene. But-1-ene has been obtained from *cis*- or *trans*-but-2-ene. Sodium hydroxide catalyses this reaction at 400°C, while LiOH, which is a weaker base, catalyses it at 440°C. The isomerisation of high-molecular-weight α-olefins with migration of the double bond in the presence of sodium isopropoxide [105] and potassium butoxide [106] has been described.

A number of workers [107-113] investigated the isomerisation of olefins under the influence of potassium amide at the boiling points of the hydrocarbons. They put forward for the first time the idea that the first stage of this reaction is the partial dissociation of hydrogen from the C–H bond in the allyl position relative to the double bond [108]:

$$R{-}CH_2{-}CH{=}CH_2 + MNH_2 \rightarrow [R{-}\overline{C}H{-}CH{=}CH_2]\,M^+NH_3 .$$

The negative charge in the resulting carbanion can shift in the direction of the double bond with formation of the carbanion (III):

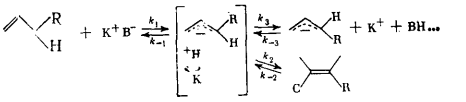
$$\underset{(II)}{[R{-}\overline{C}H{-}CH{=}CH_2]\,M^+NH_3} \rightarrow \underset{(III)}{[R{-}CH{=}CH{-}\overline{C}H_2]\,M^+NH_3} .$$

After the addition of a proton, the carbanion gives rise to an olefin with the double bond in a new position. As was to be expected on the basis of the proposed mechanism, the hexenes where the allyl position contains the maximum number of hydrogen atoms isomerise faster [109], since substitution of hydrogen by electron-donating alkyl groups entails a decrease of the mobility of the remaining hydrogen atoms.

Shatenshtein and coworkers [5,114,115] showed that not only calcium amide but also potassium amide in liquid ammonia cause the isomerisation of alkenes. Later it was noted that the reactions catalysed by these amides involve the isotope exchange of hydrogen [32] together with the migration of the double bond, which constitutes a clear confirmation of the views of Gostunskaya et al. [108]

The participation of the carbanion in the isomerisation process in the presence of basic catalysts has also been demonstrated by Astaf'ev and Shatenshtein [116]. The C–H bonds in allylbenzene $C_6H_5{-}\overset{*}{C}H_2{-}CH{=}CH_2$ located at the position marked with as asterisk are involved in conjugation with the electronic system of the aromatic ring and with the multiple bond. The hydrogen in this position therefore ionises in an ammonia solution of potassium amide and a carbanion is formed with the characteristic absorption spectrum [5]. When the amide is neutralised with an ammonium salt, mainly propenylbenzene $C_6H_5CH{=}C{-}CH_3$ is formed, i.e. the double bond migrates [117]. However, a free carbanion is by no means always formed during isomerisation. According to Shatenshtein [5], in most cases partial dissociation of hydrogen in the form of a proton is most likely to occur with its simultaneous migration, for example in the trimolecular complex in the transition state.

Certain observations confirming these views have been described [118-121]. It has been established that the isomerising activity of potassium t-butoxide depends on the nature of the solvent [119]. At a temperature as low as 40–60°C, albeit for a comparatively long contact time (24 h for linear and up to 500 h for branched olefins), it was possible to achieve thermodynamic equilibrium in butene, pentene, and 2-methylpentene isomers. The use of labelled olefins showed that the isomerisation occurring in the potassium t-butoxide–dimethylsulphoxide system proceeds within the complex of the olefin and the catalyst [118-121]. Hydrogen transfer from one molecule to another was not observed; there is only an intense isotope exchange between the olefin and the solvent–dimethyl sulphoxide. These results were interpreted on the basis of a model with a chemically bound ion pair [120]:



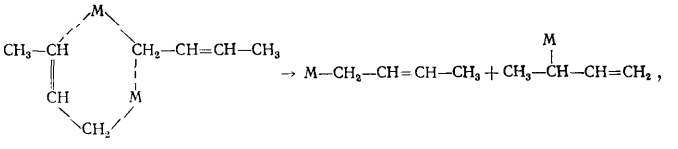
$k_3 < k_1$; k_2

$B^- = O^-$-Bu-t .

