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New Advances in the Chemistry of Methane

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The review deals with new reactions of methane in the presence of organometallic catalysts. The available data on deuterium-hydrogen exchange between methane and the methyl groups of the catalyst and on the reactions involving the addition of methane to low-valence transition metal complexes and to unsaturated hydrocarbons are surveyed. Certain other aspects of the chemistry of methane of theoretical and applied interest are considered.
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I. INTRODUCTION

Petroleum processing products constitute at present the main raw material source for the preparation of the majority of organic compounds and polymeric materials. This is the reason for the continuing increase in the rate of extraction and processing of petroleum during the last decades, which has led to the danger of exhaustion of its available resources. According to the estimates of specialists, if the present rate of development of the petroleum processing industry is maintained, the world petroleum reserves will be virtually completely exhausted after 30–40 years. The continuously increasing deficiency of petroleum and petroleum products is already facing chemists with the task of creating a new raw material source for the manufacture of organic substances and polymeric materials.

In nature there are two sources available for organic chemistry, with enormous reserves still available, namely coal and natural gas. The possibility, in principle, of obtaining hydrocarbon raw materials and natural liquid fuel from coal has been known for a long time but the imperfection of the coal processing technology, the severe conditions required for this purpose, and other, including purely economic, factors have created serious obstacles to the realisation of this process in industry. The conversion of natural gas into a hydrocarbon raw material, for example, the preparation of acetylene, have long been achieved on an industrial scale. These processes also proceed at high temperatures and pressures with very low yields and very low selectivity.

On the other hand, it is well known that enzymes exist in nature which oxidise methane (the principal component of natural gas) to methanol under the usual conditions with a high selectivity. The progress in the chemistry of alkanes in recent years is due to the endeavour to create new highly efficient and selective ways of processing natural gas.

The work of Enikolopov and Nalbandyan has made an enormous contribution to the development of the chemistry of saturated hydrocarbons. As early as the 1950's, they investigated in detail the kinetics and mechanism of the gas-phase oxidation of methane by molecular oxygen[1-19]. Since these classical studies have been described in detail in other reviews and monographs[19-21], in the present article the gas-phase reactions of methane will not be considered.

The activation of alkanes under mild conditions in the presence of soluble platinum complexes was first observed by Shilov and co-workers in 1969.[22] It was established, in particular, that the activation of the C–H bond in alkane can lead to deuterium–hydrogen exchange involving the alkanes and their chlorination or oxidation[23-26]. The publication of these studies attracted much interest to the chemistry of paraffinic hydrocarbons and new catalysts for the activation of the CH bonds in saturated hydrocarbons, mainly based on the complexes of Group VIII elements, were soon discovered[27-30].

Comparative analysis of the physicochemical characteristics of hydrogen, methane, ethylene, and other hydrocarbons indicates the possibility of employing Ziegler–Natta organometallic catalysts for the activation of the C–H bonds in the methane molecule. Table 1 presents the bond energies D, the ionisation potentials IP, the electron affinities EA, and the proton affinities PA of methane, hydrogen, ethylene, acetylene, and benzene[26]. It is seen that the C–H bond energy in methane is approximately the same as the H–H bond energy in the hydrogen molecule, but is lower than the C–H bond energies in acetylene, benzene, and ethylene. The ionisation potential of methane is higher than those of benzene, ethylene, and acetylene, but is lower than the ionisation potential of hydrogen. Methane has a smaller proton affinity than benzene and ethylene but higher than hydrogen.

In terms of the characteristics considered, methane thus occupies an intermediate position between hydrogen and ethylene. This factor led to the hypothesis that the activation of methane and its chemical reactions can be achieved in the presence of catalysts capable of activating hydrogen and ethane molecules, although methane should then manifest a lower reactivity than hydrogen owing to steric hindrance. The hydrogenation catalysts and olefin polymerisation catalysts of the Ziegler–Natta type are known to belong to this class.

Table 1. The physicochemical characteristics of hydrocarbon and hydrogen molecules[26].

Molecule	D(R-H), kcal mol^{-1}	IP, eV	EA, eV	PA, eV
H_2	104	15.4	−3.60	4.4
CH_4	104	12.7	—	5.3
C_2H_4	106	10.5	−1.81	6.9
C_6H_6	109	9.2	−1.10	7.5
C_2H_2	120	11.4	—	—

When hydrogn interacts with organometallic catalysts of this type under the usual conditions, the transition metal (M)–carbon bond undergoes hydrogenolysis:

$$M{-}R + H_2 \rightarrow M{-}H + RH \quad .$$

In the absence of the monomer, the reaction results in the evolution of alkane and the formation of a transition metal hydride derivative. In addition, it has been shown[31] that, under these conditions, D_2 molecules enter into deuterium–hydrogen exchange with the alkyl groups of the catalyst. The hydrogenolysis of the M–C bond plays a decisive role also in the hydrogenation reactions of unsaturated hydrocarbons. Analogous reactions of methane with organometallic catalysts have been observed recently for the first time.

Deuterium–hydrogen exchange reactions in methane, the addition of methane to unsaturated hydrocarbons and low-valence transition metal complexes, and reactions involving the exchange of alkyl groups between alkanes and organometallic complexes of 3*d* transition elements have been discovered in recent years. These reactions are especially interesting, because they proceed under mild conditions and in non-polar solvents such as heptane and benzene.

This review describes in detail the studies by Enikolopov's school on the activation of methane in the presence of organometallic complexes in hydrocarbon media and analyses the causes of the relatively high reactivity of methane compared with heavier homologues.

II. THE INTERACTION OF DEUTEROMETHANE WITH ZIEGLER–NATTA CATALYSTS

The interaction of methane can be conveniently studied in the presence of Ziegler–Natta catalysts in which far-reaching transformations of the system components, leading to the reduction of the transition metal with evolution of gaseous products, do not occur. It is therefore useful to employ catalytic systems containing organoaluminium components which have the weakest reducing properties but can alkylate transition metal compounds. It is known[32] that such requirements are met fairly satisfactorily by dimethylaluminium chloride. Its interaction with transition metal salts results in the formation in most cases of an alkylated complex exhibiting catalytic activity and stable in the absence of monomers[33].

