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The Mechanism of the Decomposition of Organometallic Compounds of Transition Metals and the Role of Intermediate Species in Catalysis

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The three pathways leading to the decomposition of organometallic compounds of transition metals (Mo, W, Ta, Re, Pt, Pd, Rh, Cr, Nd, Y, and Nb) at the instant of formation are examined. α-Decomposition accompanied by the formation of carbene and carbyne species is of decisive importance for methyl, benzyl, trimethylsilylmethyl, and neophyl derivatives. The decomposition proceeds without superposition of radical stages. The mechanism of the chain metathesis of olefins and cycloolefins under the influence of carbene complexes of transition metals is considered. Ideas concerning the chemical nature of the elementary steps in the hydrogenolysis and isomerisation of the carbon skeleton and the dehydrogenation and hydrogenation of hydrocarbons are put forward on the basis of the hypothesis that the primary step in the oxidative addition of hydrocarbons to zerovalent metals involves the formation of organometallic compounds.
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I. INTRODUCTION

Fairly numerous investigations have been carried out on the decomposition of organometallic compounds of transition metals. In early studies of Kondyrev and Fomin[1], published in 1915, it was shown that the products of the decomposition of the organometallic compounds formed on interaction of alkylmagnesium halides with transition metal halides are saturated and unsaturated hydrocarbons corresponding to the alkyl groups of the initial compounds RMgX. These reactions were subsequently studied in greater detail in numerous investigations by Kharasch and many other workers (see, for example, Refs. 2–10).

The decomposition of alkyl derivatives as a rule results in the formation of the corresponding hydrocarbons R + H and R − H (alkane and alkene) and a certain amount of recombination products (R − R). If R = benzyl, phenyl, neopentyl, or other groups without an H atom in the β-position relative to the C–M bond, then the main decomposition product is R − R. When methyl-lithium interacts with halides of a number of metals, the main products are methane and ethane depending on the nature of the metals[5]:

$$CH_3Li \xrightarrow[\text{Ti, Zr, Mn, Cr, La}]{} \text{mainly } CH_4, \quad \xrightarrow[\text{Au, Fe, Ni}]{} \text{mixture of } CH_4 \text{ and } C_2H_6, \quad \xrightarrow[\text{Ag, Cu}]{} \text{mainly } C_2H_6. \qquad (1)$$

The mechanisms of these reactions are considered mainly on the basis of the hypothesis of free-radical stages. The idea of intermediate radical stages in the decomposition are still used by many investigators to account for the mechanism of the formation of the final reaction products, although there is no direct experimental evidence for this. In particular, the "trapping" of these intermediate decomposition products by styrene may be due to the addition to the latter of an organometallic compound of a transition metal. The present author and his co-workers[11–13] were the first to show experimentally that, in the presence of free-radical acceptors, for example, α-methylstyrene, the composition of the products of the reactions of C_2H_5MgBr and C_2H_5Li with $NiCl_2$, $CoCl_2$, and $TiCl_4$ remains unchanged. The reactions involving $NiCl_2$ and $CoCl_2$ lead to the formation of equimolar amounts of ethane and ethylene; in the reaction with $TiCl_4$, a large proportion of ethylene disappears owing to polymerisation. The absence of radical stages has also been noted in the reactions involving the oxidative addition of ethyl bromide to zerovalent cobalt and nickel[14]. The very fact of the formation of equimolar amounts of ethane and ethylene indicates a non-radical nature of the process, since ethyl free radicals readily abstract a hydrogen atom from the solvent. It has been shown that free radical reactions proceed smoothly in those cases where the reduction of M^{n+1} to M^n in the organometallic compound takes place very readily, for example, with conversion of the stable cobalt(III) or manganese(III) complexes into unstable ionic forms[15]:

$$(acac)_3Co + CH_3COOH \rightarrow (CH_3COO)_2Co + CH_3^{\cdot} + CO_2,$$
$$(acac)_3Mn + CH_3COOH \rightarrow (CH_3COO)_2Mn + CH_3^{\cdot} + CO_2. \qquad (2)$$

Homolytic decomposition at the C–M bond, accompanied by the formation of free radicals, is known for compounds characterised by a low energy of this bond. However, in most cases the energies of the carbon–transition metal bond are 30–60 kcal mol^{-1} [16] and the instability of the above compounds at the instant of formation requires a special explanation. Apart from the decomposition pathways leading to the β-disproportionation (R − H and R + H) and recombination (R–R) products, which have been studied in detail, in many cases α-decomposition, accompanied by the formation of carbene and carbyne complexes of transition metals, is the dominant process.

The formation of the carbene complexes of tantalum in the decomposition of $[(CH_3)_3CCH_2]_5Ta$ and $(C_6H_5CH_2)_5Ta$ has been demonstrated[17,18]. The reaction products were respectively $[(CH_3)_3CCH_2]_3Ta{=}CHC(CH_3)_3$ and $(C_6H_5CH_2)_3Ta{=}CHC_6H_5$. The formation of three and more ethane molecules in the decomposition of tetramethyltitanium has been demonstrated[19]. The α-disproportionation of methyl groups, accompanied by the formation of methane, has been demonstrated in relation to the decomposition of $(CD_3)_4Ti$.[20]

Interest in a more detailed study of the α-disproportionation reactions was aroused by the development of ideas concerning the carbene and carbyne nature of the active centres in the metathetical reactions of olefinic and acetylenic hydrocarbons. The stabilisation of carbenes by transition metals tends to drive the reaction towards the formation of carbene species. The carbene stabilisation effect can be illustrated by the work of Fischer[21], who demonstrated the possibility of synthesising stable carbene complexes of transition metals. As a rule, one or two heteroatoms (O, S, and N) are attached to the carbene carbon atom, while different stabilising ligands are attached to the transition metal.

The free carbenes, formed, for example, in the decomposition of diazo-compounds, are extremely reactive and are incapable of causing the development of selective reactions, while the stable Fischer carbene complexes have a low reactivity. The carbene and carbyne complexes arising in the decomposition of organometallic compounds of transition metals at the instant of their formation and occupying an intermediate position between the above species as regards chemical reactivity are of special interest.

Below we present the experimental results of studies in our laboratory of the contributions of the α-decomposition reactions for compounds of different transition metals.

II. THE MECHANISM OF THE DECOMPOSITION OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS AT THE INSTANT OF FORMATION. THE RELATIVE CONTRIBUTIONS OF REACTIONS INVOLVING THE α-DISPROPORTIONATION AND RECOMBINATION OF GROUPS

Organometallic compounds of lithium or magnesium containing groups incapable of β-decomposition [CH_3, $C_6H_5CH_2$, $(CH_3)_3SiCH_2$, $C_6H_5C(CH_3)_2CH_2$] have been used as alkylating agents in the reactions with metal halides. The metals investigated (Pt, Pd, Cr, Rh, Mo, Re, W, Ta, Nb, Co) have found extensive applications in the catalytic reactions of hydrocarbons. In recent years some of them (Mo, W, Re, and Ta) in combination with alkylating agents have begun to be used to initiate the chain metathetical reactions of olefins and cyclo-olefins.

Table 1. The composition of the gaseous products of the reaction of CD_3Li with MCl_n.

MCl_n	CD_3Li/MCl_n	Yield, % of CD_3Li			Balance of CD_3 groups, %	$2CD_4+CD_3-CD_4^*$
		CD_4	CD_3-CD_3	$CD_2=CD_2$		
$MoCl_5$	1	60	4.2	3.8	68	124.2
$MoCl_5$	3	70	1.1	0.8	71.9	141.1
WCl_6	1	11	66	0.8	77.8	88
WCl_6	2	20	46	1.5	67.5	86
WCl_6	4	40	35	0.8	75.8	115

*The overall balance of the groups based on Eqn.(3) is presented.