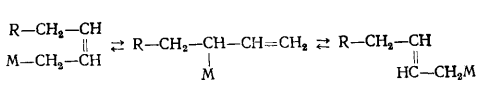
The rate of isomerisation of hydrocarbons depends both on the strength of the base and on the acidity of the allyl hydrogen atom in the olefin. For example, penta-1,4-diene, which has very acidic hydrogen atoms, isomerises under the influence of potassium t-butoxide in dimethyl sulphoxide approximately 10^8 times faster than does pent-1-ene [121]. It has been noted [118,120] that 2-methylpent-1-ene isomerises to 2-methylpent-2-ene faster than 2-methylpent-2-ene isomerises to 4-methylpent-2-ene. The authors [118,120] explained the kinetic observations by the relative stability of the carbanions formed as intermediates.

The migration of the multiple bond is also catalysed by organosodium compounds formed as a result of the reaction of sodium with the promoting agent, for example *o*-chlorotoluene or anthracene [122-125]. The possibility of using the product of the reaction of lithium with ethylenediamine as a homogeneous catalyst of this reaction has been reported [126,127]; the replacement of lithium by sodium in this instance lowers the activity of the catalyst.

Wittig [128] established that organolithium compounds are dimerised in solution. On this basis, Kropachev et al. [43] suggested that this facilitates the isomerisation step, as a result of which one of the molecules isomerises, while the other remains unchanged:



where M is the alkali metal. The direct *cis* $\rightleftharpoons$ *trans*-transition is known to require an appreciable activation energy, so that the reaction may proceed via the mechanism [43]



All the studies of the isomerisation reactions of olefins in the presence of basic catalysts have shown that the catalysts examined accelerate only the migration of the double bond in the molecule and do not affect the carbon skeleton. The alkylation of alkylbenzenes by monoolefins, catalysed by alkali metals and some of their compounds, exhibits a remarkable selectivity: olefins add only to the side chain of the alkylbenzene. A detailed

examination of these reactions suggested[1] that the characteristic features of these transformations are associated with the formation of intermediates—alkylbenzene carbanions.

Thus the investigators who studied both the hydrogen isotope exchange in hydrocarbons in the presence of bases and the base-catalysed dimerisation, codimerisation, isomerisation, and alkylation reactions of olefins concluded that all these reactions proceed via a stage involving the formation of carbanions. However, free carbanions are not as a rule produced. Only an electron shift in the direction of the formation of $\equiv C^-$ may occur in the transition state[5].

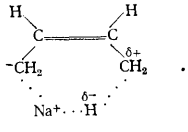
IV. REACTIONS OF OLEFINS UNDER THE INFLUENCE OF ALKALI METALS ON CARRIERS

Alkali metals on solid inorganic carriers are more effective catalysts of the isomerisation, dimerisation, codimerisation, oligomerisation, and hydrogenation reactions of olefins than dispersions of alkali metals or solutions of their compounds in hydrocarbon solvents. Thus, in their early studies of the isomerisation of olefins in the presence of basic catalysts, Pines and coworkers[129,130] already investigated a whole series of catalysts consisting of sodium or lithium on inorganic carriers and showed that alkali metals "with a large surface area as a result of their deposition on activated alumina"[1] are the most active catalysts. According to the authors, they are capable of abstracting protons from olefin molecules with formation of intermediates, stabilised as a result of the resonance involving the following structures:[130]

$$\underset{\text{(IV)}}{R-\overset{Na^+}{\overline{C}H}-CH=CH_2} \leftrightarrow \underset{\text{(V)}}{R-CH=CH-\overset{Na^+}{\overline{C}H_2}}\ .$$

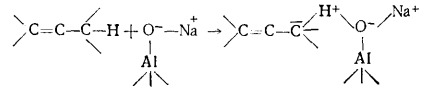
In the presence of an excess of the olefin, the metal is exchanged for an allyl proton, which leads to the formation of the isomerised olefin with structure (V) and the regeneration of the intermediate (IV). This reaction may be interrupted as a result of the formation of a compound which is insufficiently basic to metallate the olefin, for example a polyene, when a hydride ion is split off[1].

