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The Reactions of Hydrocarbons under the Influence of Transition Metal Atoms and Ions in the Gas Phase at Room Temperature

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The results of numerous experimental studies of the composition of the products fromed on interaction of hydrocarbons with transition metal atoms or ions in the gas phase at room temperature are surveyed. In all cases organometallic intermediates are formed, their decomposition leading to the final reaction products. The results presented are of great interest for the understanding of the chemical nature of the elementary steps in the reactions of hydrocarbons in heterogeneous catalysis. The bibliography includes 68 references.

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I. INTRODUCTION

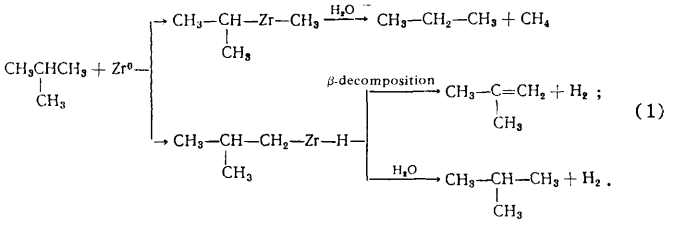
The modern ideas about the mechanisms of the elementary steps in the reactions of hydrocarbons under the influence of transition metals in heterogeneous catalysis presuppose the preliminary dissociative adsorption of the hydrocarbons on the catalyst surface with formation of radical-like fragments, which consist of hydrocarbon groups or hydrogen atoms, and are in some way linked to the heteroatoms, and are capable of migrating from one active centre of another. As a rule catalytic reactions proceed with participation of a large number of active centres; this applies particularly to the hydrogenolysis and skeletal isomerisation reactions of hydrocarbons under the influence of transition metals. In view of the lack of direct experimental approaches to the study of the chemistry of the elementary steps in heterogeneous catalysis, the idea that different active centres and intermediate hydrocarbon species, whose chemical nature is obscure, participate in different reaction stages is frequently resorted to. In earlier publications, we examined the chemistry of the elementary steps in hydrogenation, dehydrogenation, hydrogenolysis, and deuterium exchange processes on the basis of the idea that the primary reaction involves the oxidative addition of hydrocarbons to a transition metal atom on the surface with subsequent decomposition of the resulting organometallic compound.[1-3] Thus it has been suggested that hydrogenation in heterogeneous systems proceeds via stages in which the olefin adds to the H–N hydride bond and that a hydrogen molecule adds to the C–M bond with regeneration of the initial hydride derivative, while the dehydrogenation reaction includes a stage in which the hydrocarbon undergoes oxidative addition to the reduced metal with subsequent β-decomposition of the organometallic intermediate. This made it possible to explain the primary formation of but-1-ene observed in the heterogeneous catalytic dehydrogenation of butane. The specific deuterium-exchange reactions involving various hydrocarbons in the initial stages and the mechanism of the autohydrogenation of unsaturated hydrocarbons have also been examined on the basis of these ideas. The pathways leading to the decomposition of organometallic compounds of transition metals frequently used in heterogeneous catalysis (Ni, Co, Pt, Pd, W, Mo, Rh, Cr, etc.) have been recently studied in detail in relation to various alkyl and aryl derivatives. They decompose mainly via β-elimination, which leads to the formation of equimolar amounts of alkenes and alkanes, and α-decomposition accompanied by the formation of extremely reactive carbene and carbyne species and recombination products produced from the hydrocarbon groups linked to the metal. The chain metathetical reactions of olefinic hydrocarbons under the influence of W, Mo, Re, and Ta compounds are known to be initiated by the carbene complexes formed on α-decomposition of organometallic compounds. The mechanisms of all these reactions have been described in detail in a series of reviews.[4-8] Naturally, the metal atoms which retain the greatest number of free coordination sites and whose reactivity approaches that of isolated atoms are the most reactive in the oxidative addition reactions of hydrocarbons. The metal atoms on the crystal faces, in dislocations, and, as will be shown below, in the gas phase and in the hydrocarbon matrix may play a similar role.

Not only zerovalent metals but also metals in low oxidation states are sometimes fairly active in similar reactions, as shown for the addition of toluene to biscyclopentadienyltungsten[9] and of triphenylphosphine to a series of Group VIII metals.[10] The contribution of the homolytic decomposition of the organometallic compounds, accompanied by the formation of free radicals is small and thus should apparently increase with increase of reaction temperature. However, a high selectivity of the action of catalysts at elevated temperature is incompatible with the occurrence of free-radical stages in the process, which indicates the need to take account of other pathways which have been investigated for the reactions of organometallic intermediates.

Numerous publications devoted to the study of the reactions of hydrocarbons with metal atoms in hydrocarbon matrices at reduced temperatures or with metal ions in the gas phase at room temperature have appeared recently. The composition of the products of these reactions shows that the latter take place via stages in which the metal adds to the C–H or C–C bond with subsequent reaction of the organometallic intermediate. These investigations are of great interest for the understanding of the chemical nature of the elementary steps in heterogeneous-catalytic reactions of hydrocarbons and can serve as an experimental basis for the examination of the reaction mechanisms. This review presents a survey of the results of the published studies in this field.