(a) The reaction of CD_3Li with $MoCl_5$ and WCl_6.[22,23] The reaction was carried out in solution in dibutyl ether at 20 °C for 30 min. The yields of the reaction products are given in Table 1.. The products do not contain hydrogen atoms, which indicates the absence of free-radical stages. The main product is CD_4, which is formed solely as a result of the α-disproportionation reaction:

$$(CD_3)_2MX_n \rightarrow CD_4 + CD_2 : MX_n \qquad (3)$$

However, the yield of CD_4, particularly in the reaction involving $MoCl_5$, is much higher than would follow from Eqn. (3), which is confirmed by the overall balance of CD_3 groups. These results can be explained solely by the intensification of the α-decomposition reactions as far as the formation of carbyne and carbide species:

$$\begin{aligned}(CD_3)_3MX_m &\rightarrow 2CD_4 + CD \vdots MX_m ,\\ (CD_3)_4MX_y &\rightarrow 3CD_4 + \text{carbides.}\end{aligned} \qquad (4)$$

CD_2H_2, CDH_3, and CH_4 were isolated in proportions of 4 : 3 : 2 in the decomposition of the resulting precipitate with water, which confirms the formation of species of this kind. It is noteworthy that only a few methylene species are evolved in the form of ethylene or remain bound to molybdenum and tungsten. The carbyne formed is apparently mainly consumed in the reaction with the solvent or with other system components. This phenomenon is also characteristic of the other reactions derived below.

(b) The reactions of $(CH_3)_3SiCH_2Li$ and $(CH_3)_3GeCH_2Li$ with various metal chlorides[24–29]. The reaction was carried out in benzene at 20 °C. When tungsten, molybdenum, tantalum, rhenium, and niobium chlorides were used, the process began in solution, while in the case of cobalt, rhodium, platinum, and palladium chlorides the system was heterogeneous. In this case the metal chloride was taken in a tenfold excess relative to the organolithium compound, which ensured the complete consumption of the latter. The interaction of the organolithium compound with the metal halide can proceed via the following main pathways:

$$(CH_3)_3SiCH_2Li + MCl_n \begin{cases} \longrightarrow (CH_3)_3SiCH_2CH_2Si(CH_3)_3 , & (5a)\\ \longrightarrow (CH_3)_4Si + (CH_3)_3SiCH : MCl_{n-2} , & (5b)\\ \longrightarrow (CH_3)_3SiCl + CH_2 : MCl_{n-2} . & (5c) \end{cases}$$

The possibility of the occurrence of radical stages is excluded from consideration, since it has been shown[24] that, when the reaction is carried out in perdeuterobenzene, analogous products without deuterium atoms are formed. When the reactions were carried out in trideuterotoluene ($C_6H_5CD_3$), the tetramethylsilane formed also did not contain deuterium. Pathway (5a) is characteristic of the usual decomposition leading to the formation of a recombination product. Pathways (5b) and (5c) lead to the formation of trimethylsilyl and methylene–carbene complexes respectively.

Table 2 presents the experimental results. The overall balance of trimethylsilylmethyl groups was set up on the basis of twice the amount of tetramethylsilane [in conformity with Eqn.(5b) and the number of groups detected in the form of $(CH_3)_3SiCl$ and $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$]. The main pathway in the decomposition of trimethylgermylmethyl and trimethylsilylmethyl derivatives of tungsten, formed for the ratio $RLi/WCl_6 = 0.5–1.0$, is pathway (5c), leading to the formation of methylene species. In the case of tantalum, niobium, and rhodium compounds, the α-disproportionation reaction [pathway (5b)] predominates. The contribution of this reaction is fairly large for platinum and palladium compounds and even for $CoCl_2$, although the main reaction product in these cases is the recombination product R–R. The formation of appreciable amounts of $(CH_3)_3SiCl$ in the reaction of $(CH_3)_3SiCH_2Li$ with $PtCl_4$ is noteworthy.

The results obtained show that the formation of carbene species in the decomposition of organometallic compounds is characteristic also of platinum group metals and not only of transition metals involved in metathetical reactions.

(c) Reactions of benzyl derivatives of magnesium and lithium with MX_n.[30–34] The composition of the products of the interaction of benzylmagnesium chloride in diethyl ether with various metal halides was investigated. Control experiments in perdeuterodiethyl ether showed that, in the reaction with $PdCl_2$, the amount of $C_6H_5CH_2D$ formed does not exceed 5% of the overall amount of toluene produced. Apparently the formation of $C_6H_5CH_2D$ is due to the metallation of diethyl ether by organometallic palladium compounds. When the reaction of benzylmagnesium chloride with $MoCl_5$ is carried out in perdeuterodiethyl ether, $C_6H_5CH_2D$ is not formed.

Table 2. The composition of the products of the interaction of $(CH_3)_3ZCH_2Li$ with MCl_n.

MCl_n	RLi/MCl_n	Yield, % of theoretical			Overall group balance, %	Refs.
		$(CH_3)_4Z$	$(CH_3)_3ZCl$	$(CH_3)_2ZCH-CH_2Z(CH_3)_2$		
		Z = Ge				
WCl_6	0.5	11.2	55.4	—	—	[25, 26]
WCl_6	1.0	11.3	43.5	—	—	[25, 26]
WCl_6	2.0	11.2	34.5	—	—	[25, 26]
		Z = Si				
WCl_6	1.0	17.0	31.5	24—26	90.5	[24, 26]
WCl_6	2.0	23.5	23.5	24—26	95.5	[24, 26]
$MoCl_5$	2.0	31.0	10.0	14	86	[27]
$TaCl_5$	0.5	43.0	10.0	traces	96	[27]
$TaCl_5$	1.0	35.0	12.0	11	93	[27]
$ReCl_5$	0.5	7.6	9.5	81	105.7	[29]
$ReCl_5$	1.0	20.0	5.4	55	100.4	[29]
$NbCl_5$	1.0	40.0	6.0	18	104	[29]
$CoCl_2$	0.1	20.0	traces	61	101	[29]
$RhCl_3$	0.1	43.0	traces	16	102	[28]
$PtCl_4$	0.1	16.0	8.0	55	95	—
$PdCl_2$	0.1	17.0	2.0	55	91	[28]

The interaction of $C_6H_5CH_2MgCl$ with metal halides can proceed via the following principal pathways:

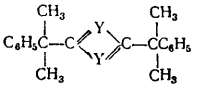
$$C_6H_5CH_2MgCl + MX_n \begin{cases} \longrightarrow C_6H_5CH_2CH_2C_6H_5\,, & (6a) \\ \longrightarrow C_6H_5CH_3 + C_6H_5CH : MX_{n-2} \rightarrow C_6H_5HC{=}CHC_6H_5\,, & (6b) \\ \longrightarrow 2C_6H_5CH_3 + C_6H_5C : MX_{n-3} \rightarrow C_6H_5C{\equiv}CC_6H_5\,. & (6c) \end{cases}$$

The carbene and carbyne fragments can be partly disposed of in the form of stilbene and toluene. The data in Table 3 show that in the reactions of organomagnesium compounds the main product is toluene, in the formation of which 40 to 70% of the benzyl groups of the organometallic compound are consumed. In the reaction with $PtCl_4$ a considerable amount (9–10%) of stilbene is formed.

Particular mention should be made of the fact that in the reactions with $NdCl_3$ and YCl_3 a stable organometallic compound soluble in hydrocarbons is formed in a yield exceeding 90%, to which the following dimeric structure has been attributed:

$$(C_6H_5CH_2)_3Nd\,(Y) \rightarrow 1.8\,C_6H_5CH_3 + 0.5\,C_6H_5C\begin{matrix}\diagup\!\!\diagup Nd\,(Y)\\ \diagdown\!\!\diagdown Nd\,(Y)\end{matrix}CC_6H_5 + \\ + 0.2\,(C_6H_5HC{=}CHC_6H_5 + C_6H_5C{\equiv}CC_6H_5)\,. \qquad (7)$$

In these compounds one fragment of the benzyl group corresponds to each Nd or Y atom. When they are treated with D_2O, $C_6H_5CD_3$ is formed quantitatively. In the reaction with neophenyl-lithium the compound



is formed quantitatively and its hydrolysis yields two t-butylbenzene molecules. In terms of their thermal stability, the complexes produced are analogous to the Fischer carbene complexes.

Table 3. The composition of the products of the interaction of organolithium and organomagnesium compounds (A) with MCl_n in diethyl ether at 20 °C.