Study of the isomerisation kinetics[130] showed that, after a short contact time, but-1-ene is converted preferentially into *cis*-but-2-ene and not into the thermodynamically more stable *trans*-isomer. The stereospecificity of the catalyst may be accounted for either by the fact that but-1-ene reacts faster with the *cis*-butenyl carbanion or by the fact that the *cis*-butenyl carbanion is present in the reaction mixture at higher concentrations. The latter interpretation is more probable[130], which may be accounted for by the additional resonance stabilisation of the structure[1]



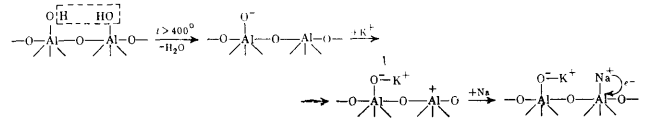
It has been shown[123] that a dispersion of lithium on γ-Al_2O_3 is not as active as the corresponding sodium catalyst. The authors[130] believe that one of the causes of the high activity of the latter catalyst may be the formation of organosodium compounds from the alkali metal and reactive impurities in the olefin. This view is based on data[122,123,129,131-134] showing that sodium isomerises olefins much more readily in the presence of such an organic compound, for example chlorobenzene and chlorotoluene.

Another cause may be the replacement of the protons of the hydroxy-groups on the surface of alumina by sodium, which leads to the suppression of the Brønsted acidity with the simultaneous appreciable enhancement of the basicity of the oxygen anions[130,135]. The formation of carbanions can be explained in this case by the mechanism[135]



This hypothesis makes it possible to explain also the increased activity of the "Na on γ-Al_2O_3" catalyst in reactions involving the migration of the multiple bond in hexenes and vinylnorbornene {5-vinylbicyclo[2,2,1]hept-2-ene} when alumina is modified by solutions of potassium carbonate[136-140]. Preliminary vacuum heat treatment or treatment in a stream of inert gas is known to entail the dehydration of the surface of this oxide and the formation of Lewis acid or basic centres[141,142]. The K^+ ions in the potassium carbonate solution deactivate the Lewis basic centres and the residual Brønsted acid centres[143,144], while sodium apparently forms an ion linked by a one-electron bond to the Al_2O_3 surface[102]. The ionisation of sodium is clearly demonstrated by the appearance of a blue colour when it is deposited[102]. A similar pattern of colour changes is observed when alkali metals are dissolved in ammonia. The formation of ions under these conditions is known and has been confirmed by many methods, in particular by the high electrical conductivity of the solution[145].

The increase of the activity of the "Na on γ-Al_2O_3" catalyst when the carrier has been thermally activated at 400–500°C is probably associated with the fact that the sodium atom forms with a surface-unsaturated aluminium atom (a Lewis acid centre) an active catalytic complex, for example of the kind represented schematically below[102]:



Other workers[146], who investigated the isomerisation of α-butene on potassium deposited on γ-, η-, and α-Al_2O_3 and quartz, reached similar conclusions.

The use of not only the "sodium on γ-alumina" catalysts[147-151] or others where sodium is deposited on molecular sieves[152,153] but also catalysts of a similar type, namely potassium or potassium amide on γ-Al_2O_3[154-156] and a complex of graphite with an alkali metal[157], has been recommended for the isomerisation of butenes, pentenes, and hexenes[157]. The enhancement of the isomerising capacity of the "Na on γ-Al_2O_3" catalyst has been observed when the latter is flushed with air[151]. The kinetics of the isomerisation of vinylnorbornene on potassium amide in liquid ammonia have been described[158]. In contrast to the thermal isomerisation of this hydrocarbon[159], which leads to the formation of tetrahydroindene {bicyclo[4,3,0]-nonadiene}, the base-catalysed reaction leads only to the migration of the multiple bond without affecting the ring.