The interaction of deuteromethane with catalytic systems based on titanium tetrachloride, biscyclopentadienyltitanium dichloride, diacetylacetonatiotitanium dichloride, vanadium trichloride, and vanadium triacetylacetonate in combination with dimethylaluminium chloride has been investigated in the temperature range 20–70 °C and in the pressure range 0.4 to 10 atm.[34] The results of the mass-spectrometric analysis of the products have shown that the interaction of deuteromethane with the above catalysts results in deuterium–hydrogen exchange between methane and the alkyl groups of the catalytic system. Dideuteromethane is then formed preferentially; however, mono- and tri-deuteromethane are also found in the products together with CH_2D_2. It is noteworthy that, in the presence of deuteromethane, fairly large amounts of methane are found in the gas phase. Fig.1 shows that the amount of methane in the gas phase increases with time almost linearly, while the accumulation of di- and trideuteromethane takes place after an appreciable induction period. The evolution of methane evidently occurs in the stage involving the formation ot the active centres responsible for the deuterium-hydrogen exchange.

The accumulation of methane in the presence of deuteromethane can be caused by the reversibility of the intramolecular or intermolecular disproportionation of the methyl groups bound to the transition metal atom:

$$\rangle M\langle^{CH_3}_{CH_3} \rightleftarrows M{=}CH_2 + CH_4 \quad ;$$

$$2\,\rangle M{-}CH_3 \rightleftarrows \rangle M{-}CH_2{-}M\langle + CH_4 \quad .$$

The formation of carbene complexes in such systems has now been rigorously demonstrated[35,36]. In the catalytic systems investigated these equilibria are apparently displaced largely to the left under the usual conditions. The hypothesis of the reversibility of the disproportionation of the alkyl groups[34] makes it possible to explain not only the accumulation of methane in the presence of an excess of deuteromethane but also the formation of di- and tri-deuteromethanes. Indeed the addition of deuteromethane to the carbene complexes of transition metals should lead to the formation of deuteromethyl derivatives whose disproportionation leads to the formation of di- and tri-deuteromethanes, for example, in accordance with the mechanisms

$$\rangle M{=}CH_2 + CD_4 \rightarrow \rangle M\langle^{CH_2D}_{CD_3} \rightarrow \begin{cases} \rangle M{=}CD_2 + CH_2D_2 \quad ; \\ \rangle M{=}CHD + CHD_3 \quad ; \end{cases}$$

$$\rangle M{-}CH_3 + \rangle M{-}CH_3 + 2CD_4 \rightarrow 2\,\rangle M{-}CD_3 + CH_2D_2 \quad .$$

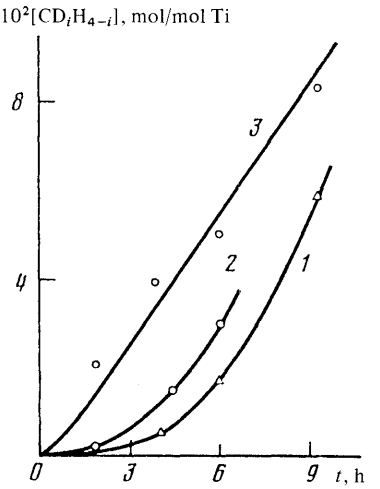


Figure 1. Kinetics of the deuterium–hydrogen exchange between CD_4 and the $TiCl_4$–$Al(CH_3)_2Cl$ catalytic system[34]: 1) dideuteromethane; 2) trideuteromethane; 3) methane; 20 °C, 3 atm, $[TiCl_4] = 5 \times 10^{-2}$ M, Al/Ti = 4.

The formation of monodeuteromethane can be readily explained by taking into account the possibility of the exchange of the methyl groups bound to the transition metal and the aluminium atom[37]; however, the possibility of the direct interaction of deuteromethane with the transition metal complex containing the M–CH_3 σ-bond is of greatest interest[34]:

$$\rangle M{-}CH_3 + CD_4 \rightarrow \rangle M{-}CD_3 + CH_3D \quad .$$

This reaction, which takes place most readily in the case of vanadium catalysts, is analogous to the hydrogenolysis of the M–C σ-bond.

It must be emphasised that the interaction of gaseous deuterium with the $TiCl_4$–$Al(CH_3)_2Cl$ system under identical conditions also results in the formation of the same deuteromethanes as in the reactions of deuteromethane with this system (Table 2)[31]. The identical proportions of the deuteroproducts in the interaction of gaseous deuterium and deuteromethane with Ziegler–Natta catalysts indicates the similarity of the mechanisms of the activation of the hydrogen and methane molecules in the coordination sphere of the transition metal. In the presence of small amounts of pyridine the deuterium–hydrogen exchange involving methane is fully suppressed. Evidently pyridine enters into the coordination sphere of the transition metal, forming a stable complex and preventing thereby the coordination and activation of methanes.

Table 2. The yields Q of the gaseous products of the interaction of deuterium with the $TiCl_4$–$Al(CH_3)_2Cl$ catalytic system[31]*.

τ, h	10^2Q, mol/mol Ti			
	CHD_3	CH_2D_2	CH_3D	CH_4
2	0.2	0.1	0.4	2.3
4	0.4	1.7	0.3	3.6
8	1.9	6.5	—	11.0
10	2.9	7.2	—	14.7

*Solvent—heptane; 50 °C; $[TiCl_4] = 2.5 \times 10^{-2}$ M; Al/Ti = 4.

The validity of the above ideas about the mechanism of the interaction of deuteromethane with Ziegler–Natta catalysts has been confirmed by the results of mass-spectrometric analysis of the gaseous products of the hydrolysis of the catalytic system where mono-, di-, and tri-deuteromethanes were detected[34]. The formation of deuterated methyl groups in the catalytic systems is possible only as a result of the activation of the C–D bond in the deuteromethane molecule when the latter interacts with the active centres of the catalyst. Thus the above results indicate the activation of the methane molecule in the coordination sphere of the transition metal.

The proposed mechanism of the deuterium–hydrogen exchange presupposes two possible pathways in the interaction of methane with organometallic complexes: (1) the reaction which is the reverse of the disproportionation of alkyl groups and (2) the exchange of alkyl groups between methane and the organometallic compound. Recently it has been possible to obtain direct evidence for the possibility of the occurrence of that reaction with participation of methane.

III. THE ACTIVATION OF METHANE BY LOW-VALENCE TRANSITION METAL COMPOUNDS

The disproportionation of alkyl groups containing a β-carbon atom in dialkyl compounds of transition metals proceeds via the scheme

$$\rangle M\langle^{C_2H_5}_{C_2H_5} \rightarrow \rangle M + C_2H_6 + C_2H_4 ,$$

according to which the oxidation state of the metal changes at once by two units and an alkane and an alkene are formed[33,37].