MCl_n	A/MCl_n	Yield, % of theoretical				Refs.
		toluene	stilbene	tolane	bibenzyl	
		A = $C_6H_5CH_2MgCl$				
$MoCl_5$	3.0	14—16	0.8—1.5	0.3—0.7	25—27	[30]
WCl_6	0.7	22	0.1	0	7.7	[31]
WCl_6	4.0	17.7	0.5	0	19.1	[31]
$ReCl_5$	3.0	22—27	1.7—2.0	0	18—20	[31]
$RnCl_3$	2.8	26—29	1.2—1.6	0	29—33	[32]
$PdCl_2$	1.5	30—34	0.8—1.2	0	20—38	[32]
$PtCl_4$	4.0	33—34	9—10	0	14—18	[32]
$CrCl_3$	2.5	32—36	1.1—1.4	0	13.8—14.3	[32]
		A = $C_6H_5CH_2Li$				
$NdCl_3$*	2.0	33—57	1.8	0.8	4.2	[33, 34]
YCl_3*	3.0	46	5.0	7.5	4.0	[33, 34]

*In tetrahydrofuran.

Table 4. The composition of the products of the interaction of organolithium and organomagnesium compounds (A) with transition metal chlorides at room temperature.

MCl_n	A/MCl_n	Contribution of reaction, %	
		α-decomposition	recombination (R–R)
	A = CD_3Li		
$MoCl_5$	1—3	96—99	1—4
WCl_6	1—4	34—65	35—66
	A = $(CH_3)_3GeCH_2Li$		
WCl_6	0.5—2.0	46—67	—
	A = $(CH_3)_3SiCH_2Li$		
WCl_6	1—2	74—76	24—26
$MoCl_5$	2	86	14
$TaCl_5$	0.5—1.0	100	0
$ReCl_5$	0.5—1.0	19—45	55—81
$NbCl_5$	0.5—1.0	82—85	15—18
$CoCl_2$	0.1	39	61
$RhCl_3$	0.1	86	14
$PtCl_4$	0.1	45	55
$PdCl_2$	0.1	45	55
	A = $C_6H_5CH_2MgCl$		
$MoCl_5$	3	73—75	25—27
WCl_6	0.7—4.0	81—92	8—19
$ReCl_5$	3	80—82	18—20
$RhCl_3$	2.8	67—71	29—33
$PdCl_2$	1.5	62—71	29—38
$PtCl_4$	4	82—86	14—18
$CrCl_3$	2.5	86	14
	A = $C_6H_5CH_2Li$		
$NdCl_3$	2—3	96	4
YCl_3	3	96	4
	A = $C_6H_5C(CH_3)_2CH_2Li$		
YCl_3	3	100	0

When the reaction of $(CH_3)_3SiCH_2Li$ with $NdCl_3$ was carried out in bromine, stable products were obtained[35] to which the structure

$$(CH_3)_3SiHC{=}Nd{-}CHSi(CH_3)_3\,.\\ \qquad\qquad\qquad\qquad\quad |\\ \qquad\qquad\qquad\qquad Nd{=}CHSi(CH_3)_3$$

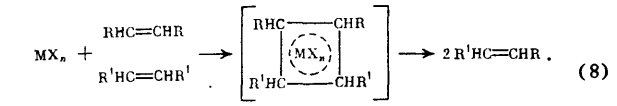
was attributed. When this compound is decomposed with deuterated water, $(CH_3)_3SiCHD_2$ is produced quantitatively.

Particular mention should be made of the considerable contribution of the α-decomposition reaction in the presence of platinum, palladium, and chromium, which are widely used in the catalysis of the reactions of hydrocarbons. Table 4 summarises data characterising the contribution of the α-decomposition reactions leading to carbene species and the contribution of the group recombination reactions (the formation of R–R). It lists the minimum and maximum yields of products obtained for different proportions of organolithium (organomagnesium) compounds and transition metal chlorides.

Thus the α-disproportionation of groups leading to the formation of carbene and carbyne species is in many instances the main pathway in the decomposition of the organometallic compounds of transition metals when the latter do not have hydrogen atoms at the β-carbon atom. As mentioned above, the carbene and carbyne species formed apparently disappear mainly as a result of the reaction with the solvent and only a small proportion are detected as recombination products ($D_2C{=}CD_2$, $C_6H_5HC{=}CHC_6H_5$, and $C_6H_5C{\equiv}CC_6H_5$) and bound as complexes with the transition metal. It will be shown below that the decomposition of the alkyl derivatives of certain transition metals can involve some α-decomposition as well as the main β-decomposition reaction.

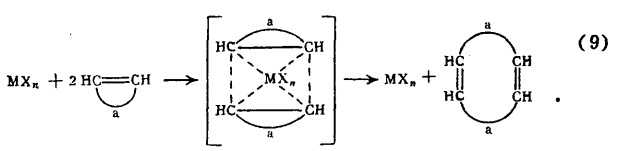
III. THE CHAIN METATHETICAL PROCESS UNDER THE INFLUENCE OF CARBENE COMPLEXES OF TRANSITION METALS

The metathesis of olefins under the influence of molybdenum and tungsten compounds on alumina was first observed by Banks and Bailey[36]. Subsequently systems based on molybdenum, tungsten, and rhenium compounds in combination with organometallic compounds of aluminium, tin, etc. were used widely for these reactions. In their composition, they resemble the Ziegler systems used for the polymerisation of olefins and dienes. The metathetical reactions of olefins in homogeneous systems proceed at the usual temperatures at a very high rate without heat changes. The mechanism proposed initially for this unusual reaction provided for a stepwise process via intermediate stages with formation of quasi-cyclobutane rings having four equivalent carbon atoms[37]:



(8)

Simultaneously and independently Natta and co-workers[38,39] developed their research into the opening of cyclo-olefins under the influence of the same catalytic systems. They showed that the metathesis catalysts initiate the polymerisation of cyclo-olefins at the usual temperatures with formation of polymers in which the double bonds are retained quantitatively. The hypothesis of the intermediate formation of a quasi-cyclobutane ring was used[40] to explain the mechanism of the opening of cyclo-olefins:



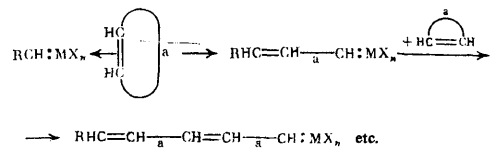
(9)

Calderon et al.[41] were the first to demonstrate that the metathesis of olefins proceeds via a C=C bond dissociation reaction:

$$CD_3DC{=}CDCD_3 + CH_3HC{=}CHCH_3 \rightarrow 2\,CD_3DC{=}CHCH_3\,. \qquad (10)$$

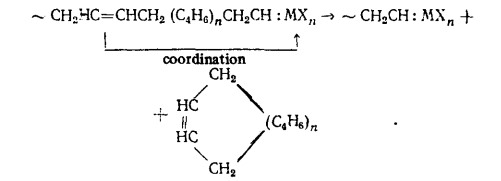
It has been shown in studies[42,43] of the composition of products of the decomposition of the ozonides of a copolymer of a ^{14}C-labelled cyclopentene with cyclo-octene that the polymerisation of cyclo-olefins also takes place with dissociation of the double bonds.