As a rule, in the processes described alkenes with the double bond in an internal position are obtained from α-olefins. However it has been suggested[160,161] that

α-alkenes be obtained from their β- and γ-isomers using the shift of thermodynamic equilibrium, by distilling from the reaction zone the required α-olefins, which are as a rule more volatile than their isomers. Although this idea arouses no objections in principle, when it is applied one encounters the difficulty of isolating the required products from the equilibrium mixture where their content is relatively small. A more effective procedure involves the formation of 4-methylpent-1-ene from 2-methylpent-1-ene and 2-methylpent-2-ene by the method of the so called "antithermodynamic isomerisation" in the presence of borides, which Ziegler developed[162,163]. The products of this reaction contain 45–70% of the required compound.

The vapour-phase dimerisation and codimerisation of alkenes in the presence of catalysts on carriers containing an alkali metal or its compound is characterised by a high degree of conversion of the starting material, improved selectivity, and long duration of the continuous operation of the catalyst. Potassium and sodium or their mixtures and more rarely lithium, rubidium, and caesium are usually recommended for the preparation of such catalysts. Inorganic oxides, for example MgO, Al_2O_3, CaO, ZnO, alumino- and magnesio-silicates[164-175], inorganic acid salts (K_2CO_3, K_2SiF_6, NaCl, KCl, etc.)[173,176,177], alkaline earth metal hydrides[179], metallic aluminium, magnesium, copper, silver, iron, cobalt, nickel, and their mixtures[180-184], and crystalline zeolites[185] are used as the carriers.

An active catalyst for the conversion of olefins was obtained by depositing potassium on magnesium oxide. It is pointed out that the selectivity of the dimerisation and codimerisation of alkenes with respect to the required α-olefin improves when the carrier has been heat-treated at 500–1000°C.[166] It has also been suggested[167-173] that potassium and potassium amide on alumina be used. The authors believe that the composition of the propene dimer obtained in the presence of these catalysts is determined by the specific surface of the carrier. Judging from the data which they quote, the highest yield of α-olefins is attained when the oxide has a small specific surface. The surface was reduced by the heat-treatment of the carrier at temperatures up to 1200°C, but the authors[167-169] did not take into account the fact that this entails also the conversion of the γ-form of the oxide into the α-form, i.e. a change not only in the specific surface but also in other surface properties for example, acidity.

The study of the influence of the porosity of the carrier on the yield of 4-methylpent-1-ene in the dimerisation of propene[74] showed that, with decrease of pore radius, the content of this α-olefin in the dimerised product diminishes and the yield of its β-, γ-, and ω-isomers increases.

Alkali metal hydrides are more advantageous than the pure alkali metals because of the higher rate of dimerisation and the greatly reduced period required for the formation of the catalyst[186-191]. It is suggested that not all alkali metal hydrides but only the hydrides of the most reactive metals (potassium, rubidium, caesium, or their mixtures) be used on the following carriers: carbon black, potassium, rubidium, and caesium carbonates, or powdered glass[186,189,190]. A high activity of the catalyst and selectivity of the dimerisation of propene to 4-methylpent-1-ene (approximately 90–92%) were attained on a catalyst consisting of a mixture of potassium, copper, and sodium[192] or potassium[183] alkoxide. Catalysts comprising alkali metals or their hydrides and charcoal have been described[193-210]. Mainly methylpentenes with the multiple bond in an internal position have been obtained in their presence. Exceptions are catalysts containing an amino-group[193] as well as layer complexes having the overall formula MC_X with a definite alkali metal : carbon ratio[195,197,198,209,210]. The physicochemical principles of the reactions in the presence of such complexes have been examined[211].