A reversible reaction can be achieved in the oxidative addition of an alkane to a complex of a transition metal in a low oxidation state. The analogous reaction with hydrogen is well known and takes place under the usual conditions at a high rate, for example, in the hydrogenation of olefins[38]:

$$\rangle M + H_2 \rightarrow \rangle M\langle^{H}_{H} \xrightarrow{C_2H_4} \rangle M\langle^{H}_{C_2H_5} \rightarrow \rangle M + C_2H_6 .$$

It is easy to estimate that the oxidative addition of methane should be less exothermic by ~10 kcal mol^{-1} than the addition of hydrogen. Steric hindrance may be an additional obstacle in the case of methane.

The oxidative addition of methane to low-valence transition metal complexes should entail the formation of alkyl hydride derivatives:

$$\rangle M + CH_4 \rightleftarrows \rangle M\langle^{H}_{CH_3} .$$

Under the usual conditions, this equilibrium is known to be displaced to the left[39], so that the isolation of the product of the oxidative addition of methane is not a simple task and the occurrence of the reaction can be inferred only from the results of the study of isotope exchange involving methane.

The possibility of the oxidative addition of alkanes to platinum(II) has been postulated by Shilov and co-workers[26]. Recently the same workers were able to isolate and investigate the σ-aryl complexes of platinum(IV) from a solution of hexachloroplatinic acid and hydrocarbons in a CF_3COOH + H_2O mixture, although the mechanism of the formation of the Pt–R bond was not rigorously demonstrated[40–44].

It has been established[45–47] that deuterium–hydrogen exchange between methane and deuterium takes place in a benzene solution of vanadocene (Cp_2V), leading to the formation of CH_3D, CH_2D_2, CHD_3, and CD_4 in the proportions 1.0 : 0.2: 0.3 : 0.12. The yield of deuteromethanes (for a methane content in the initial mixture of 35% and a pressure of 250 mmHg) after 24 h is 2–6%. Here one should note that repeated deuteration of the solvent (benzene) takes place simultaneously with formation of hexa- and penta-deuterobenzenes.

The formation of methanes deuterated to different extents in the isotope exchange between D_2 and CH_4 may be due to the oxidative addition of methane, for example, via the mechanism

$$\rangle M + CH_4 \rightleftarrows \rangle M\langle^{H}_{CH_3} ;$$

$$\rangle M\langle^{H}_{CH_3} + D_2 \rightarrow \begin{cases} \rightleftarrows \rangle M\langle^{D}_{CH_3} \rightleftarrows \rangle M\langle^{H}_{CH_2D} \\ \rightarrow \rangle M\langle^{H}_{D} + CH_3D \end{cases} .$$

The preferential formation of monodeuteromethane may be associated with the simultaneous occurrence of the oxidative addition of deuterium:

$$\rangle M + D_2 \rightarrow \rangle M\langle^{D}_{D} \xrightarrow{CH_4} \rangle M\langle^{D}_{H} + CH_3D .$$

The oxidative addition of methane becomes thermodynamically more favourable when the process is accompanied by the simultaneous rupture of the double bond in the olefin (for example, ethylene) molecule in the coordination sphere of the metal. In this case a methyl derivative should be formed in which the disproportionation reaction, leading to

the reformation of methane and ethylene, is faciliated:

$$>M\leftarrow\overset{CH_2}{\underset{CH_2}{\|}}+CH_4\rightleftarrows >M<\begin{matrix}CH_3\\C_2H_5\end{matrix}.$$

On the other hand, if one of the hydrocarbons contains deuterium atoms, the reversibility of this reaction leads to deuterium–hydrogen exchange between methane and ethylene.

Table 3. The products of the deuterium–hydrogen exchange between C_2D_4 and CH_4 under the influence of Cp_2V.[45]*

C_2D_4/CH_4	Yield, mol/mol Cp_2V								
	C_2HD_3	C_2HD_2	C_2H_3	C_2H_4	CHD_3	CH_2D_2	CH_3D	C_6D_6	C_6D_5H
0.88	—	—	0.2	33.5	0.5	2.4	—	30.2	4.1
0.34	0.1	0.9	—	10.7	0.7	—	1.6	6.4	1.5

*Solvent—benzene; 70 °C; 40 atm; 100 h; $[Cp_2V] = 3.5 \times 10^{-2}$ M.

Table 4. The multiple deuterium–hydrogen exchange factor (M) in the $Cp_2V + CH_4 + C_2H_4 + C_6H_6$ system at 70 °C.[47]

Amount of initial hydrocarbon			$10^3\cdot[Cp_2V]$, M	τ, h	Deuterating agent	M		
$10^3[CH_4]$, mol	$10^3[C_6H_6]$, mol	$10^3[C_2H_4]$, mol				CH_4	C_6H_6	C_2H_4
23.70	112.50	20.78	35.4	100	C_2D_4	2.2	5.9	3.9
43.62	112.50	15.04	35.4	100	C_2D_4	1.1	5.8	3.8
15.36	107.0	18.00	30.7	80	CD_4	2.0	5.8	4.0
6.92	123.0	9.17	11.7	80	CD_4	1.0	4.5	4.0
13.40	56.25	18.05	32.0	80	C_6D_6	2.3	4.5	3.7
56.70	56.25	—	73.0	44	$(C_5D_5)_2V$	0	4.2	—
9.17	56.25	17.5	73.0	44	$(C_5D_5)_2V$	0	0	2.3
—	112.5	32.0	35.4	100	C_2D_4	—	5.9	—

Table 3 presents data for the isotope exchange between methane and ethylene in the presence of vanadocene at 70 °C. Evidently benzene is also involved in the exchange reaction and in the methane–deuteroethylene–benzene system the deuterium–hydrogen exchange results in the formation mainly of fully deuterated benzene and "light ethylene", while methane gives rise to simple exchange products. Table 4 shows that the multiple deuterium–hydrogen factor is on average 1.7 for methane, while under the same conditions it reaches 5.9 for benzene and 4.0 for ethylene[47].

It follows from the data of Shestakov et al.[47] presented in Table 5 that less than 10% of the benzene employed and up to 44% of the ethylene participate in the deuterium–hydrogen exchange reactions. On this basis, one may claim that in the presence of Cp_2V the benzene and ethylene molecules are involved in multiple exchange reactions.

The deuterium–hydrogen exchange between methane and benzene in the absence of ethylene proceeds much more slowly. This fact together with the results of the study of the H–D exchange in the C_2D_4–CH_4–C_6H_6, C_2H_4–CD_4–C_6H_6, and C_2D_4–C_6H_6 systems (Tables 5 and 6) shows that benzene is deuterated as a result of its reaction with deuteroethylene, while methane is involved in exchange with ethylene in a parallel pathway[46].

In the C_2H_4–CD_4–C_6H_6 system the ethylene molecule transfers deuterium atoms from methane to benzene. Indeed the rate of deuteration of benzene in this system is much higher than in the system where the deuterating agent is deuterethylene and the multiple exchange factor is the same in both cases.