The present author and his co-workers[44–46] showed for the first time that the polymerisation of various cyclo-olefins under the influence of metathesis catalysts results in the formation of high-molecular-weight products at low conversions, oligomers being absent, which constituted direct confirmation of the chain mechanism of the process. The polymerisation of cyclo-olefins initiated by diazo-compounds, which decompose under the influence of WCl_n, was the first experimental evidence for the carbene nature of the active centres[47,48]. The following mechanism of chain propagation under the influence of carbene complexes of transition metals was proposed:



(11)

The polymerisation process consists of consecutive stages in which the monomer is coordinated to the active centre (the carbene complex of the transition metal) and is incorporated in the chain with regeneration of the active centre. The formation of high-molecular-weight products indicated a small number of effective active centres and their comparatively long lifetime. It was shown that unsaturated polymers are readily destructured in solution via the same mechanism with formation of a set of cyclic oligomeric molecules[49–53]:

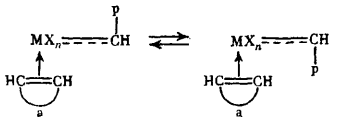


(12)

Thus, high-molecular-weight polybutadiene (molecular weight 200 000) is converted into cyclic oligomers with a number-average molecular weight of 1600 in solution (concentration of raw rubber 8–10%) under the influence of metathesis catalysts after 15 min at room temperature. In the R_2AlCl–$MoCl_3(OCOC_{17}H_{35})_2$ system the oligomers formed retain the *cis*-configuration of the units[53], while in the R_2AlCl–WCl_6 system the ratio of the *cis*- and *trans*-units in the oligomers corresponds approximately to equilibrium. The initial stage of the polymerisation of cyclo-olefins involves the formation of a polymer with a narrow molecular-weight distribution (MWD),[54] which corresponds to a process via a live chain mechanism. The contribution of intramolecular reactions [Eqn.(12)] increases with the degree of polymerisation, which leads to a gradual widening of the MWD.

The $(CH_2{=}CHCH_2)_4Si$–WCl_6 system has been used for the polymerisation of cyclopentene. At −30 °C it gives rise to a polymer containing 98% of *cis*-units, while at +30 °C the product is a polypentenamer with a predominant (~80%) *trans*-configuration of the units[55]. The formation of units with the *cis*- and *trans*-configurations in metathetical reactions is

apparently associated with the rotation of the carbene about the C=M bond:



(13)

where p is the polymer chain.

The energy of rotation of carbenes in the complex $(C_6H_5CH_2)_3Ta{=}X$, where X represents carbene species, has been estimated[56] as 15–22 kcal mol^{-1}. For metathesis catalysts, it is apparently significantly lower and depends on the nature of the transition metal and the ligands surrounding it. The hypothesis of the possibility of such an isomerisation mechanism was first put forward by Ivin et al.[57]

As in other radical anionic chain processes, the metathetical reaction is inhibited by impurities leading to the formation of more stable carbene complexes than those of the growing chain. It has been shown[58–60] that ethyl vinyl ether, butyl vinyl sulphide, and trimethylvinylsilane fully inhibit the cyclopentene ring opening reaction even when present in an amount corresponding to two moles per mole of tungsten:

$$\begin{gathered}
\mathrm{pHC:MX}_n + \mathrm{H_2C{=}CHSi(CH_3)_3} \xrightarrow{(a)} \mathrm{pHC{=}CH_2} + \\
+ \mathrm{(CH_3)_3SiHC:MX}_n \xrightarrow{(b)} \mathrm{p'HC:MX}_n \ , \\
\mathrm{pHC:MX}_n + \mathrm{H_2C{=}CHOR} \xrightarrow{(a)} \mathrm{pHC{=}CH_2} + \\
+ \mathrm{ROHC:MX}_n \xrightarrow{(b)} \mathrm{p'HC:MX}_n \ ; \\
\mathrm{pHC:MX}_n + \mathrm{H_2C{=}CHSR} \xrightarrow{(a)} \mathrm{pHC{=}CH_2} + \mathrm{RSHC:MX}_n \xrightarrow{(b)} \mathrm{p'HC:MX}_n \ .
\end{gathered} \tag{14}$$

The reaction is inhibited in stages (14b) involving the transition from the relatively stable complex to the more reactive complex formed after the incorporation of the monomer.

It has been shown[51] that in the cometathesis of α-olefins the reaction proceeds preferentially towards the exchange of methylene fragments [degenerate metathesis—reaction (15a)]:

$$\mathrm{R'HC{=}CH_2} + \mathrm{RHC{=}CD_2} \begin{cases} \longrightarrow \mathrm{RHC{=}CH_2} + \mathrm{R'HC{=}CD_2} \ ; & (15a) \\ \longrightarrow \mathrm{R'HC{=}CHR} + \mathrm{H_2C{=}CD_2} \ . & (15b) \end{cases}$$

The rate of reaction (15a) is higher by a factor of 10^2–10^3 than that of reaction (15b). The mechanism of this phenomenon was examined and confirmed by the present author and his co-workers[62]. Reaction (15b) can proceed via intermediate stages involving the formation of secondary and primary carbene complexes differing in reactivity:

$$\underline{\mathrm{R'HC:MX}_n\uparrow} \quad \underline{\overset{\mathrm{H_2C:MX}_n}{\downarrow}\mathrm{RHC:MX}_n\uparrow} \quad \underline{\overset{\mathrm{H_2C:MX}_n}{\downarrow}\mathrm{R'HC:MX}_n} \ \text{etc.} \tag{16}$$

Under the conditions of the chain process, even small differences between the reactivities of the primary and secondary carbenes cause a marked retardation of the reaction. Reaction (15a) proceeds via a stage in which secondary carbene complexes with identical reactivities are formed:

$$\mathrm{R'HC:MX}_n \longrightarrow \mathrm{RHC:MX}_n \longrightarrow \mathrm{R'HC:MX}_n \longrightarrow \mathrm{RHC:MX}_n \ \text{etc.} \tag{17}$$

Therefore its rate is much higher than that of reaction (15b).

This mechanism has been confirmed experimentally by the results obtained in the cometathesis of β-butene with α-pentene in equimolar amounts under the influence of the R_2AlCl–WCl_6 system at 20 °C. The following reactions can take place in the initial stage:

$$\mathrm{C_3H_7HC{=}CH_2} + \mathrm{CH_3HC{=}CHCH_3} \rightarrow \mathrm{C_3H_7HC{=}CHCH_3} + \mathrm{CH_3HC{=}CH_2} \ ; \tag{18a}$$

$$2\,\mathrm{C_3H_7HC{=}CH_2} \rightarrow \mathrm{C_3H_7HC{=}CHC_3H_7} + \mathrm{H_2C{=}CH_2} \ . \tag{18b}$$

Reaction (18a) should proceed via consecutive stages involving the formation of the carbene complexes $CH_3CH_2.CH_2HC:MX_n$ and $CH_3HC:MX_n$, while reaction (18b), accompanied by the formation of ethylene, proceeds via stages in which $C_3H_7CH:MX_n$ and $CH_2:MX_n$ are formed. It has been established experimentally that the initial reaction product is only propene and not ethylene.

In the first section of this review, pathways leading to the formation of carbene species in the decomposition of organometallic compounds of transition metals capable of β-disproportionation were considered. In metathesis systems alkyl derivatives of aluminium (tin) are used in which there is a possibility of the α- and β-disproportionation of groups. It appeared important to explain the relatively small contribution in the above systems of α-decomposition reactions leading to the formation of carbene active centres. For this purpose, a study was made of the composition of the products formed in the reaction of $(C_2H_5)_2AlCl$ with $MoCl_3(OCOC_{17}H_{35})_2$ and of $C_2H_5AlCl_2$ with $WCl_4(OR)_2$ in the presence of trimethylvinylsilane[58,63]:

$$\mathrm{C_2H_5Mo\,(W)\,X}_n \begin{cases} \longrightarrow \mathrm{C_2H_4} + \mathrm{C_2H_6} \ ; & (19a) \\ \longrightarrow \mathrm{C_2H_6} + \mathrm{CH_3HC{:}\,Mo\,(W)\,X}_n \ . & (19b) \end{cases}$$

In the presence of trimethylvinylsilane, the reaction leading to the formation of the more stable trimethylsilylcarbene species and propene should take place:

$$\mathrm{CH_3HC:MX}_n + \mathrm{H_2C{=}CHSi(CH_3)_3} \rightarrow \mathrm{(CH_3)_3SiHC:MX}_n + \mathrm{C_3H_6} \ . \tag{20}$$

It has been shown that 3(10)% of propene relative to molybdenum (tungsten) is formed in the reaction. Hence it follows that reaction (19b) plays an appreciable role in the systems considered.