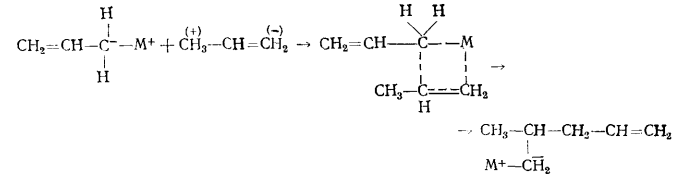
Comparison of various catalysts for the dimerisation of propene to 4-methylpent-1-ene[102,212-236] led to the conclusion that elemental alkali metals on alkali metal carbonates are the most effective catalysts[177,213-232]. It has been noted that the composition of the products of this reaction changes only slightly on passing from one alkali metal to another. The nature and surface properties of the carrier have a decisive influence on the direction of the reaction towards the formation of a particular isomer[102]. Thus, when the alkali metal is deposited on potassium carbonate (specific surface $S = 0.15$ m^2 g^{-1}), propene dimerises mainly to 4-methylpent-1-ene[213-220], while in the presence of γ-Al_2O_3 ($S = 250$ m^2 g^{-1}) the product is 2-methylpent-2-ene[167]. Mainly *cis*- and *trans*-4-methylpent-2-enes are formed on the "Na on α-Al_2O_3" catalyst ($S = 14$ m^2 g^{-1}).[102,169]

However, the surface area is not apparently the only factor determining the efficiency of the carrier. For example, sodium deposited on a ceramic, pumice, or a faience carrier with a low surface area proved to be inactive in the dimerisation of propene[102].

Catalysts containing an alkali metal on inorganic alkali metal salts (halides, sulphates, silicates, and carbonates) showed a high activity[213,228].

The experimental data described cannot be accounted for in terms of a reaction mechanism providing for the intermediate formation of carbanions as separate kinetic species[58]. Evidently, when a carbanion is really the reaction centre, then in such a mechanism of the propagation reaction the capacity for oligomerisation should be shown only by electron-accepting vinyl compounds, because a carbanion is an electron-donating agent. Ethylenic and diethylenic hydrocarbons, which are electron-donating substances[237,238], should not combine with a carbanion and should not therefore oligomerise under the influence of substances capable of forming carbanions[237].

These findings can be best explained in terms of an anionic-coordination mechanism[239] based not on a carbanion but on an ionic aggregate containing the metal ion as well as the carbanion. In this case, the transition state consists of a four-membered ring[239] and the dimerisation of propene can be represented schematically as follows[102]:

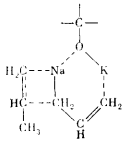


A definite coordination in the addition of the monomer to the active centre is probably promoted also by the polarisation of the olefin molecule as a result of the $\pi-\delta$ conjugation, which has been observed in many ways, for example with the aid of isotope exchange[5,240,241].

It was shown previously[212] that sodium catalysts show a low activity in the dimerisation of propene in the presence of alkali metals dispersed in inert hydrocarbon solvents. However, when sodium is deposited on an inorganic acid salt (for example, on potassium carbonate) or γ-Al_2O_3, catalysts for the dimerisation of propene more effective

than the potassium catalysts are obtained[228]. This phenomenon has been attributed by some workers to the displacement of potassium from the inorganic acid salt by sodium[74,242]. However, the hypothesis[243] that the activation of allylsodium compounds by inorganic acid salts proceeds in consequence of the formation on the surface of the carrier of the so called "double coordination complex" appears more likely. Such complexes are formed with compounds where the metal–carbon bond is conjugated with a double bond or a phenyl group[17,243]. They consist of ionic aggregates, where alkali metal atoms exhibit both basic and coordination valences[237,244]. The reaction is believed[244] to proceed via the adsorption of a monomeric molecule on the ionic aggregate with the coordination and activation of the former on the surface of the latter and the subsequent interaction with the anion located on the same site. The increase of activity is attributed to the enhancement of the polarisation of the $M^{\delta+}-\overset{\delta-}{C}\!\!\swarrow$ bond on formation of the complex. It has been shown that the activity of the catalyst increases when the distance r in the inorganic salts employed, equal to the sum of the ionic radii, is greater than 2.75 Å and the complex contains different alkali metals[245].