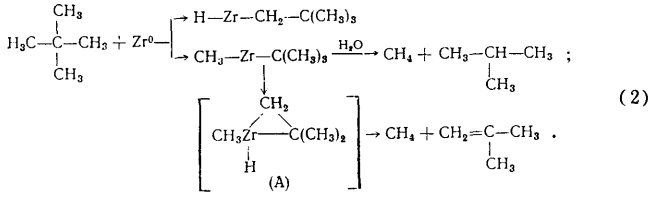
II. THE REACTIONS OF HYDROCARBONS WITH METAL ATOMS

The possibility of the chemical interaction of metal atoms with alkanes was established for the first time in 1979.[11] The authors showed that the reaction of zirconium atoms, obtained by evaporation in a high vacuum, with isobutane or neopentane in a matrix begins already at −196 °C. Heating of the hydrocarbon matrix to room temperature is accompanied by the evolution of a certain amount of hydrogen and of traces of methane. Subsequent hydrolysis of the matrix leads to the formation of considerable amounts of hydrogen and C_1–C_4 hydrocarbons in the case of isobutane and C_1–C_5 hydrocarbons in the case of neopentane. The main products of the first reaction were isobutene and methane and those of the second were methane, isobutane, and isobutene. The results enabled the authors to conclude that the zirconium undergoes oxidative addition to the C–H or C–C bonds of isobutane and neopentane with subsequent decomposition of the organometallic compounds formed:



(1)

The following reaction mechanism has been proposed for neopentane:



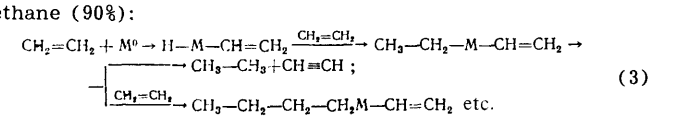
(2)

The presence of isobutane in the products of the reaction of zerovalent zirconium with neopentane is apparently associated with the hydrolysis of the organometallic compounds formed as a result of the insertion of the metal in the C–C bond. Although the hypothesis of the formation of the intermediate state (A) is controversial, it is difficult to imagine other pathways leading to the formation of isobutene and methane—products which are characteristic of the reaction of neopentane under the conditions of heterogeneous catalysis at high temperatures.

It has been shown[11] that many other transition metals (Ti, V, Cr, Mn, Fe, Ni, Co, Mo, and W) can undergo oxidative addition to isobutane under the same conditions with formation of the decomposition products of the organometallic intermediates.

The decomposition products of organometallic intermediates have been detected in studies[12,13] of the condensation of zerovalent nickel vapour on pentane, 2,3-dimethylbutane, methylcyclopentane, and cyclopentane at −196 °C.

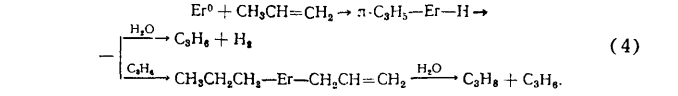
The interaction of the vapours of metallic ytterbium, samarium, and erbium, with ethylene, propene, and allene and also the reaction of erbium with cyclopropane at −196 °C have been investigated.[14] Organolanthanide compounds stable at room temperature were obtained. The product of the reaction of erbium with propene, apparently a π-allyl complex, proved to be soluble in tetrahydrofuran (THF). A small amount of hydrogen was found among the products of the hydrolysis of the organometallic compounds obtained in all the systems. The composition of the main hydrolysis products depended on the nature of the metal and the hydrocarbon. Thus the hydrolysis of the ethylene matrix with ytterbium and samarium led to the formation of C_1–C_6 hydrocarbons, which indicates the oligomerisation of ethylene under the influence of organometallic lanthanide compounds. The main hydrolysis product in the erbium–ethylene system was methane (90%):



(3)

The methane formed is apparently the product of the hydrolysis of the carbide produced as a result of the interaction of the zerovalent metal with acetylene. An analogous explanation was put forward by ourselves[3] in a study of the mechanism of the autohydrogenation of olefins.

Propyne, propane, propene, and the initial allene were found among the principle hydrolysis products in the reaction involving allene or in this reaction the products were propane, propyne, and the initial propene. On the basis of the considerations concerning the role of the organometallic intermediates and their decomposition pathways put forward in our earlier studies,[1–3] the reactions of propene can be accounted for in terms of the mechanisms



(4)

The hydrolysis of the erbium–cyclopropane matrix led to the formation of mainly the propane–propene fraction, propyne, and the initial cyclopropane. The data obtained led to the conclusion that the reactions in the systems investigated have a complex mechanism and that oxidative addition of the metal to the C–H bond takes place in all cases.

The oxidative addition of lanthanides to the C–H bond has been observed for hydrocarbons containing weakly acidic hydrogen. Thus the interaction of ytterbium, samarium, and erbium with hex-1-yne at −196 °C leads to the formation of lanthanide hydride compounds.[15] The formation of neodymium hydride in the decomposition of its butyl derivatives, obtained by the exchange reaction of $(C_5H_5)_3Nd$ with n-BuLi, has been observed.[16]

An infrared spectroscopic study of the photoinitiated reaction of copper atoms in a methane matrix at −261 °C demonstrated[17] the formation of organometallic compounds of the type CH_3MH. The formation of analogous compounds on photoinitiation had been observed earlier[18,19] in the reactions of iron, cobalt, copper, manganese, and lanthanide atoms with methane at −253 °C.

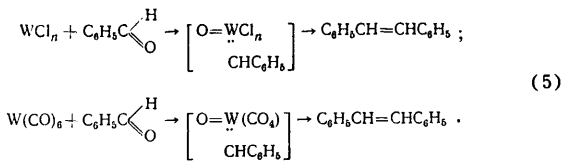
The infrared spectroscopic method made it possible to establish the insertion of a photoexcited iron atom in the C–H bond of ethane and propane at −263 °C.[20] The formation of a metallocyclobutane derivative, the product of the insertion in the C–C bond, was observed for cyclopropane.