It was noted above that the $(H_2C{=}CHCH_2)_4Si + WCl_6$ system is used for the polymerisation of cyclopentene at −30 °C. It has been shown[64] that the reaction of $H_2C{=}CHCH_2SI(CH_3)_3$ with WCl_6 at room temperature in the absence of the monomer is rapidly completed by the formation of propene in an amount significantly exceeding that permitted by the equation

$$\mathrm{(H_2C{=}CHCH_2)_2WX}_n \rightarrow \mathrm{C_3H_6} + \mathrm{H_2C{=}CHCH{:}\,WX}_n \ . \tag{21}$$

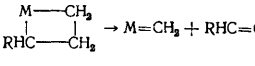
Hence it follows that the reaction of WCl_6 with $H_2C{=}CHCH_2.Si(CH_3)_3$ as well as CD_3Li is more far reaching and involves the formation of the carbyne species $H_2C{=}CHC{\vdots}WX_m$.

A series of studies describing the reactions involving the redistribution of acetylenic hydrocarbons under the influence of carbyne complexes of transition metals have been published recently[65,66]. It has been shown[67] that in the metathesis of acetylenic hydrocarbons under the influence of $(CH_3)_3CC{\equiv}W[OC(CH_3)_3]_3$ the equilibrium composition of product is attained after only 2 min at room temperature:

$$2\mathrm{R'C{\equiv}CR} \rightleftarrows \mathrm{RC{\equiv}CR} + \mathrm{R'C{\equiv}CR'} \ , \tag{22}$$

where R and R′ = C_2H_5 or C_3H_7.

The metathetical reaction is initiated by the metal–cyclobutane complexes, which form carbene active centres on dissociation[68]:



(23)

This served as a basis for the hypothesis that metal–cyclobutane intermediates are involved in the chain metathetical process, which is hardly justified, since metal–cyclobutane

complexes are relatively stable and chain propagation in metathetical reactions proceeds at enormous rates.

The unusual metathetical reactions of olefinic and acetylenic hydrocarbons have attracted the attention of investigators to a new class of active centres arising in the chemical reactions—the carbene and carbyne complexes of transition metals. In many instances they are apparently intermediates in the catalytic reactions of hydrocarbons.

IV. THE MECHANISMS OF THE ELEMENTARY STEPS IN THE CATALYTIC REACTIONS OF HYDROCARBONS UNDER THE INFLUENCE OF TRANSITION METAL COMPOUNDS

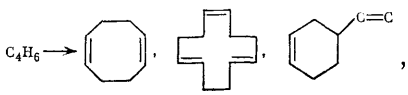
It is well known that many catalytic reactions of hydrocarbons proceed at low temperatures via stages involving organometallic compounds. Apart from the polymerisation of olefins, dienes, and their derivatives, one may quote instances of many other reactions in which the formation of organometallic intermediates has been established. For example, the dimerisation (linear oligomerisation) proceeds via consecutive stages involving the formation of HMX and the corresponding organometallic compound[69,70]:

$$HNiX + H_2C{=}CH_2 \rightleftarrows CH_3CH_2NiX \xrightarrow{C_2H_4} CH_3CH_2CH_2CH_2NiX \rightarrow C_2H_5HC{=}CH_2 + HNiX \quad (24a)$$

$$HNiX + H_2C{=}CH \rightleftarrows \underset{\displaystyle C_6H_5}{CH_2CHNiX} \xrightarrow{H_2C=CH-C_6H_5} \quad (24b)$$

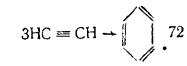
$$CH_3\underset{\displaystyle C_6H_5}{CH}CH_2\underset{\displaystyle C_6H_5}{CHNiX} \rightarrow CH_3\underset{\displaystyle C_6H_5}{CH}{-}CH{=}CH\underset{\displaystyle C_6H_5}{|} + HNiX \ .$$

Other reactions, in particular the cyclic oligomerisation of olefins, dienes, and acetylenic compounds under the influence of reduced transition metal (Ni, Co, Ti, etc.) compounds (the formation of vinylcyclohexene, cyclo-octadiene, cyclododecadiene, aromatic derivatives of acetylenic compounds, etc.), proceed cooperatively at a transition metal atom, sometimes without explicit stages with formation of organometallic σ-compounds,



(25a)

linear dimers and trimers being produced[71]:



(25b)

The same applies to the dienylation reactions occurring under the influence of reduced cobalt, palladium, rhodium, etc. compounds (see, for example, Müller et al.[73]):

$$H_2C{=}CHCH{=}CH_2 + \underset{\displaystyle COOR}{H_2C{=}CH} \rightarrow H_2C{=}CHCH{-}\underset{\displaystyle COOR}{CHCH_2CH_2} \ ; \quad (26a)$$

$$H_2C{=}CHCH{=}CH_2 + C_2H_4 \rightarrow CH_3CH{=}CHCH_2CH{=}CH_2 \ ; \quad (26b)$$

$$2H_2C{=}CHCH{=}CH_2 \xrightarrow{Pd} H_2C{=}CHCH{-}\underset{\displaystyle CH_3}{CH}{=}CHCH{=}CH_2 \ . \quad (26c)$$

All the above reactions take place with migration of a hydrogen atom.

The oxo synthesis under the influence of cobalt and rhodium compounds is also related to reactions proceeding via stages with formation of organometallic compounds[74,75]:

$$HCo(CO)_3 + C_2H_4 \rightarrow CH_3CH_2Co(CO)_3 \xrightarrow{CO} CH_3CH_2COCo(CO)_3 \rightarrow$$

$$\xrightarrow{H_2} CH_3CH_2C\overset{H}{\underset{O}{\diagdown\!\!\diagup}} + HCo(CO)_3 \ . \quad (27)$$

Many other catalytic reactions of hydrocarbons under the influence of transition metals at elevated temperatures should proceed, according to their character, via stages involving the formation of organometallic compounds. This applies to the dehydrogenation, hydrogenation, skeletal isomerisation, and hydrogenolysis of hydrocarbons.

The pathways in the chemical reactions involved in heterogeneous catalysis are usually represented by pathway mechanisms which are convenient for the kinetic description of the process but in many instances fail to elucidate the chemical significance of the elementary steps. The study of the mechanisms of the reactions of organometallic compounds in model systems can apparently yield additional information about the chemical nature of the individual stages of the reaction. On the basis of experimental data on the decomposition pathways of organometallic compounds of transition metals, it is possible to consider the chemical nature of the hydrogenolysis and isomerisation of the carbon skeleton via stages involving the formation of carbene species and cyclopropane derivatives respectively.

1. Hydrogenolysis and Skeletal Isomerisation of Hydrocarbons

The mechanisms of hydrogenolysis usually employed involve the adsorption of adjacent carbon atoms on adjacent metal atoms with dissociation of the C–H bond. It is assumed that the dissociation of the C–C bonds requires that the hydrocarbon groups linked to the metal must undergo further dehydrogenation up to the complete elimination of hydrogen from the carbon atoms[76–78] in $-CH_2C-C$ (with M M). The ruptured fragments are then hydrogenated. The hydrogenolysis belongs to the type of catalytic reactions which are believed to require the simultaneous involvement of a complex *ensemble* of active centres in the reaction. Furthermore the metathetical reaction of olefins indicates the possibility of its occurrence in the presence of hydrogen at one of the metal atoms:

$$RHC{=}MX_n + H_2 \rightarrow RCH_3 + MX_n \ (\text{or } H_2MX_n) \quad (28)$$

As studies on metathetical reactions have developed, it has become clear that almost all transition metals can take part in them. The catalysts of metathesis are usually believed to be only those metals (Mo, W, Re, Ta) in the presence of which the reaction proceeds with a long chain. For the metals indicated, the chain length reaches 10^6–10^7. Although the formation of carbene species is characteristic of almost all other transition metals, the metathetical reactions in their presence do not occur or develop with a short chain.

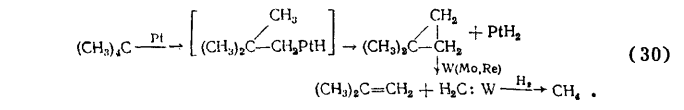
Free carbons in solution combine at the instant of formation with a hydrogen molecule[79]. It has been shown[80] that hydrogen adds at 49 °C to the stable carbene complex $(CO)_5W{=}C(C_6H_5)_2$. A similar reaction in the presence of deuterium should lead to the appearance of two deuterium atoms at a single carbon atom in the initial stage.