Table 5. The yields of deuterohydrocarbons and the specific rates of isotope exchange ν_{sp} in various systems in the presence of vanadocene[47].

System	Amount of hydrocarbons involved in exchange, mole %			$10^2\nu_{sp}$, litre $mol^{-1}h^{-1}$		
	methane	benzene	ethylene	methane	benzene	ethylene
C_2D_4–CH_4–C_6H_6	2.5	7.8	43.8	11.9	11.4	44.3
	0.7	2.4	26.2	5.2	4.2	20.2
C_2D_4–$^{13}CH_4$–C_6H_6	0.6	1.7	—	11.9	9.4	—
C_2H_4–CD_4–C_6H_6	0.8	0.1	11.0	24.1	1.1	24.8
C_2H_4–CH_4–C_6D_6	2.0	0.5	4.5	16.4	1.0	4.8
C_2D_4–C_6H_6	—	3.7	0.5	—	6.3	39.4
C_6H_6*	—	0.002	—	—	0.1	—
C_2H_4–CH_4–C_6H_6*	0	0	0.05	0	0	3.7

*The experiments were performed in the presence of $(C_5D_5)_2V$.

Table 6. The specific rates and the multiple deuterium–hydrogen exchange factors in the $CH_4 + C_2D_4 + C_6H_6$ system in the presence of various metallocenes[45–47]*.

Catalyst	M			$10^2\nu_{sp}$, litre $mol^{-1}h^{-1}$		
	CH_4	C_6H_6	C_2H_4	CH_4	C_6H_6	C_2H_4
Bz_2Ti	2.6	4.9	3.0	40.1	91.4	14.8
Cp_2V	2.2	5.9	3.9	11.9	11.4	44.3
Cp_2Mn	1.1	4.8	3.5	1.1	7.9	9.0
Cp_2Fe	1.0	4.9	3.5	0.1	1.5	6.0
Cp_2Co	1.0	4.7	2.9	0.3	0.3	5.0
Cp_2Ni	1.0	4.7	3.0	0.2	0.1	0.5

*Solvent—benzene; 70 °C; 2.5 atm; 100 h.

Presumably the formation of deuterocarbons is due to their metathesis reaction involving the dissociation of the C=C double bond in ethylene. Indeed the methyl hydride complex formed in the oxidative addition of methane[26,45] can be converted into a carbene complex[48], which is the active centre of metathesis according to the authors[49]. The formation of deuterated hydrocarbons can then be represented schematically as follows:

$$>M+CH_3\rightleftarrows \underset{H}{\overset{CH_3}{>M<}}\rightleftarrows >M=CH_2+H_2,$$

$$\underset{D_2C=CD_2}{\overset{M=CH_2}{}}\longrightarrow >M=CD_2+H_2C=CD_2.$$

When [^{13}C] methane was used, the transfer of carbon-13 atoms to the ethylene molecules should have been observed: however, mass-spectrometric studies showed that the interaction of the C_2H_4, $^{13}CH_4$, and C_6H_6 hydrocarbons with Cp_2V

does not lead to the isotope exchange of carbon between the system components[47]. The replacement of methane by [^{13}C]-methane hardly affects also the rate and degree of the deuterium–hydrogen exchange between deuteroethylene and methane. These data show that in the system investigated there are no metathesis reactions and that the hydrocarbons are deuterated due to the isotope hydrogen–deuterium exchange.

It is noteworthy that, on passing from benzene to deuterobenzene or from methane to deuteromethane, the rate of deuterium–hydrogen exchange with ethylene falls appreciably other conditions being equal. The kinetic isotope effect k_H/k_D is 3.6 for benzene and 3.1 for methane. The occurrence of a significant isotope effect confirms that the dissociation of the C–H bond in the benzene and methane molecules takes place in the rate-determining stage of the process[45–47].

Table 5 lists the specific rates of the deuterium–hydrogen exchange defined as the numbers of steps in the H–D exchange adjusted to unit concentrations of the catalyst and the corresponding hydrocarbon, i.e.

$$\nu_{sp} = \frac{\sum i d_i}{[Cp_2V]\,[RH]\,\tau},$$

where $\Sigma i d_i$ is the number of steps in the deuterium–hydrogen exchange in the given hydrocarbon, $[Cp_2V]$ the amount of the catalyst in moles, [RH] the molar concentration of the hydrocarbon, and τ the experimental time (h).

It is of interest that, in the presence of vanadocene under the conditions of the experiments presented in Table 5, the specific rates of the deuterium–hydrogen exchange between methane and benzene, on the one hand, and the deuteroethylene, on the other, are almost equal and in certain cases ν_{sp} for methane is actually higher (Table 6). The anomalously high reactivity of methane compared with benzene is evidently due to the specific features of the mechanism of the activation of the C–H bond in these hydrocarbons by vanadocene.

The cyclopentadienyl rings of the catalyst also participate in the H–D exchange reactions. Table 4 shows that methane is hardly involved in this exchange, while benzene exchanges with the cyclopentadienyl groups only in the absence of ethylene.

The H–D exchange between benzene and C_5D_5 rings results in the formation mainly of hexadeuterobenzene and small amounts of C_6H_5. When ethylene is present in the system, the isotope exchange between benzene and C_5D_5 rings is fully inhibited and there is exchange between the latter and ethylene, which results in the formation of mainly $C_2H_2D_2$. Although the factor associated with the multiple exchange of methylene and benzene with the C_5D_5 rings separately is fairly large, the contribution of this exchange is insignificant in both cases. This is also indicated by the observed satisfactory deuterium atom balance in the exchange between the hydrocarbons investigated in the presence of "light" Cp_2V.[47]

The principal experiment data indicating the multiple character of the H–D exchange between benzene and deuteroethylene in the presence of vanadocene with the preferential formation of C_6D_6 and C_2H_4 show that the coordination of the benzene and ethylene molecules in these intermediate complexes ensures the equivalence of the C–H bonds. The residence time of the benzene and ethylene molecules in the intermediate complexes should then be sufficient for the exchange of all the hydrogen atoms. For example, the complex $(\eta^5\text{-}C_5H_5)_2(\eta^6\text{-}C_6H_6)(\eta^2\text{-}C_2H_4)V$, which has the required symmetrical coordination of benzene and ethylene molecules, can be considered as the intermediate; however, its existence is doubtful for both steric and electronic reasons, because 23 electrons should be present in the transition metal orbitals.

The electronic structue of the complex Cp_2V has been considered[47] for different angles θ between the directions of the V–Cp bonds. Fig. 2 illustrates schematically the positions of the d levels of Cp_2V for different values of θ found by calculations based on the extended Hückel method[50,51].