The reaction of ethylene with cobalt, rhodium, nickel, and palladium atoms at −261 °C was investigated by infrared spectroscopy under conditions involving matrix isolation.[21] The formation of only the π-complex with ethylene was observed in all cases; this may be regarded as the primary reaction stage leading to the insertion of the metal in the C–H bond at higher temperature.

III. THE REACTIONS OF CARBONYL COMPOUNDS WITH METALS IN LOW OXIDATION STATES

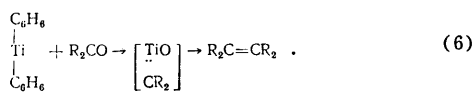
Not only the atoms of transition metals but also their other forms corresponding to low oxidation states can enter into the oxidative addition reactions. This has been established

for the interaction of aldehydes and ketones with tungsten and titanium compounds in which the metal is in a reduced state. Thus it has been shown that the addition of benzaldehyde to the WCl_6–2RLi system in THF at room temperature induces the rapid formation of stilbene.[22] According to the data of Fujiwara et al.,[23] the WCl_6–$LiAlH_4$ system is just as active in this reaction, while tungsten and molybdenum carbonyls have somewhat lower activities. The formation of olefins from carbonyl compounds in the electrochemical reduction of WCl_6 has been observed.[24] The formation of stilbene as a result of the oxidative addition of benzaldehyde to reduced metals can be represented schematically as follows:



(5)

Ledon et al.[25] investigated the reductive dimerisation of aldehydes and ketones under the influence of a zerovalent titanium complex–bisbenzenetitanium. The reactions of benzophenone and acetone with bisbenzene-titanium at 75–80 °C in THF led to the formation of tetraphenylethylene and tetramethylethylene respectively in quantitative yields. Presumably the reaction proceeds via the mechanism



(6)

IV. OXIDATIVE ADDITION OF HYDROCARBONS TO TRANSITION METAL IONS

Numerous studies devoted to the gas-phase reactions of hydrocarbons at room temperature and in a high vacuum with the univalent ions of a whole series of transition metals (Rh^+, Fe^+, Co^+, Ni^+, Cr^+, and Sc^+) have been published recently. The reactions of alkanes,[26–36] alkenes,[31,37–40] cyclic hydrocarbons,[26,27,35,41,42] and their derivatives, namely alkyl halides,[43–47] alcohols,[44,45] aldehydes and ketones,[48–50] ethers,[48,49] amines[51,52] and nitro-compounds,[53] have been investigated. Transition metal ions have been obtained with the aid of laser radiation,[26–28,37,41,46] by thermal ionisation,[32–36,40,42,50,53] or under the influence of the electron impact.[29–31,38,39,43,45,47–49,51,52] The gas-phase reactions of the ions were investigated mass-spectrometrically. Naturally, the energy levels of the metal ions transferred to the gas phase differ significantly depending on the nature of the metal and the conditions of their formation which indicates influence on the character of the product formed, in particular on the relative contributions of the reactions involving insertion in the C–H and C–C bonds. In this connection, the high reactivity of the isolated metal atoms and ions in the gas phase means that their interaction with hydrocarbons at room temperature leads to the formation of the same products as in heterogeneous catalysis at high temperatures.

The composition of the primary products of the interaction of hydrocarbons with Rh^+, obtained by irradiating rhodium foil with a laser beam in the presence of the reacting hydrocarbon, has been investigated mass-spectrometrically.[26] The contribution by secondary reactions does not exceed 10%. The results of this study, presented in Table 1, are of significant interest for the understanding of the chemical nature of the elementary steps in the catalytic reactions of hydrocarbons under the influence of individual metal atoms or ions.

In the reactions of ethane and propane, olefins bound in complexes are formed quantitatively (or almost quantitatively), while the reactions of n-butane, n-pentane, and 2,3-dimethylbutane give rise to dienes with evolution of the corresponding amount of H_2. Trienes bound in complexes are formed from n-heptane and n-octane with evolution of three H_2 molecules.

Table 1. The composition of the primary products of the reactions of Rh^+ with alkanes at room temperature.[26]

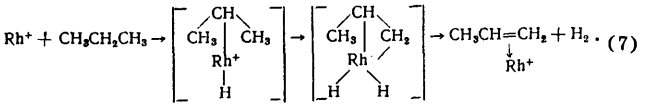
Alkane	$(RhA)^+$	Yield $(RhA^+)^*$, %	Neutral products
C_2H_6	$RhC_2H_4^+$	100	H_2
C_3H_8	$RhC_3H_6^+$	94	H_2
$n\text{-}C_4H_{10}$	$RhC_4H_6^+$	100	$2H_2$
$iso\text{-}C_4H_{10}$	$RhC_4H_8^+$	43	H_2
	$RhC_4H_6^+$	48	$2H_2$
$n\text{-}C_5H_{12}$	$RhC_5H_8^+$	88	$2H_2$
$iso\text{-}C_5H_{12}$	$RhC_5H_8^+$	97	$2H_2$
$neo\text{-}C_5H_{12}$	$RhC_5H_{10}^+$	15	H_2
	$RhC_5H_8^+$	29	$2H_2$
	$RhC_4H_8^+$	13	CH_4
	$RhC_4H_6^+$	34	H_2, CH_4
$n\text{-}C_6H_{14}$	$RhC_6H_{10}^+$	49	$2H_2$
	$RhC_6H_8^+$	33	$3H_2$
	$RhC_6H_6^+$	18	$4H_2$
$CH_3{-}CH(CH_3){-}CH(CH_3){-}CH_3$	$RhC_6H_{10}^+$	100	$2H_2$
$n\text{-}C_7H_{16}$	$RhC_7H_{10}^+$	94	$3H_2$
$n\text{-}C_8H_{18}$	$RhC_8H_{12}^+$	91	$3H_2$
Cyclopropane	$RhC_3H_4^+$	76	H_2
	$RhCH_2^+$	11	C_2H_4
Cyclopentane	$RhC_5H_6^+$	100	$2H_2$
Cyclohexane	$RhC_6H_8^+$	65	$2H_2$
	$RhC_6H_6^+$	35	$3H_2$

*Relative to theoretical yield.