The activating effect of small amounts of reduced tungsten, rhenium, and molybdenum compounds in the hydrogenolysis of ethane and neopentane in the presence of a platinum catalyst[81,82] may be caused, as mentioned in our communications[83,84], by their activity in metathetical reactions. The fact that the first stage in the hydrogenolysis of paraffins involves the formation of C=C bonds is also correlated with this fact:

$$RCH_2CH_2R \underset{(a')}{\overset{Pt\ (a)}{\rightleftarrows}} H_2 + RHC{=}CHR \xrightarrow{(b)} \begin{cases} \xrightarrow{W\ \text{etc.}} RHC{=}W \\ \xrightarrow{Pt} RHC{=}Pt \end{cases} \xrightarrow{H_2} RCH_3 \ . \quad (29)$$

In the absence of tungsten, molybdenum, and rhenium compounds, the excess hydrogen retards the hydrogenolysis by shifting the equilibrium towards the starting material [reaction (29a')]. The decrease of the inhibiting effect of

hydrogen in the presence of the above metals is associated with the fact that the latter are more effective in metathetical reactions than platinum. The accelerating effect of tungsten and other metals active in metathetical reactions on the hydrogenolysis of neopentane under the influence of platinum agrees with the extremely effective decomposition of cyclopropane groups by metathetical catalysts:

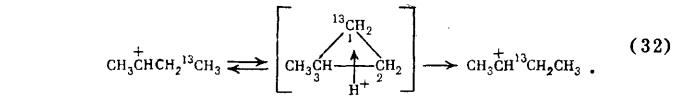


(30)

Numerous studies have been devoted to the skeletal isomerisation of hydrocarbons under the influence of cationic systems. It has been shown[85] that n-[1-^{13}C]butane isomerises rapidly to n-[2-^{13}C]butane under the influence of solutions of superacids (HF + SbF_5):

$$CH_3CH_2CH_2^{13}CH_3 \rightleftarrows CH_3CH_2^{13}CH_2CH_3 . \qquad (31)$$

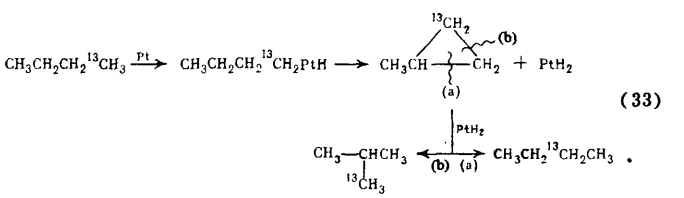
The rate of migration of the ^{13}C atom in n-butane is approximately equal to the rate of isomerisation of n-pentane to isopentane in the presence of the same catalyst. It has been suggested[85] that protonated cyclopropane, which can be formed from a classical carbonium ion, is an intermediate:



(32)

The addition of H^+ to the carbon atom (1) with dissociation of the C(1)–C(3) bond leads to the reformation of the initial cation; the addition of H^+ to the C(2) atom with dissociation of the C(2)–C(3) bond leads to the formation of a carbon skeleton with migration of ^{13}C to a neighbouring position; on the other hand, the addition of H^+ to the C(1) atom with dissociation of the C(1)–C(2) bond results in the formation of an iso-skeleton with the ^{13}C atom in the methyl group. These ideas were used to explain the mechanism of the rapid skeletal isomerisation of n-pentane to isopentane under the influence of cationic systems[86]. The nature of the intermediate state, consisting of protonated cyclopropanes, has been examined[87–89].

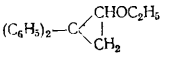
Cyclopropane derivatives can be formed also in the α-decomposition of the organometallic compound. This apparently determines the possibility of skeletal isomerisation also in the presence of non-acid catalysts. It has been established[90] that n-[1-^{13}C]butane is converted on platinum films into isobutane (containing the label only in the methyl group) and n-[2-^{13}C]butane, the isobutane/n-[2-^{13}C]butane ratio remaining constant in the course of the reaction. Hence it follows that the above product should arise from a single intermediate. Thus the above migration of the ^{13}C atom on acid catalysts is also possible on metallic catalysts without cationic components. Such reactions can proceed via stages involving the formation of an organometallic compound with subsequent formation of the cyclopropane ring:



(33)

The usual reactions (decomposition of diazo-compounds etc.) leading to carbene species in solution are as a rule accompanied by the formation of cyclopropane derivatives and olefins (iso-olefins), which arise also as a result of the decomposition of the cyclopropane derivatives formed as the primary products. The ratio of the cyclopropane derivatives and olefins depends in the first place on the structure of the carbene and to a certain extent on the method of its synthesis. According to the data quoted by Kirmse[91], the yields of cyclopropane derivatives are as follows for different carbenes (expressed in percentages of the theoretical yield): 80–96% for $(CH_3)_3CCH$:, 25–51% for $(CH_3)_2CHCH$:, 41% for $C_2H_5CH(CH)_3CH$:, and 43–65% for $(CH_3)_3C-C(CH_3)$:.

So far there are no data on the specific character of the reactions of carbene complexes of transition metals, but one may expect that the ability to form cyclopropane derivatives will also be manifested in such cases. The formation of cyclopropane and its derivatives in metathetical reactions has been noted in a number of studies[36,63,92]. Diphenylcarbenepentacarbonyltungsten reacts with ethyl vinyl ether to form the cyclopropane derivative



in 65% yield[93].

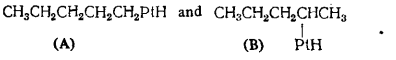
The reactions described above presuppose the primary formation of an organometallic compound via the oxidative addition of hydrocarbons to active zerovalent metals. The possibility of such reactions is considered below. The reaction involving the isomerisation of n-pentane to isopentane, which is the starting material for the synthesis of isoprene, has been studied in a number of investigations. In order to account for the mechanism of this process in the presence of a platinum/alumina catalyst, the following pathway mechanism has been proposed[94]:

$$n\text{-}C_5H_{12} + 2Z_1 \rightarrow C_5H_{11}Z_1 + HZ_1 ; \qquad (34a)$$

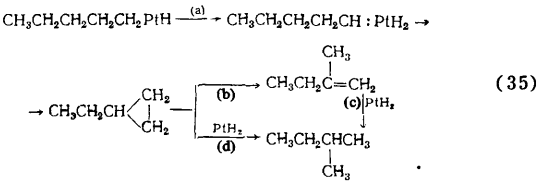
$$C_5H_{11}Z_1 + Z_2 \rightarrow C_5H_{11}Z_2 ; \qquad (34b)$$

$$C_5H_{11}Z_2 \xrightarrow{H_2} \text{iso-}C_5H_{12} . \qquad (34c)$$

The mechanism presupposes the presence of two types of active centres on the catalyst (Z_1 and Z_2). A group of the type of an organometallic compound arises in reaction (34a), while in reaction (34b) the group [C_5H_{11}] is transferred to the active centre Z_2 on which the isomerisation step takes place with participation of hydrogen. The chemical significance of this stage of the reaction as well as the role of hydrogen in it remain obscure. In the absence of a considerable excess of hydrogen (5–10 moles per mole of pentane) the catalyst becomes covered in coke and is rapidly deactivated. In the discussion the chemical nature of the dehydrogenation reactions of hydrocarbons, arguments are adduced below in favour of the initial occurrence of the oxidative addition of hydrocarbons to the metal. For the reactions considered, the primary step may lead to organometallic compounds of two types:

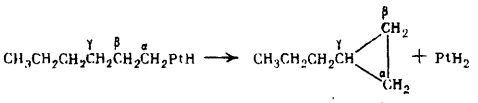


The main pathway in the decomposition of the compounds indicated (β-disproportionation) leads to pentene with a normal carbon skeleton, while α-decomposition, accompanied by the formation of carbene species can lead to the isomerisation of the carbon skeleton:



(35)

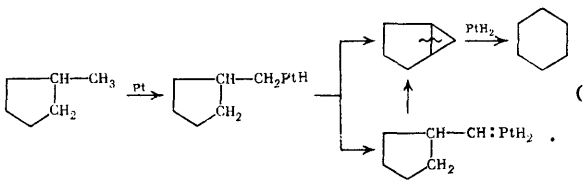
One cannot rule out the possibility of the formation of cyclopropane derivatives as a result of a γ-elimination reaction, as noted by Davidson et al.[16]



(36)

On the basis of the mechanism proposed, the saturation of the catalyst with coke can be accounted for by the formation of an extremely reactive analogue of isobutene, namely $CH_3CH_2C(CH_3)=CH_2$. Hydrogen converts it into isopentane, which prevents the saturation of the catalyst with coke.