The results of studies on the selection of catalysts for the dimerisation and codimerisation of olefins agree well with the investigations of polymerisation processes carried out by Morton[243,244]. This justifies the hypothesis that the activation of allylsodium by potassium carbonate is associated with the formation of a "double coordination complex" and that the selectivity of the reaction can be explained by the selective adsorption of a monomeric molecule in its field and that the transition state in the dimerisation of propene may be represented schematically as follows[102]:



These views on the reaction mechanism are confirmed by data[246] showing that the addition of mercury or transition metals to the "sodium on potassium carbonate" catalyst alters fairly appreciably the rate but not the proportions of reaction products. The authors concluded[246] that the rate-limiting stage of the reaction is the adsorption of propene. It has been shown[102,247] that the rate and selectivity of the dimerisation of propene depend on the content of metallic sodium in the catalyst. Hambling[247] attributed the change in selectivity to the isomerisation of 4-methylpent-1-ene catalysed by allylsodium. However, this mechanism appears unlikely, since the allyl carbanion is a comparatively weak base, while 4-methylpent-1-ene is a very weak acid. The Shaw mechanism[69], with chain termination via the dimer, where a strong base, namely the isohexenyl carbanion

$$M^+[CH_3-\underset{\displaystyle CH_2}{\underset{|}{CH}}-CH-CH=CH_2]^-$$

acts as the metallating agent, appears to be more likely.

The study of the composition of high-molecular-weight side products of the dimerisation of propene in the presence of the "sodium on potassium carbonate" catalyst showed that they consist mainly of C_9 olefins, formed via the mechanism involving the addition of the dimer to the active allyl centre responsible for the dimerisation[248].

In contrast to the dimerisation of propene, that of ethylene in the presence of the "Na on K_2CO_3" catalyst proceeds at insignificant rates, apparently owing to the difficulty of the substitution of a proton in the vinyl group[100]. The reaction products consist mainly of but-1-ene and 3-methylpent-1-ene. The latter is probably formed via the mechanism involving the addition of an ethylene molecule to the *s*-butenyl carbanion† [100,247].

But-1-ene dimerises at a higher rate than ethylene, because, as already pointed out, but-1-ene is metallated faster. The two structures of the carbanions formed under these conditions,

$$Na^+\left[\begin{array}{l}CH-CH=CH_2\\ |\\ CH_3\end{array}\right]^- \leftrightarrow Na^+\left[\begin{array}{l}CH=CH-CH_2\\ |\\ CH_3\end{array}\right]^-,$$

give rise to 3,4-dimethylhex-1-ene and 5-methylhex-2-ene following the addition of the next but-1-ene molecule[100], as was to be expected on the basis of the postulated mechanism.

The codimerisation of ethylene and but-1-ene in the presence of the "Na on K_2CO_3" catalyst is approximately an order of magnitude faster than the dimerisation of butenes. This can be explained by the involvement in the given reaction of a readily metallated alkene (but-1-ene and ethylene), which adds to the carbanion at a higher rate. The principal products of this reaction—3-methylpent-1-ene and hex-2-enes (with the former predominating)—are formed as a result of the addition of ethylene to the first or second structure of the s-butenyl carbanion respectively[100,247]. The codimerisation of ethylene with propene in the presence of this catalyst at 80–120°C gave 92 wt.% of pentenes, 5.2 wt.% of heptenes, and only 2.6 wt.% of hexenes. Thus the addition of ethylene to the allyl anion in the above temperature range is approximately 40 times faster than the addition of propene (pent-1-ene and 4-methylpent-1-ene predominate in the pentene and hexene fractions respectively)[247].

The yield of high-molecular-weight olefins, particularly C_7 and C_8 olefins, is much higher in the codimerisation reactions involving ethylene. Furthermore, the rate of formation of octenes in the codimerisation of ethylene and but-1-ene increases with increase of the content of ethylene in the starting material[103]. The composition of the C_8 olefins (the main products are 3-methylhept-1-ene, oct-4-enes, 3-ethyl-3-methylpent-1-ene, 3-methylhept-3-ene, 4-ethylhex-2-ene, and 5-methylhept-3-ene) shows that these alkenes are formed as a result of the successive addition of two ethylene molecules to the butenyl carbanion and not as a result of the dimerisation of butenes[103].