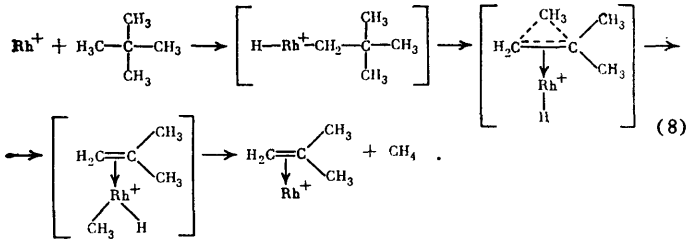
The principle products of the reaction of n-hexane are complexes of a diene and triene as well as benzene, which is apparently formed from the linear triene via the intermediate cyclohexadiene. It has been shown[54,55] that the dehydrocyclisation of hexane to benzene in heterogeneous catalysis at high temperatures proceeds via consecutive stages involving the formation of an olefin, a diene, a triene, and cyclohexadiene. Complexes of isobutene and butadiene are formed in approximately equal amounts from isobutane. The formation of butadiene indicates the occurrence of skeletal isomerisation together with dehydrogenation. The neopentane reaction products are of special interest. Apart from the isopentene and isoprene complexes, arising as a result of consecutive steps involving the isomerisation of neopentane and its dehydrogenation, complexes of butene and butadiene with the metal, formed as a result of the decomposition of the hydrocarbon skeleton with the simultaneous evolution of CH_4 and H_2, were also detected. As expected, a complex of cyclopentadiene is formed in a quantitative yield from cyclopentane, while the complexes of cyclohexadiene and benzene are formed from cyclohexane. It is of interest to note that

a complex of methylene carbene was formed in a yield of approximately 11% from cyclopropane. All these reactions are characteristic of heterogeneous catalysis by transition metals at high temperatures.

It has been concluded[26] that the primary step is the oxidative addition of the hydrocarbon with formation of the organometallic derivative and the decomposition of the latter leads to the final reaction products. Thus the following mechanisms have been proposed for propane and neopentane:



(7)

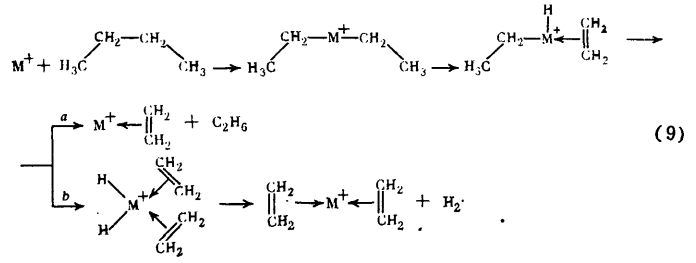


(8)

It is noteworthy that the insertion of the metal in a C–H bond in the methyl group, and not in the methylene group as in Eqn.(7), appears to us preferable, since this involves the formation of a more stable primary organometallic intermediate. The decomposition of the latter via the β-elimination pathway leads to the formation of the same reaction products.

The reactions of normal and branched alkanes as well as cycloalkanes with Ti^+ ions obtained by the action of laser radiation on titanium foil were investigated in a subsequent study.[27] The Ti^+ ions are inserted mainly in the C–H bonds of hydrocarbons, leading to the formation of products similar to those obtained in the presence of Rh^+ ions.

The reactions of Fe^+, Co^+, and Ni^+ ions with a series of normal alkanes ranging from propane to heptane have been investigated.[28] The Fe^+, Co^+, and Ni^+ ions were obtained by the same method as the Rh^+ and Ti^+ ions. It was found that the Ni^+ and Co^+ ions are mainly inserted in a C–C bond with formation of unsaturated products of the decomposition of the carbon skeleton:



(9)

If the metal is inserted in the CH_2–CH_3 bond in n-butane, then the same reaction leads to the formation of propene and methane. Diethylcobalt, obtained by the reaction of ethyllithium with $CoCl_2$, is known to decompose only via pathway (9a), leading to the formation of equimolar amounts of ethane and ethylene.[56] Such products can arise not only via each stage involving the formation of a hydride derivative, as in reaction (9a), but also as a result of the disproportionation of two ethyl groups bound to the metal. Reaction (9b), which leads only to ethylene, does not occur in this case. It may be that this reaction is specific to metal ions. In the case of Fe^+, the insertion in a C–H bond with subsequent formation of an olefin is observed together with the above reaction.

The study of the reactions of a series of olefins, ranging from ethylene to hexene isomers, in the presence of Fe^+ ions obtained with the aid of laser radiation has shown that the composition of the primary reaction products depends on the nature of the olefin.[37] Ethylene, propene, and isobutene did not react with Fe^+ ions under these conditions. n-Butenes give rise to quantitative yields of products of the insertion in a C–H bond. In contrast to n-butenes, methylbutenes produce considerable amounts of products of the insertion in a C–C bond. In the reactions of n-pentenes and hexenes, the last of the reactions indicated becomes the main one.

The reactions of Fe^+, Co^+, and Ni^+ ions with cyclic hydrocarbons, namely cycloalkanes and cycloalkenes, have also been investigated.[41] In this case the reaction involving the insertion of the metal ion in a C–C bond is the main one, which is the reason for the formation of products of the dehydrogenation and rupture of the carbon skeleton, as has been noted for the reactions of Co^+ and Ni^+ with n-alkanes.