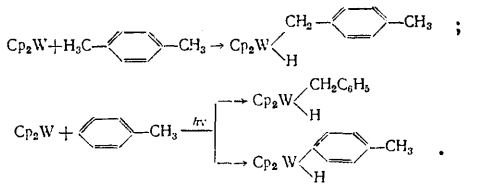
The mechanism of the reversible isomerisation of methylcyclopentane to cyclohexane in the presence of a platinum catalyst can be treated analogously. In the given instance the reaction also requires a considerable excess of hydrogen:



(37)

2. Dehydrogenation of Hydrocarbons

The reaction involving oxidative addition to reduced forms of metals is nowadays well known. The addition of alkenyl halides to nickel carbonyl has been used[95] to obtain the corresponding π-allyl complexes. Alkyl and alkenyl halides readily add to arene complexes of zerovalent vanadium[96] with formation of primary organometallic derivatives. Green has shown[97] that *p*-xylene adds to biscyclopentadienyltungsten even at 60 °C, while toluene reacts with the latter at the usual temperature under the influence of light in accordance with the equation



(38)

The oxidative addition of triphenylphosphine to zerovalent metals (Pd, Ir, Rh, Pt) has been described[98-100]:

$$Ph_3P + Pd^0 \rightarrow Ph_2P{-}Pd{-}Ph \ . \qquad (39)$$

Since the least coordination saturated metal atoms, located on the crystal faces and in the defects, participate preferentially in the dehydrogenation reactions of hydrocarbons, it may be expected that at high temperatures the primary step is oxidative addition accompanied by the formation of an organometallic compound, since decomposition leads to the dehydrogenation products:

$$CH_3CH_2CH_2CH_3 + M^0 \rightarrow CH_3CH_2CH_2CH_2MH \rightleftarrows CH_3CH_2CH{=}CH_2 + MH_2 \ ; \qquad (40a)$$

$$C_6H_5CH_2CH_3 + M^0 \rightarrow C_6H_5\underset{\displaystyle MH}{\underset{|}{C}}HCH_3 \rightleftarrows C_6H_5CH{=}CH_2 + MH_2 \ ; \qquad (40b)$$

$$CH_3CH_2CH_2CH{=}CHR + M^0 \rightarrow CH_3CH_2\underset{\displaystyle MH}{\underset{|}{C}}HCH{=}CHR \rightleftarrows$$

$$\rightleftarrows CH_3CH{=}CHCH{=}CHR + MH_2 \ . \qquad (40c)$$

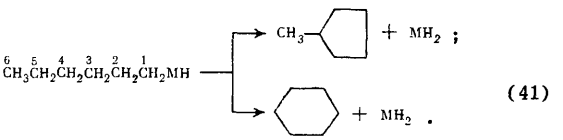
The oxidative addition of butane [reaction (40a)] takes place most readily with participation of the methyl group, since this entails the formation of a more stable primary organometallic compound and the dehydrogenation step involves the usual decomposition pathway of alkyl derivatives (β-decomposition). The finding that the primary product of the dehydrogenation of butane is α-butene, which isomerises further to β-butenes, is consistent with the above considerations. In the case of paraffins containing a large number of CH_2 groups, the fraction of such groups participating in the oxidative addition step increases, which leads to the primary formation of inner double bonds.

The reaction of benzene derivatives [reaction (40b)] takes place with participation of the α-methylene group, since this results in the formation of a more stable compound in which the C–M bond is conjugated with the benzene ring. This fact is correlated with the finding that the α-methylene group at the benzene ring is the first to undergo deuterium exchange under dehydrogenation conditions (deuterium adds to the C–M bond).

In unsaturated hydrocarbons the α-methylene group at the double bond is most reactive, which leads to the π-allyl coordination of the olefin to the transition metal in the primary step. As a consequence of the migration of the double bonds in the allyl system, all the hydrogen atoms are involved in deuterium exchange.

In all the examples presented the dehydrogenation mechanism reflects the main pathway in the decomposition of alkyl and a number of aryl derivatives of organometallic compounds of transition metals—β-decomposition. The mechanism of the dehydrogenation of hydrocarbons at a single metal atom as a result of β-decomposition operates most explicitly in the thoroughly investigated dimerisation (oligomerisation) reactions of ethylene, styrene, and other olefins[69,70]. The decomposition of organolithium and organoaluminium compounds at comparatively low temperatures with formation of olefins and metal hydrides proceeds analogously.

The possible decomposition pathways become more complex with increase in the length of the carbon skeleton. The mechanism under discussion for hydrocarbons becomes just as probable for the reaction at the C–H bond of the fifth or sixth carbon atom, starting from C_5 (and particularly C_6) hydrocarbons:



(41)

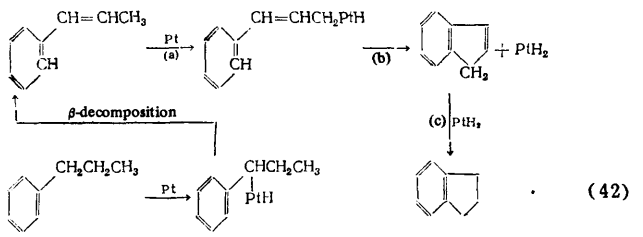
The abstraction of a hydrogen atom from C(5) and C(6) does not entail steric hindrance, while the abstraction of hydrogen atoms from C(3) and C(4) is accompanied by the formation of strained three- and four-membered rings. The contribution of α-decomposition, leading to carbene complexes, is extremely small for alkyl derivatives. One cannot rule out the possibility that the mechanism described reflects the mechanism of the dehydrocyclisation of hexane to methylcyclopentane.

The α-decomposition of organometallic compounds becomes possible in those cases where the reaction leads to the formation of a relatively stable carbene complex, for example, in the dehydrogenation of alkyl ethers, dialkyl sulphides, tetramethylsilane, etc.

It was shown above that the carbene pathway leading to the decomposition of organometallic compounds of platinum, palladium, and many other metals predominates when these have no β-hydrogen atoms. Such a decomposition pathway

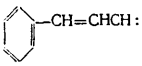
is apparently rate-determining in the dehydrogenation of toluene, tetramethylsilane, neopentane, etc. when the removal of hydrogen from the system is ensured. The oxidative addition of toluene to a zerovalent metal should lead to the formation of bibenzyl.

The main initial products of the reactions of n-propylbenzene and ω-methylstyrene in the presence of Pt/Al_2O_3 at 450–500 °C are indene and indan, while the formation of other products (the hydrogenolysis and isomerisation products) is associated with the reactions of intermediates[101]. The CH_3 group in ω-methylstyrene and the α-methylene group in n-propylbenzene should be extremely reactive in oxidative addition to platinum. It is therefore possible to consider a reaction mechanism involving oxidative addition stages, which leads to one intermediate:



(42)

Reaction (42) can proceed via ω-elimination or via a stage in which a carbene species is formed:



3. Hydrogenation of Olefins

The addition of olefinic and diene hydrocarbons to a hydrogen-transition metal bond is known to occur in many instances. Nickel, cobalt, and chromium hydrides in ether combine with butadiene to form π-allyl complexes, which dissolve[102]:

$$\begin{aligned} &NiH_2 \xrightarrow{C_4H_6} (\pi\text{-}C_4H_7)_2Ni \ ; \\ &CoH_n \xrightarrow{C_4H_6} (\pi\text{-}C_4H_7)_3Co \ ; \\ &CrH_3 \xrightarrow{C_4H_6} (\pi\text{-}C_4H_7)_3Cr \ . \end{aligned} \qquad (43)$$