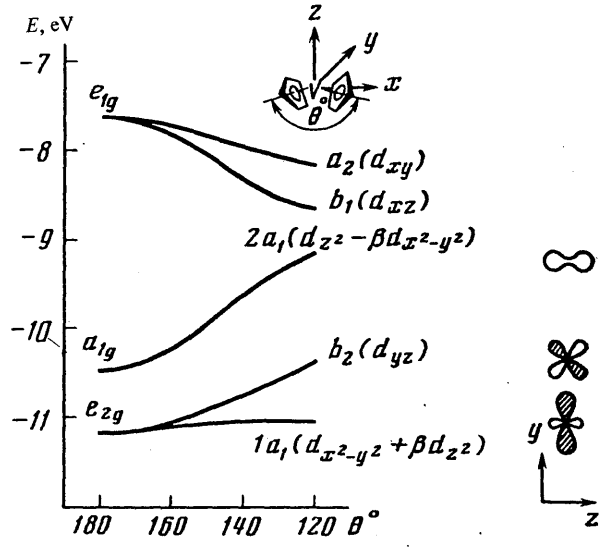
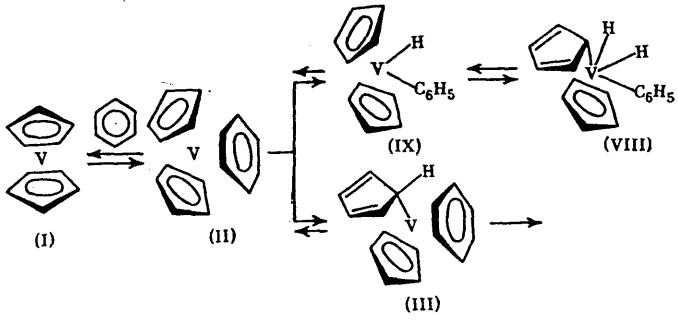
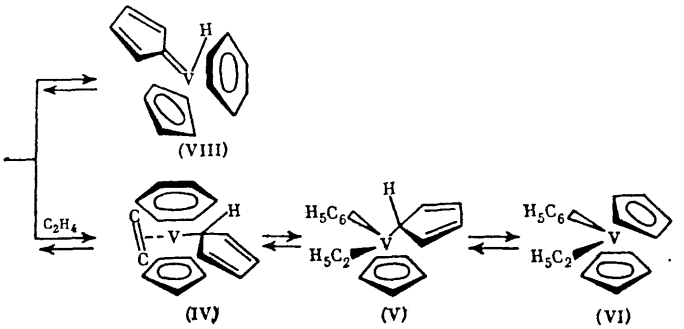


Figure 2. Schematic illustration of the variation of the energy of the d levels in the complex Cp_2V as a function of the variation of the angle θ between the axes of the Cp rings[47].

The distorted Cp_2V complex has three low lying weakly antibonding orbitals: $1a_1$, b_2, and $2a_1$,[47,51,52] which are responsible for the formation of bonds between Cp_2V and ligands of the σ or π type. The sterically accessible electron density maxima in all three orbitals are located in the zy plane. The $1a_1$, b_2, and $2a_1$ orbitals can then ensure the formation of a σ-bond at angles of ±90°, ±45°, and 0° relative to the z axis respectively. The b_2 and $1a_1$ orbitals are suitable for the π interaction at angles of 0°, ±90°, and ±45° relative to the z axis respectively.

The following scheme has been proposed to interpret the main experimental facts observed in the study of deuterium exchange between benzene, on the one hand, and ethylene and Cp rings, on the other[47]:





The first stage is the addition of benzene to Cp_2V; the possibility of complex formation is ensured by the interaction of $2a_1$ and b_2 orbitals of Cp_2V with the orbitals of a_{2u} and e_{1g} of benzene respectively (Fig. 3). The overall energy gain is not very great, since it is made up of the decrease of the energies of two orbitals occupied by four electrons and the increase of the level of one one-electron orbital. Furthermore, there exists also definite steric hindrance to the accommodation of three rings around the vanadium atom.

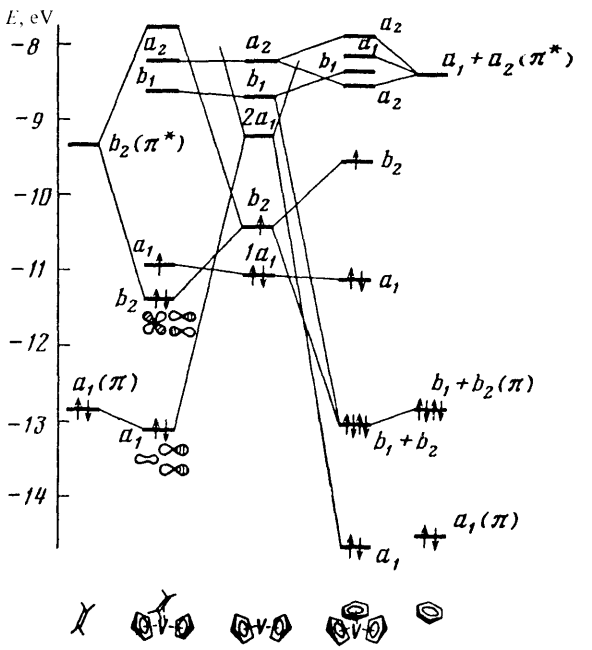


Figure 3. Energy scheme for the interaction of the complex Cp_2V with ethylene and benzene molecules[47].

The presence of a *d* electron in the complex (II) in a high antibonding orbital renders it unstable and reactive, in particular, it tends to be oxidised. The easiest way of employing the reactivity of the complex (II) and of removing an electron from the antibonding *d* orbital consists in attack by the positively charged vanadium atom on the negatively charged rings with formation of the complex (III) or (IX). Attack on the cyclopentadienyl ring is preferred both from the standpoint of the larger negative charge an in view of the possibility of a smooth conversion of η^5-Cp into η^1-Cp via η^3-Cp; this reaction pathway is simplified because there is no need for the dissociation of a C–H bond.