It has been established that the presence of the hydride ligand[57] influences significantly the reactivity of the metal ions. This conclusion was reached on the basis of the study of the reactions of FeD^+, CoD^+, and NiD^+ with a series of alkanes (C_1–C_5) and alkenes (C_2 and C_3) in the gas phase. The FeD^+, CoD^+, and NiD^+ ions were generated by the reaction of the Fe^+, Co^+, and Ni^+ ions, obtained by laser radiation, with deuteriated nitromethane or methyl nitrite:

$$M^+ + CD_3NO_2 \xrightarrow{-NO} MOCD_3^+ \xrightarrow{-CD_2O} MD^+ ;$$
$$M^+ + CD_3ONO \xrightarrow{-NO} MOCD_3^+ \xrightarrow{-CD_2O} MD^+ . \qquad (10)$$

It was found that the FeD^+, CoD^+, and NiD^+ ions are inserted mainly in C–H bonds of the alkanes, in contrast to the Co^+ and Ni^+ ions, which, as shown above, give rise mainly to products of the insertion in a C–C bond. NiD^+ and CoD^+ are then capable of reacting with ethane, while NiD^+ is capable of oxidative addition even to methane.

It was noted above that the Fe^+ ion does not react with ethylene and propene. On the other hand, FeD^+ and CoD^+ can undergo oxidative addition to the C=C bond of propene and NiD^+ also to the C=C bond of ethylene.

According to the data of Jacobson and Freiser,[58] $CoCH_3^+$ as well as MH^+ ions are inserted solely in a C–H bond of aliphatic alkanes, starting with propane. This fact has been established in a study of gas-phase reactions of $CoCH_3^+$ with a series of alkanes ranging from methane to hexane isomers. The $CoCH_3^+$ ions were obtained by the reaction of Co^+, generated by laser radiation, with methyl iodide:

$$Co^+ + CH_3I \rightarrow CoCH_3^+ + I . \qquad (11)$$

The authors showed that methane and ethane do not react with $CoCH_3^+$. The evolution of mainly methane and the formation of dehydrogenation products were observed in the reactions with participation of C_3–C_6 alkanes. In the reactions of 2,2-dimethylpropane and 2,2-dimethylbutane, methane is the main neutral reaction product (insertion in a C–C bond).

The $FeCH_3^+$ ions, obtained by the same method as the $CoCH_3^+$ ions, do not react with aliphatic alkanes.[58] The reactions of the $NiCH_3^+$ ions have not been investigated, since they could not be obtained by the above method. The formation of NiI^+ and not $NiCH_3^+$ was observed in the reaction of Ni^+ with methyl iodide.

The gas-phase reactions of the $CoCH_3^+$ and $FeCH_3^+$ ions with a series of cyclic hydrocarbons—cycloalkanes ranging from C_3 to C_6 as well as cyclopentene and cyclohexane—were subsequently investigated.[59] These ions are inserted mainly in C–C bonds of cyclopropane and cyclobutane, forming alkyl (ethyl or propyl) complexes and ethylene. It had been shown earlier that the Fe^+ and Co^+ ions, obtained by means

of laser radiation, do not react with cyclopropane.[41] In the reactions of cyclopentane, cyclohexane, cyclopentene and cyclohexene with $CoCH_3^+$, the formation of only the dehydrogenation products (the complexes of cycloalkenes or cycloalkadienes) and the corresponding neutral products (methane and hydrogen) was observed. The $FeCH_3^+$ ions do not enter into this reaction. In the case of cyclopentene and cyclohexene the oxidative addition to a C–H bond is the only reaction for both $CoCH_3^+$ and $FeCH_3^+$.

In one of the most recent studies,[60] the gas-phase reactions of the $FeCH_2^+$ and $CoCH_2^+$ ions with aliphatic alkanes are investigated. The method of preparation of the MCH_2^+ ions was based on the reactions of the Fe^+ and Co^+ ions, generated by laser radiation, with epoxyethane or cycloheptatriene:

$$M^+ + C_2H_4O \rightarrow MCH_2^+ + CH_2O$$
$$M^+ + \text{cyclo-}C_7H_8 \rightarrow MCH_2^+ + C_6H_6 \qquad (12)$$

The study of the reactions of the $CoCH_2^+$ and $FeCH_2^+$ ions with alkanes, ranging from methane to hexane isomers, led to the conclusion that the oxidation addition of the hydrocarbon to the metal ion proceeds predominantly via the insertion into the C–H bonds of the alkanes and to a lesser extent the C–C bonds. The $CoCH_2^+$ ion reacted with all the alkanes investigated except methane, while the $FeCH_2^+$ ions reacted with alkanes starting from propane.

The gas-phase reactions of the $FeCH_2^+$ and $CoCH_2^+$ ions with olefins, ranging from ethylene to hexene, and also with butadiene, acetylene, and propyne have also been studied.[61] The reactions of $FeCH_2^+$ and $CoCH_2^+$ with ethylene lead to the formation of only the M^+ ion and the corresponding neutral product C_3H_6. The authors suggest that the interaction of $CoCH_2^+$ with ethylene may entail its insertion both in a C–H bond with formation of propene and in the C=C bond with formation of cyclopropane. The reaction of the $FeCH_2^+$ ion may result in the formation of propene alone. The study of the interaction of ethylene with MCD_2^+ ions established the occurrence of a metathetical reaction, which was inferred from the presence of the products MCH_2^+ and $C_2H_2D_2$. Thus two processes take place:

$$MCD_2^+ + CH_2{=}CH_2 \rightarrow MCH_2^+ + CD_2{=}CH_2 \; ; \qquad (13a)$$

$$MCH_2^+ + CH_2{=}CH_2 \rightarrow M^+ + \triangledown \text{ or propene} . \qquad (13b)$$