The heptenes formed as side products in the codimerisation of ethylene and propene in the presence of the "sodium on potassium carbonate" catalyst contain mainly 3-pent-1-ene and also admixture of *cis*- and *trans*-hept-3-enes and *cis*- and *trans*-4-methylhex-2-enes[247,249]. The formation of these alkenes can be explained by the addition of ethylene to three types of anions, which may be produced on metallation of straight-chain pentenes:

$$Na^+\left[\begin{array}{l}CH-CH=CH_2\\ |\\ CH_2\\ |\\ CH_3\end{array}\right]^- ; \quad Na^+\left[\begin{array}{l}CH_2-CH=CH\\ |\\ CH_2\\ |\\ CH_3\end{array}\right]^- ; \quad Na^+\left[\begin{array}{l}CH_3-CH-CH\\ \|\\ CH\\ |\\ CH_3\end{array}\right]^-$$

(VI) (VII) (VIII)

† Here and henceforth the abbreviation "...addition to carbanion..." has been adopted, which will be understood as "addition of an olefin molecule to the active centre containing the given carbanion".

The same olefins have been obtained in a direct synthesis of heptenes from ethylene and pent-1-ene [247,249]. However, the contents of 3-ethylpent-1-ene and hept-3-enes are approximately 86 and 11 wt.% respectively, which gives a somewhat higher ratio than that of the carbanions (VI) and (VII) in metallation products, which is 4 : 1.[17] The content of 4-methylhex-2-enes, the products of the addition of ethylene to the carbanion (VIII), is lower still, namely 2.6 wt.%, which might be accounted for by the low content of pent-2-enes in the reaction zone. However, in the codimerisation of ethylene and pent-2-enes, the reaction rate was somewhat higher, but the content of 4-methylhex-2-enes increased insignificantly [249]. An improved yield of straight-chain heptenes in this reaction was achieved only after the simultaneous alteration of the nature of the alkali metal as the "active component" and of the catalyst carrier. Thus, on replacing the "Na on K_2CO_3" catalyst by the "K on Li_2CO_3" catalyst, the yield of linear C_7 olefins was sharply increased (up to 50%).[250]

These results can be explained on the basis of a mechanism taking into account not only the relative stabilities and reactivities of various anions but also the influence of the cations derived from the organometallic compound and the inorganic carrier. The decisive factors responsible for the specificity of the action of the catalyst are apparently the stability and reactivity of the complex formed by the anion, the cation, and the inorganic alkali metal salt [102].

The possibility of employing β-olefins as the starting materials for codimerisation reactions is extremely attractive, since it makes it possible, in the first place, to obtain on their basis valuable α-olefin monomers for the synthesis of heat-resistant plastics (with melting points in the range 350–420°C) [251] and, in the second place, to make use of new sources of starting materials, for example industrial petroleum fractions [252] and the disproportionation [253–255] or isomerisation products of lower mono-olefins [249]. By altering the composition of the starting material and the carrier for the alkali metal, a number of workers [254,256–261] obtained a wide range of methylpentene and ethylpentene positional isomers.

Reactions involving the addition of propene to olefins in the presence of the "Na on K_2CO_3" catalyst require the use of more severe temperature conditions (140–170°C) [262] than the reactions in which ethylene adds to the same alkenes (80–100°C) [247]. It has been shown that, for an equimolecular mixture of propene and but-1-ene, the rate of addition of propene to a mixture of allyl and butenyl anions is approximately 15 times higher than the rate of addition of but-1-ene. The presence of a methyl substituent at the butenyl anion lowers the rate of addition of olefins by a factor of seven compared with the allyl anion [247].

The effective oligomerisation reaction on catalysts with an acid-free carrier is as a rule preceded by a fairly long period involving the formation of the complex during which the olefins are metallated and active centres containing carbanions are formed. The duration of this period diminishes in the presence of alkali metal catalysts with an acid carrier. It can be shortened by treating the catalyst with hydrogen or a readily metallated olefin before the start of the reaction [223,256]. It has been suggested that alkali metal hydrides themselves be deposited instead of the treatment with hydrogen [191]. At the end of the induction period, the rate of reaction is stabilised for a long time [225,247], which supports the hypothesis that the reaction proceeds in the presence of a constant number of active centres. Activity is lost owing to the gradual shielding of the surface by the extensive condensation products, which are probably formed as a result of the dehydrogenation [63], dehydrocyclisation, and the so called "internal alkylation" described by Richey and coworkers [263]. As a result of the last reaction, cyclic compounds, for example methylcyclopentane, may be formed [68].