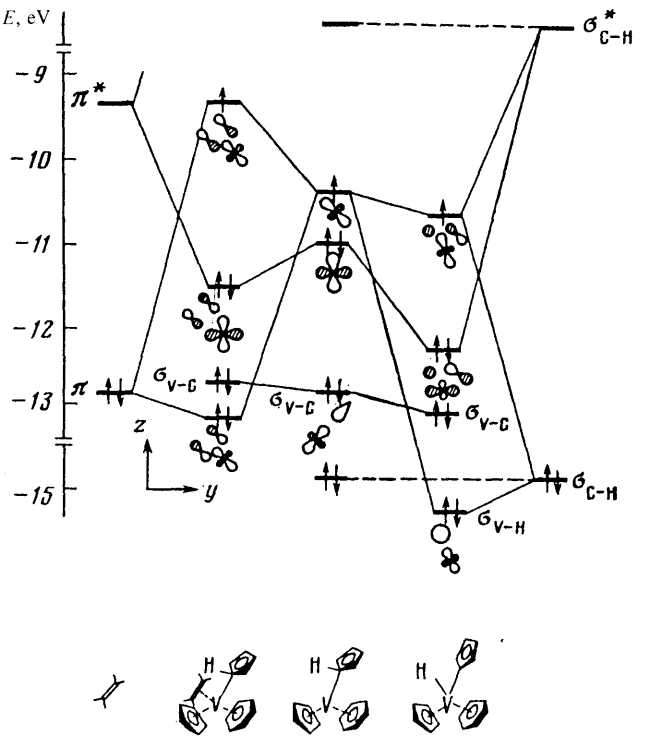
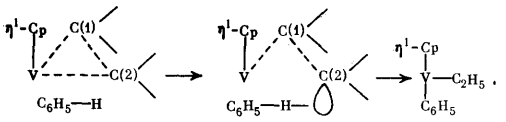


Figure 4. Energy scheme for the interaction of the complex $(\eta^1\text{-Cp})(\eta^5\text{-Cp})(\eta^6\text{-}C_6H_6)V$ with an ethylene molecule and the rearrangement of the orbitals of the complex when a hydrogen atom migrates from η^1-Cp to the vanadium atom[47].

The corresponding low lying orbitals are used for the formation of the V–η^1-Cp or V–H and V–C_6H_5 σ-bonds in the final products of the rearrangement—the complexes (III) and (IX) (Fig. 2). The remaining electrons (three or one) are accommodated in orbitals not involved in interactions with the ligands and for this reason there is no destabilising contribution to the energy in the complex (III) and (IX), in contrast to the initial complex (II). The complex (IX) is apparently thermodynamically somewhat more stable than the complex (III); the latter has orbitals ensuring the σ- and π-binding of C_2H_4 as a result of its interaction with the π and π* orbitals (Fig. 4).[47] A symmetrical coordination of benzene and ethylene obtains in the complex (IV) formed (provided that their rotation in the coordination sphere of the vanadium atom is unhindered). According to calculations by the extended Hückel method, the carbon atoms in the coordinated C_2H_4 molecule are not equivalent. This non-equivalence of the C(1) and C(2) atoms should lead to a difference between the bond lengths, i.e. $l_{V-C(1)} > l_{V-C(2)}$, which facilitates the abstraction of a hydrogen atom from the benzene ring in

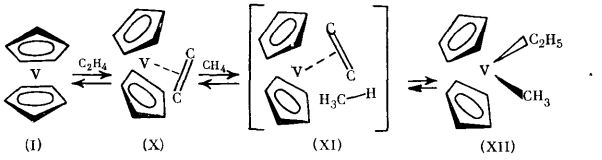
accordance with the scheme[47]



This mechanism agrees with the observed considerable kinetic isotope effect. The complex (V) formed can apparently be converted into the more stable complex (VI) via the shift η^1-Cp → η^3-Cp → η^5-Cp. The reverse transition (VI) → (V) is favoured by the steric hindrance due to the fairly large C_2H_5 and C_6H_5 ligands. The ease of rotation of the fragment η^6-C_6H_6 in the complex (IV) is fairly evident. The possibility of the rotation of the C_2H_4 fragment in the complex $Cp_2V.C_2H_4$ about the V–C_2H_4 axis is due to the electronic factor, since rotation by an angle of 90° results in the disappearance of the stabilising interaction of the b_2 orbital of the vanadium atom with the π* orbital of ethylene (Fig.2). In the complex (IV) there is no symmetry plane owing to the non-equivalence of the five- and six-membered rings and the b_1 and b_2 states are therefore partly mixed. This ensures some stabilisation of the occupied level on rotation of the ethylene molecule by 90° and thereby a decrease of the barrier to the rotation. The results of a semiempirical quantum-mechanical calculation thus confirm a significant decrease of the barrier to rotation.

The occurrence of deuterium exchange between benzene and the C_5D_5 rings, also with the preferential formation of C_6D_6, can be accounted for within the framework of the proposed scheme by the conversion of the complex (III) into the carbene complex (VII).[47]

The difference between the characters of the deuterium–hydrogen exchange reactions of benzene (multiple exchange) and methane (simple exchange) with ethylene supports the view that the proceeds in parallel reactions via different mechanisms. In the case of methane the following scheme appears the most natural:



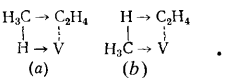
(I) (X) (XI) (XII)

The complex (X) should be fairly stable because Cp_2V has orbitals suitable for the effective π and σ binding of the ethylene molecule (Fig.3). It is evident from the above scheme that, on passing from CH_4 to CD_4, a considerable kinetic isotope effect should be observed.

The sequence of the C_2H_4 and CH_4 addition steps illustrated in the scheme follows from the sharp difference between the coordination properties of these molecules and the instability of the allyl hydride sandwich complexes[48]. In the transition (X) → (XI) → (XII) the cleavage of the double bond in the ethylene molecule facilitates additionally the loosening of the stable C–H bond in methane.

The replacement of methane by benzene immediately precludes the (X) → (XI) stage owing to the steric hindrance, since in the presence of the C···H–C_6H_5 and V···C_6H_5 interactions the ethylene and benzene molecules occupy such a considerable proportion of the space around the vanadium atom that either benzene or ethylene must fall within the region of the van der Waals contact between the Cp rings, which is impossible without a significant increase of the Cp–V bond length and hence without an appreciable energy expenditure[47].

Two possible versions of the addition of the methane molecule can be postulated in the intermediate complex (XI) in conformity with thermodynamics (for the direct abstraction of a hydrogen atom from a CH_4 molecule by the vanadium complex):



(a) (b)

Higher aliphatic hydrocarbons (C_3, C_4, etc.) could not be detected by chromatographic and mass-spectrometric methods in the $Cp_2V + CH_4 + C_2H_4 + C_6H_6$ reaction products. This finding shows that the addition of type (b), in which the interaction between the vanadium atom and a carbon atom is significant, is preferred. The methane molecule should apparently be subjected to preliminary thermal activation and should be made to assume an excited conformation with a partial increase of the H–C–H angle due to deformation vibration. A donor orbital is then formed along the second-order axis of the distorted CH_4 molecule, which determines the interaction with the electropositive vanadium atom.