In the case of ethylene the contribution by reaction (13*a*) is small, amounting to 20% for the $FeCH_2^+$ ions and only 2% for the $CoCH_2^+$ ions. However, the contribution of the metathetical reaction increases significantly in the case of propene and isobutene. Thus the main product of the reaction of MCH_2^+ with propene is the ion of ethylene bound in a complex, while isobutene gives rise mainly to the ions of ethylene and propene bound in complexes:

$$MCH_2^+ + (CH_3)_2C{=}CH_2 \rightarrow \begin{cases} M^+ \leftarrow \text{complex} + C_2H_4 \; ; \\ M^+ \leftarrow \text{complex} + C_3H_6 . \end{cases} \qquad (14)$$

Apart from the ions indicated, the M^+ ions were found in the products of the reactions of MCH_2^+ with propene and isobutene, as well as the compounds C_4H_8 in the former case and C_5H_{10} in the latter. The authors[61] believe that the $CoCH_2^+$ ions can be inserted both in a C–H bond of propene to form but-1-ene, and in the C–C bond to form methylcyclopropane:

$$CoCH_2^+ + CH_3CH{=}CH_2 \rightarrow \begin{cases} Co^+ + CH_3CH_2CH{=}CH_2 \; ; \\ Co^+ + \triangledown CH_3 . \end{cases} \qquad (15)$$

In the reaction of $FeCH_2^+$, only the insertion in a C–H bond is possible. In contrast to propene, isobutene gives rise to an appreciable amount of $MC_4H_6^+$ ions. n-Butenes give rise to the same main reaction product as isobutene. A complex set of products has been obtained in the reactions of pentenes and hex-1-ene. The main products of the reaction of the MCH_2^+ ions with butadiene were the M^+ ion and the corresponding neutral compound C_5H_8, which is cyclopentene according to the authors. In the case of acetylene and propyne, a single reaction leading to the formation of M^+ was observed in each case together with the products C_3H_4 (from acetylene) or C_4H_6 (from propyne). The authors[61] suggest that only the insertion of the carbene in a C–H bond with formation of an allene or propyne is possible in the first of the above reactions.

The reactions of alkanes with the Fe^+, Co^+, and Ni^+ ions[32–35] and of alkenes and cycloalkanes with Co^+[40,42] have been investigated by the method of ion beams. The ions were obtained by the thermal ionisation of metals formed on decomposition of the corresponding chlorides. The composition of the products of the reactions of alkanes ranging from butane to octane with the Fe^+, Co^+, and Ni^+ ions having a kinetic energy of approximately 0.5 eV permitted the same conclusion as that reached by Jacobson and Freiser,[28] namely that the Ni^+ and Co^+ ions are inserted preferentially in a C–C bond and that this is accompanied by insertion in a C–H bond in the case of Fe^+.

The study of the interaction of Co^+, having a kinetic energy of approximately 1 eV, with alkenes ranging from ethylene to hexenes[40] showed that ethylene and propene do not react with the metal ions under these conditions. In the case of isobutene the products of the insertion of Co^+ in a C–C bond was found. The reactions of n-butenes with Co^+ led to the formation of mainly a diene bound in a complex and of the corresponding neutral product (H_2). In the reactions of pentenes and hexenes, the insertion in both C–H and C–C bonds was observed.

The results obtained in a study[42] of the gas-phase reactions of Co^+ ions, having a kinetic energy of approximately 1 eV, with cycloalkanes ranging from cyclopropane to cyclohexane diverge somewhat from the data of Jacobson and Freiser.[41] Under these conditions, the Co^+ ions react with cyclopropane with formation of $CoCH_2^+$ and ethylene:

$$Co^+ + \triangledown \rightarrow CoCH_2^+ + C_2H_4 . \qquad (16)$$

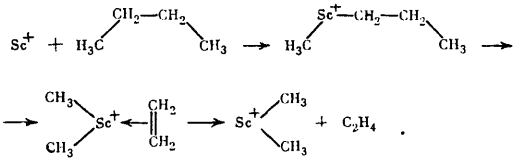
The absence of the reactions of cyclopropane with Fe^+, Co^+, and Ni^+, generated by the influence of laser radiation, is apparently associated with the fact that these ions exist mainly in the ground and insufficiently excited electronic states and do not have a high kinetic energy compared with the ions used in the ion beam method.

The reactions of Co^+ with cyclobutane, cyclopentane, and cyclohexane lead to the formation of dehydrogenation products and the products of the dissociation of the ring C–C bond according to Armentrout and Beauchamp.[42] For example, the reaction of Co^+ with cyclobutane proceeds as follows:

$$Co^+ + \square \rightarrow \begin{cases} CoC_2H_4^+ + C_2H_4 \; ; \\ CoC_4H_6^+ + H_2 . \end{cases} \qquad (17)$$

The gas-phase reactions of the FeH^+ ions, obtained by electron impact from 1,1-dimethylferrocene, with methane, ethane, and butane have been investigated for low kinetic energies of the ions.[62] It has been shown that methane and ethane do not react with FeH^+. The reaction of n-butane leads to the formation of the products of the insertion of FeH^+ in a C–H bond of the alkane, which agrees with data[57] for the analogous reactions of the FeD^+, CoD^+, and NiD^+ ion obtained by the reaction of metal ions with nitromethane or metal nitrite.