This type of catalyst may be regenerated with hydrogen [220,221], but this probably entails the hydrogenation of condensation products with a deficiency of hydrogen (one hydrogen atom for two carbon atoms) [68]. Although alkali metals are not transition metals, they catalyse the hydrogenation of aromatic molecules and their catalytic activity increases from lithium to rubidium. The most active catalyst of this reaction is sodium on potassium carbonate [242]. The possibility of the regeneration of alkali metal catalysts on carriers combined with the long period of their operation between regenerations (not less than 800 h) and high selectivity and activity [217,224,247,264], make these catalysts promising for the oligomerisation of olefins. It is not fortuitous that the first industrial process involving the dimerisation of propene to 4-methylpent-1-ene has in fact been achieved in the presence of these catalysts [264]; studies on their modification are being continued [180–185,246,265–287].

A tendency has arisen to employ alkali metals on carriers, particularly "Na on K_2CO_3" [268] or alkali metal complexes with carbon [269], in alkylation reactions which had been studied previously in the presence of dispersions of alkali metals or their complexes with aromatic hydrocarbons.

So many studies have been devoted to the polymerisation of diolefins in the presence of basic catalysts that even their simple enumeration is difficult within the framework of the present review. We shall only note that the view according to which these reactions proceed via "anionic-coordination" [239] or "coordination" [237] mechanisms, presupposing the formation of active centres containing organometallic compounds of alkali metals [270], has predominated in recent years. The reactions of dienes, which occur at higher rates, are undesirable side processes in the reactions of the less reactive mono-olefins, since the formation of dehydrocyclisation of high-molecular-weight diene polymers lead to the rapid deactivation of the catalyst. It is therefore recommended that the content of diene and acetylenic impurities in the olefinic starting materials be kept at the level of five parts per million [213]. It has been shown [271,272] that, in the presence of mono-olefins, dienes form not only homopolymers but also copolymers with the alkenes on the alkali metal catalysts.

Although the synthesis of polyolefins in the presence of alkali metal catalysts on carriers was achieved as early as 1954, [273] these studies were not developed further and research was continued mainly on the dimerisation and codimerisation of olefins. Reports concerning the preparation of C_{10}–C_{16} oligomers with a narrow molecular weight distribution appeared only recently [274]. Using the "Na on γ-Al_2O_3" catalyst containing 0.2–2.1% of OH groups, it is possible to obtain detergent olefins [274] containing up to 50% of α-olefins. This comparatively high content of surface hydroxyls distinguishes the above catalyst from those for the dimerisation of olefins, where the OH content is reduced to a minimum by the thermal activation of the carrier at 500°C.

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Thus examination of certain reactions of alkenes in the presence of basic catalysts has shown that they probably

occur with the intermediate formation of organic compounds of the alkali metals, the characteristics of the synthesis and reactions of which are of decisive importance for the specificity of the reactions investigated and the composition of their products. Being highly reactive compounds in consequence of the ionic character of the C–M bond, these substances accelerate the dimerisation, codimerisation, oligodimerisation, isomerisation, alkylation, and hydrogenation reactions of low-molecular-weight mono-olefins. The interaction of the carbanionic and metallic components of these compounds is most likely to be determined not only by electrostatic but also by exchange forces and depends significantly both on the structure of the carbanion and on the nature of the alkali metal. Free carbanions are apparently not formed in the transition state and there is merely an electron shift in the direction of the formation of $\rangle C^-$. The involvement of two catalyst centres in the transition state tends to increase the selectivity of the reaction. Modification of the catalysts (organic derivatives of alkali metals) by inorganic carriers and additives to the latter makes it possible to increase the activity and selectivity of the catalysts and in many cases constitutes an effective method for altering the mode of reaction. The results achieved using alkali metal catalysts on carriers show that promising methods for the processing of olefins can be devised on their basis.

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