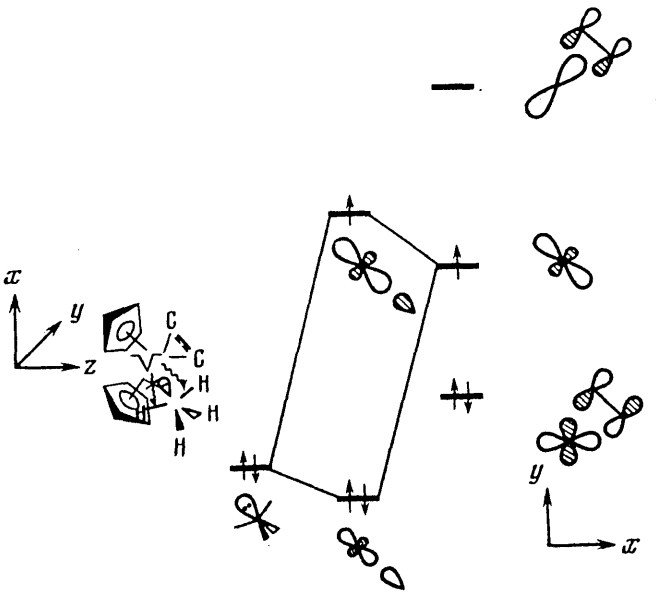


Figure 5. The interaction of the orbitals of a conformationally excited methane molecule with the complex $Cp_2V.C_2H_4$.[47]

The formation of the C_2H_4–CH_3 bond is possible only when the vanadium atom attacks a C–H bond remote from ethylene. However, Fig.5 shows that the presence of a hydrogen atom between the carbon atoms of methane and ethylene gives rise to steric hindrance. When the methyl group is bound to the vanadium atom, this hindrance eliminated, since an H atom from CH_4 naturally adds to C_2H_4. The rotation of the methane molecule about the V–CH axis, which could, in principle, ensure conditions for the formation of a propyl hydride derivative, is energetically unfavourable owing to the considerable increase of the repulsion of methane from the Cp rings and the lack of suitable orbitals for the formation of

the V–H bonds outside the bisector plane. The absence of the above obstacles favours the addition of methane to ethylene, which is apparently characteristic of the $Ti(OR)_4$–AlR_3 system, where the formation of propane from methane and ethylene has been observed[53].

It is natural to expect that ethylene remains in the coordination sphere of the vanadium atom longer than methane. Therefore, and also in view of the asymmetry of the addition of methane relative to ethylene, only mono- and di-deuteromethanes should be observed in the deuterium exchange products, which is consistent with experimental data[45–47] (Table 6).

Comparison of the mechanism of the parallel deuterium–hydrogen exchange reactions between methane and ethylene and between benzene and ethylene shows that the formation of an active centre in the case of benzene requires a longer expenditure of energy. This is in fact the reason for the observed high reactivity of methane compared with benzene in the exchange reaction of ethylene. The hindrance of the H–D exchange following the replacement of methane by heavier alkanes is also to be expected from these ideas.

It follows from the data presented above for the mechanism of the oxidative addition of methane that a decrease of the catalytic activity should be observed in the series of 3*d* transition metal metallocenes with enhancement of the electron-donating properties of the metal atom. The results of a study of the H–D exchange between deuteroethylene and methane and benzene in the presence of different metallocenes (Table 6) show that a sharp decrease of the rate of the H–D exchange involving methane is observed with enhancement of the electron-donating properties of the 3*d* transition metal atom in the sequence Ti > V > Mn > Fe > Co > Ni, while the multiple exchange factor changes insignificantly.

These results confirm yet again that the isotope exchange between methane and ethylene takes place as a result of the oxidative addition of methane to the transition metal complex of ethylene, i.e. as a result of the reaction which is the opposite of the disproportionation of the alkyl groups bound to the metal atom.

IV. THE "ALKANOLYSIS" OF THE TRANSITION METAL–CARBON BOND

The studies by Enikolopov and co-workers of the activation of methane by organometallic Ziegler–Natta catalysts demonstrated for the first time that, by analogy with hydrogen, methane can also participate in the dissociation of the transition metal–carbon σ-bond[34,53].

As mentioned above, the hydrogenolysis of the M–C bond plays an important role in the hydrogenation reactions of unsaturated hydrocarbons[38] and in the processes involving the regulation of the molecular weight of polyolefins during their synthesis in the presence of Ziegler–Natta catalysts[54]. In this case the reaction leads to the formation of the corresponding alkane and a metal–hydride linkage.

The reaction of methane with the M–C σ-bond leads to the formation of a methyl derivative of the transition metal and an alkane molecule:

$$\rangle M{-}R + CH_4 \rightarrow \rangle M{-}CH_3 + RH \quad .$$

By analogy with hydrolysis, hydrogenolysis, alcoholysis, etc., this reaction can be called "alkanolysis" (although for other alkanes a reaction of this type has not so far been observed) or the hydromethylation of the M–C bond.

"Alkanolysis" is observed in various catalytic systems based on $TiCl_4$, Cp_2TiCl_2, VCl_4, $V(acac)_3$, $Fe(acac)_3$, and many other transition metal derivatives in combination with various organoaluminium compounds. The rate of the process depends on the nature of the transition metal, the length of the hydrocarbon group bound to it, and other factors.

The most convincing demonstration of the occurrence of "alkanolysis" was achieved in the study of the interaction of methane, carefully freed from traces of moisture and oxygen, with catalytic systems. It is known[3] that in the interaction of the components of Ziegler–Natta systems containing triethylaluminium or diethylaluminium chloride the evolution of ethane and ethylene is observed, the amount of the latter being much smaller than that of ethane. Fig. 6 presents as an example data for the kinetics of the evolution of ethane in the $Fe(acac)_3$–$Al(C_2H_5)_3$ catalytic system[53].

Fig. 6 shows that ethane is evolved in an amount almost equivalent to the initial iron content over a period 5–10 min in the absence of methane; subsequently the evolution of ethane ceases. In the presence of methane the "alkanolysis" of the Fe–C_2H_5 σ-bond results in the evolution of a much larger amount of ethane. Trideuteromethane (CD_3H/Fe = $2{,}2 \times 10^{-4}$) is detected in the products of the hydrolysis of the catalytic system treated with tetradeuteromethane, which indicates the formation of a methyl derivative of iron in the "alkanolysis" of the Fe–C_2H_5 bond. According to preliminary data, the rate constants for the "alkanolysis" of the M–R bond are smaller by a factor of 30–50 than the rate constants for the hydrogenolysis of the same bond. "Alkanolysis" is a reaction which can already find an important practical application, for example, in the manufacture of polyolefins.