As mentioned above, the dimerisation reactions of ethylene and styrene proceed via a stage in which the olefin adds to HNiX. In the polymerisation of dienes and olefins under the influence of Ziegler–Natta systems containing titanium, cobalt, nickel, and other metal halides as well as organoaluminium compounds, hydrogen is used as the chain transferring agent:

$$pCH_2MX + H_2 \rightarrow pCH_3 + HMX \xrightarrow{\text{olefin}} RMX \ . \qquad (44)$$

Thus there are sufficient grounds to assume that the first stage in the hydrogenation reaction is the addition of the olefin to the M–H bond with formation of an organometallic derivative. This is consistent with the concept of the semihydrogenated state adopted in catalysis. On the basis of the available data for the reaction pathways of organometallic compounds of transition metals, the hydrogenation mechanism can be represented as follows in relation to metal dihydrides:

$$\begin{aligned} &H{-}M{-}H + 2H_2C{=}CHR \rightarrow RCH_2CH_2MCH_2CH_2R \rightarrow \\ &\quad \xrightarrow{2H_2} 2RCH_2CH_3 + H{-}M{-}H \ ; && (45a) \\ &\quad \longrightarrow RHC{=}CH_2 + RCH_2CH_3 \ ; && (45b) \\ &\quad \longrightarrow RCH_2CH_3 + RCH_2CH : M \xrightarrow{D_2} RCH_2CHD_2 \ ; && (45c) \\ &\quad \longrightarrow RCH_2CH_2CH_2CH_2R \ . && (45d) \end{aligned}$$

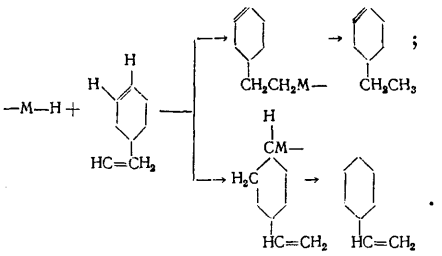
Reaction (45a) leads to the hydrogenation of both olefinic molecules. Reaction (45b), which proceeds via the β-decomposition mechanism, regenerates one olefinic molecule. The contribution of reaction (45c) can increase on formation of relatively more stable carbenes and can be estimated from the number of molecules containing two deuterium atoms at a single carbon atom at low conversions.

The semihydrogenated state in the case of styrene, 1,1-diphenylethylene, or compounds of the type of alkyl vinyl ethers and acrylonitrile corresponds to an addition product in which the C–M bond is conjugated with the benzene ring or other groups:

$$\begin{aligned} &{-}M{-}H + C_6H_5HC{=}CH_2 \rightarrow {-}M{-}\underset{C_6H_5}{CHCH_3} \ ; \\ &{-}M{-}H + (C_6H_5)_2C{=}CH_2 \rightarrow {-}M{-}\underset{(C_6H_5)}{C}{-}CH_3 \ ; \\ &{-}M{-}H + H_2C{=}CHOR \rightarrow {-}M{-}\underset{OR}{CHCH_3} \ ; \\ &{-}M{-}H + H_2C{=}\underset{CN}{CH} \rightarrow {-}M{-}\underset{CN}{CH}{-}CH_3 \ . \end{aligned} \qquad (46)$$

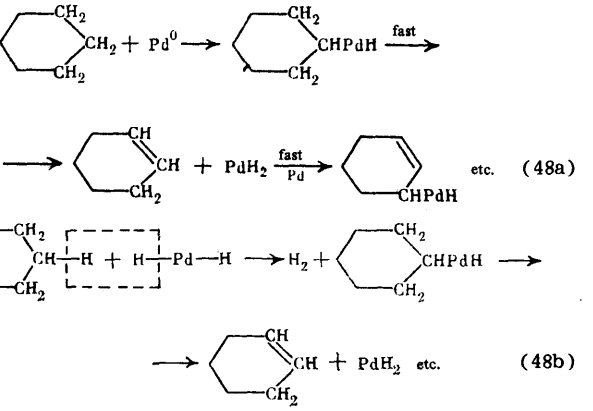
This mode of addition of styrene to HNiX has been demonstrated[70].

It has been shown that, in the hydrogenation of vinylcyclohexene derivatives over platinum and nickel, the vinyl group is hydrogenated faster than the double bond in the cyclohexene ring[103]:



Pathway (47a) leads to the formation of a more stable primary organometallic compound than pathway (47b). For the same reason, the hydrogenation of α-olefins is always faster than that of olefins with inner double bonds.

The accelerating effect of a small amount of hydrogen on the dehydrogenation of cyclohexane in the presence of a palladium catalyst has been noted[104]. These somewhat unexpected results can be explained by considering two reaction pathways via stages involving the formation of organometallic compounds:

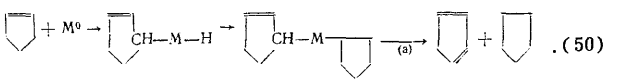


If reaction (48b) is faster than (48a), then the activating effect of hydrogen can apparently be explained by the formation of the hydride PdH_2, which accelerates the stage in which the organometallic compound is formed.

The autohydrogenation phenomenon, observed in the reactions of ethylene, butadiene, and cyclopentene over nickel, palladium, and iron[105–108] can be explained solely in terms of organometallic intermediates:

$$H_2C{=}CH_2 + M^0 \rightarrow H_2C{=}CH{-}M{-}H \xrightarrow[(a)]{C_2H_4} H_2C{=}CH{-}M{-}CH_2CH_3 \rightarrow \rightarrow HC{\equiv}CH + CH_3CH_3 \ . \quad (49)$$

Analogous subsequent reactions of acetylene lead to the formation of carbide species:



. (50)

The above equations presuppose the consecutive occurrence of the reaction via stages involving oxidative addition to the zerovalent metal (M^0), the addition of the olefin to the M–H bond, and the β-decomposition of the organometallic compound. Numerous examples of deuterium exchange involving olefins and dienes, observed in hydrogenation with deuterium[108], are consistent with the above ideas:

$$H_2C{=}CH_2 + D{-}M{-}D \rightarrow CH_2D{-}CH_2M{-}CH_2CH_2D \xrightarrow[\beta\text{-decomposition}]{} HDC{=}CH_2 + CH_3CH_2D \ . \quad (51)$$

Reactions (49) and (50) lead to analogous products of single-stage exchange in olefins and dienes if deuterium adds to the C–M bond in stages (a).

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Thus studies of the composition of the decomposition products of methyl, benzyl, trimethylsilylmethyl, and certain other derivatives of transition metals (Mo, W, Re, Ta, Pt, Pd, Cr, Rh, Nd, Y, Nb) established that the main pathway leading to the decomposition of the above organometallic compounds at the instant of their formation is α-decomposition accompanied by the formation of carbene and carbyne species. The absence of radical stages in the decomposition of the above compounds has been demonstrated.

The metathetical reactions of olefins and the ring opening reactions of cyclo-olefins proceed via a chain mechanism under the influence of carbene complexes of transition metals. The mechanisms of the elementary stages of the process, namely initiation, chain propagation, and chain transfer, have been examined. It has been established that the above reactions obey the usual rules characteristic of chain processes.

Analysis of experimental data for the reaction pathways of organometallic compounds of transition metals led to hypotheses concerning the chemical nature of the elementary steps in the catalytic reactions of hydrocarbons at a single metal atom. It has been suggested that the hydrogenolysis of the carbon skeleton proceeds via consecutive stages involving dehydrogenation (the formation of C=C bonds), the formation of carbene complexes, and addition of hydrogen to the latter.

The skeletal isomerisation reactions proceed via a stage in which cyclopropane groups are formed. The mechanism of the dehydrogenation reaction includes a stage involving the oxidative addition of the hydrocarbon to a zerovalent metal followed by the β-decomposition of the organometallic compound.

A two-stage mechanism, providing for the addition of the olefin to the M–H bond and of hydrogen to the C–M bond, has been proposed for the hydrogenation reactions. The above considerations explain the mechanism of the autohydration reactions. The above considerations explain the mechanism of the autohydrogenation of olefins and dienes and the mechanism of the deuterium exchange involving such compounds.

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