The reactions of Sc^+ ions having a kinetic energy of approximately 0.5 eV with alkanes ranging from propane to hexane in the gas phase have been recently investigated.[36] The Sc^+ ions were obtained by the thermal emission method at 2500 K. It was found that the reaction of propane with Sc^+ proceeds similarly to the reactions of alkanes with the Fe^+, Co^+, and Ni^+ ions. The main products are complexes of Sc^+ with propene (68%) and ethylene (27%). The reaction of n-butane leads to the formation of large amounts of the complex $Sc(C_2H_6)^+$ and ethylene respectively. Analysis of the thermochemical data led the authors[36] to the conclusion that the complex $Sc(C_2H_6)^+$ had the dimethylscandium structure. $Sc(CH_3)_2^+$ may be formed on insertion of Sc^+ to the terminal C–C bond of n-butane:



(18)

or to a C–H bond in the CH_2 group, which also leads to the formation of the dimethylethylene intermediate. The insertion of Sc^+ in a C–H bond leads to the formation of dehydrogenation products, which are, according to the authors' hypothesis, metallocyclobutane derivatives and not olefins and dienes bound in complexes as for other ions.

The gas-phase reactions of the Fe^+, Co^+, Ni^+, Cr^+, and Ti^+ ions with alkanes have also been investigated in other studies.[29,30] The metal ions were obtained by electron impact on the corresponding carbonyls (the Fe^+, Co^+, Ni^+, and Cr^+ ions) or the chloride (the Ti^+ ions). In their studies of the reactions of the Fe^+, Co^+, Ni^+, and Cr^+ ions with perdeuteriobutanes having the normal or isostructure, the authors concluded that the composition of the reaction products depends on the nature of the metal and the alkane. Table 2 presents the relative rate constants for the reactions of M^+ with butanes in the initial stage and shows that, in the presence of the Cr^+ ions, approximately 60% of the reaction steps involve the insertion of the metal in a C–D bond with subsequent formation of an olefin and a diene bound in complexes with Cr^+, while about 40% involve the insertion in the C_2–C_3 bond of butane with subsequent formation of ethylene. The insertion in the C_1–C_2 and C_3–C_4 bonds is not observed. The contribution by the reaction involving the insertion in the C_2–C_3 bond of n-butane increases sharply for Fe^+ and Co^+ with the corresponding fall of the rate of insertion in the C–H bonds. The formation of small amounts of complexes of propene with Fe^+ and Co^+ indicates the partial occurrence of the reaction also involving the C_1–C_2 (C_3–C_4) bonds. The reaction in which Fe^+, Co^+, and Ni^+ are inserted in a C–C bond is decisive for isobutane; the decomposition of the organometallic intermediate leads to the formation of a propene complex. The contribution by reactions involving the insertion in a C–H bond, which lead to an isobutene complex, is comparatively small.

In reactions of the Ni^+ ions with n-butane[29] and also with the C_4–C_7 alkenes, only insertion in a C–H bond takes place with subsequent β-decomposition of the organometallic compound and the formation of an olefin and hydrogen.

V. OXIDATIVE ADDITION OF OTHER ORGANIC COMPOUNDS TO TRANSITION METAL IONS

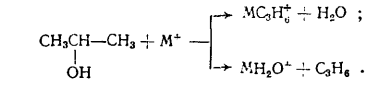
In conclusion we shall consider briefly the reactions of metal ions with derivatives of hydrocarbons containing various functional groups.

The gas-phase reactions of transition metal ions with aryl halides have been studied in relation to the interaction of the Fe^+ and Co^+ ions with CH_3I,[43] CH_3Br,[43] C_2H_5I,[44] and iso-C_3H_7Cl,[45] of the Ni^+ ions with CH_3I[44,45] and C_2H_5I,[45,45] of the Cr^+ ions with C_2H_5I,[44] and of the Fe^+ ions with C_6H_5Cl.[47] The above ions were obtained by electron impact on the corresponding metal carbonyls. The gas-phase reactions of Ti^+, obtained by laser radiation, with CH_3X (X = Cl, Br, or I), C_2H_5Cl, C_6H_5Cl, and $(CH_3)_2CHCl$ have been investigated.[46] The formation of the products of the oxidative addition to the C–Hal bond were observed in all cases. It is well known that RHal add analogously to active zerovalent metals in solution. The addition of alkenyl halides to $Ni(CO)_4$, leading to the formation of π-allyl derivatives,[63] and the addition of alkyl halides to zerovalent cobalt and other zerovalent metals[64,65] may serve as examples.

Table 2. The relative rate constants for the formation of the products of the reactions of M^+ with butanes.[30]

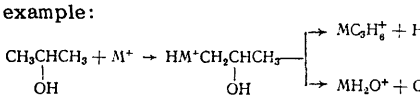
M^+	n-C_4D_{10}				iso-C_4D_{10}	
	$MC_4D_4^+$	$MC_3D_6^+$	$MC_4D_6^+$	$MC_4D_8^+$	$MC_3D_6^+$	$MC_4D_8^+$
Cr^+	0.22	0	0.16	0.16	0	0.09
Fe^+	0.53	0.07	0.04	0.04	0.46	0.09
Co^+	0.53	0.09	0	0.13	0.82	0.15
Ni^+	0.14	0.02	0	0.07	0.29	0.04

The gas-phase reactions of the Fe^+, Co^+, and Ni^+ ions, arising as a result of the electron impact on the corresponding metal carbonyls, with methyl, ethyl, and isopropyl alcohols have been studied.[44,45] The above ions induce the formation of mainly the products of oxidative addition to the C–OH bond with subsequent dehydration of the alcohols. $MC_2H_4^+$ ions were the main products of the reactions of the Fe^+, Co^+, and Ni^+ ions with ethyl alcohol, while approximately equal amounts of the $MC_3H_6^+$ and MH_2O^+ ions were found in the products of the reaction with isopropyl alcohol:



(19)

In the given instance the reaction proceeds via the classical pathway involving the β-decomposition of the organometallic compounds. It is noteworthy that the analogous decomposition products can arise also when M^+ is inserted in a C–H bond, for example:



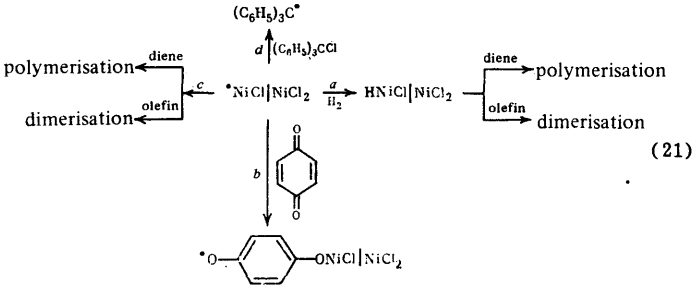
(20)

The gas-phase reactions of Fe^+ and Co^+ ions with acetaldehyde, acetone, ethyl methyl ketone, and isopropyl methyl ketone have been studied[49,50] as well as the reactions of Fe^+ ions with a series of other ketones—simple, mixed, unsaturated, and cyclic, also propionaldehyde and butyraldehyde.[49] The reaction of Co^+ ions with formaldehyde has been investigated.[50] Fe^+ ions have been obtained by the action of laser radiation,[49] while Co^+ ions have been generated by thermal ionisation.[50] The reactions involving Co^+ ions have been studied using a low kinetic energy of the ions. The composition of the products of the reactions with aldehydes and ketones depends on the nature of the carbonyl compound.

Thus acetone, formaldehyde and acetaldehyde give rise to only the $M(CO)^+$ ions—the products of oxidative addition to the C–C=O or H–C=O bonds. In the reactions with participation of ketones and aldehydes, there is a longer alkyl chain and the fraction of the products of oxidative addition to a C–H bond increases, while in the reactions with ketones having substituents at the α-carbon atoms and cyclic ketones there is an increase in the fraction of the products of oxidative addition to a C–C bond.

The gas-phase reactions of Fe^+ ions, obtained by the action of laser radiation, with ethers (dimethyl, diethyl, and di-isopropyl ethers, two mixed ethers—butyl methyl and isopropyl methyl ethers, and a cyclic ether—tetrahydrofuran) have been investigated.[49] The composition of reaction products depends on the nature of the ether. Thus dimethyl ether gives rise to only $FeCH_2O^+$ ions and correspondingly CH_4 (insertion in the C–O bond). The oxidative addition to the C–O bond predominates also for diethyl, di-iso-propyl, and isobutyl methyl ethers. For butyl methyl ether, the dehydrogenation reaction leading to the formation of $FeC_5H_{10}O^+$ and correspondingly H_2 is the dominant process.

It was already noted above that metal ions entering the gas phase under the influence of laser and especially electron irradiation are much more reactive than the ions of the same metals on the surfaces of catalysts and that even at room temperature hydrocarbons undergo more extensive reactions in the presence of such ions even at room temperature than in heterogeneous catalysis at not unduly high temperatures. It is noteworthy that metal subhalides, obtained on heating salts at 200–300 °C in a high vacuum and remaining in the matrix comprising halides, are to some extent analogous of metal ions. They are known to function as catalysts with selective activity in reactions with olefins at the usual temperatures. It has been shown[66,67] that small amounts of the ·NiCl species, detected by EPR in an $NiCl_2$ matrix, exhibit catalytic activity in diene polymerisation and ethylene dimerisation reactions at low temperatures.



(21)

The reactions via pathways *a* and *c* lead to the polymerisation of dienes and the oligomerisation of olefins, while along pathways *d* and *b* the system loses activity and triphenylmethyl and semiquinonoid radicals appear respectively. Analogous subhalides with catalytic activity in the above reactions arise when other metal halides are used.[66] One can also note that certain metal oxides, heated in a high vacuum at 400–500 °C for a long time, acquire the ability to catalyse deuterium exchange in hydrocarbons at low temperatures.[68] It may be that under the given conditions defects due to the formation of a small number of metal atoms in a more reduced state can arise in the catalyst matrix and are able to participate in the oxidative addition of hydrocarbons and deuterium.

The metal atoms formed on vaporisation in a high vacuum with their subsequent condensation in the hydrocarbon matrix[11] approach heterogeneous metallic catalysts as regards the character of their action on hydrocarbons although in this instance too isolated atoms are naturally more reactive than the atoms on the surface. It is well known that in the latter case the active centres are distributed on the crystal faces or in dislocation, where the metal atom retains a fairly large number of coordination vacancies and is able to pass to the oxidised state after combining with the hydrocarbon to form an organometallic intermediate.

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It follows from the data presented that, on coming into contact with an isolated metal atom at low temperatures, hydrocarbons undergo reactions analogous to their reactions in heterogeneous catalysis at higher temperatures. The reaction intermediates are in all cases organometallic compounds of transition metals, whose decomposition pathways have been thoroughly investigated in the temperature range 20–100 °C. Complex reactions of hydrocarbons (hydrogenation, dehydrogenation, skeletal isomerisation, hydrogenolysis, and deuterium exchange) can take place not only on an *ensemble* of metal atoms but also at an individual atom via stages involving the formation of organometallic intermediates arising as a result of the addition of the metal atom to C–H, C–C, and C–O bonds. The experimental data presented in this review are therefore of special interest for the understanding of the chemical nature of the elementary steps in heterogeneous catalysis.

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