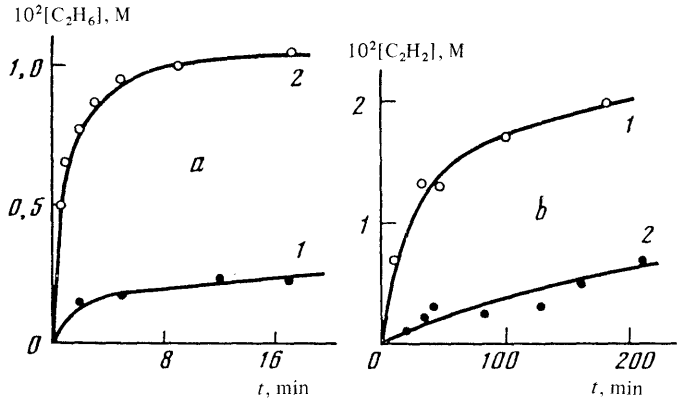


Figure 6. Kinetics of the accumulation of ethane (*a*) and of the absorption of acetylene (*b*) in the $Fe(acac)_3$–$Al(C_2H_5)_3$ catalytic system in the absence (curves *1*) and presence (curves *2*) of methane[53].

V. THE ADDITION OF METHANE TO UNSATURATED HYDROCARBONS

The discovery of the deuterium–hydrogen exchange reaction involving methane and of the "alkanolysis" of the M–C bond, which proceeds analogously to the corresponding reactions of hydrogen with organometallic catalysts, led to the task of finding new ways for the transformation of methane.

The most characteristic and important reaction of hydrogen in the presence of Ziegler–Natta catalysts is hydrogenation of unsaturated hydrocarbons. The mechanism of the hydrogenation reaction involves stages in which the transition metal–carbon bond undergoes hydrogenolysis and a hydrocarbon molecule is inserted in the metal–hydride bond formed[38]. For example, the mechanism of the hydrogenation of ethylene can be represented schematically as follows:

$$\rangle M{-}R + H_2 \rightarrow \rangle M{-}H + RH\ ,$$
$$\rangle M{-}H + C_2H_4 \rightarrow \rangle M{-}C_2H_5 + H_2\ ,$$
$$\rangle M{-}C_2H_5 + H_2 \rightarrow \rangle M{-}H + C_2H_6\ .$$

The discovery of "alkanolysis" led to the idea that hydrogen may be replaced by methane in the hydrogenation reactions of ethylene and acetylene[53 55]. Indeed, the "alkanolysis" of the M–R σ-bond in the catalytically active complex results in the formation of a new $M{-}CH_3$ σ-bond. It is known[33] that the insertion of an ethylene molecule in the bond results in the formation of a propyl derivative of the transition metal:

$$\rangle M{-}CH_3 + C_2H_4 \rightarrow \rangle M{-}C_3H_7\ .$$

This reaction is much faster than the insertion of ethylene in an M–H bond[53]. The "alkanolysis" of the $M{-}C_3H_7$ bond obtained should result in the formation of a propane molecule—the product of the addition of methane to ethylene:

$$CH_4 + C_2H_4 \rightarrow C_3H_8\ .$$

The possibility, in principle, of the occurence of this reaction was first demonstrated in the presence of the $Ti(C_4H_9O)_4{-}Al(C_2H_5)_3$ catalytic system in benzene at 20 °C and a pressure of 1 atm.[55] Under these conditions, in the absence of methane, ethylene dimerises with formation of but-1-ene. The subsequent addition of the monomer, leading to the growth of the polymer chain, is hardly observed in this system[57].

If the catalytic system is maintained in an atmosphere of ethane in the absence of ethylene, then ethane, the product of the "alkanolysis" of the $Ti{-}C_2H_5$ bond, accumulated in the gas phase[55,58]. As a result of this reaction, a small amount of the methyl complex of titanium is formed in the system. After the supply of ethylene to the system in proportions $CH_4/C_2H_4 > 10$, its absorption with formation of propane is observed. This is accompanied by the simultaneous formation of a small amount of but-1-ene, whose yield can be reduced by increasing the molar ratio of methane and ethylene or by altering the conditions in the treatment of the catalyst with methane. Under the conditions indicated, the yield of propane after 10 h is 15–20% of the amount of ethylene in solution. It is noteworthy that the efficiency of the catalyst is not high and that approximately 1 mole of propane is formed in the presence of 4–5 moles of the initial titanium[55].

The formation of propane is not observed in the absence of methane or ethylene. When methane is replaced by deuteromethane, tetradeuteropropane $C_3H_4D_4$ is detected mass-spectrometrically in the gaseous products[55]. Thus there is no doubt about the formation of propene from methane and ethylene.

In order to achieve the addition of methane to acetylene, i.e.

$$CH_4 + C_2H_2 \rightarrow CH_3{-}CH{=}CH_2\ ,$$

studies were made of various catalysts of the hydrogenation of acetylene based on titanium(IV), iron(III), cobalt(II), and nickel(II) complexes in combination with organoaluminium compounds[53]. Among these, catalytic activity in the reaction involving the addition of methane to acetylene was shown only by the $Fe(acac)_3{-}Al(C_2H_5)_3$ system in benzene solution. It is known from the literature[59] that acetylene polymerises in the presence of this catalyst. However, after the treatment of the catalytic system with carefully purified methane, the polymerisation of acetylene is not observed and the rate of its absorption falls significantly[53] (Fig. 6b).

Thus, by interacting with the active centres of the catalyst, methane converts them into a form inactive for polymerisation. Bearing in mind that ethane is evolved in this process, the decrease of the catalytic activity can be attributed to the formation of a methyl derivative of the transition metal with a much lower reactivity in the initiation of the polymer chain[33,37]. Evidently the presence of the relatively inactive $M{-}CH_3$ bond in an excess of methane ($CH_4/C_2H_2 \geq 30$) ensures the necessary condition for the single insertion of an acetylene molecule in this bond and the formation of propene in the system[53].

In a dilute solution of the catalyst propene accumulates after an appreciable induction period whose duration depends on the catalyst concentration. Table 7 shows that the yield of propene increases with time and with temperature. With increase of the molar ratio Al/Fe, the yield of propene falls and, when Al/Fe > 8, whereupon the rate of exchange of the alkyl groups bound to the iron and the aluminium atoms increases significantly, its formation is not observed and acetylene polymerises[53].

Table 7. The yields of propene Q in the reaction of methane and acetylene under the influence of the $Fe(acac)_3{-}Al(C_2H_5)_3$ catalytic system[53]*.

10^3[Fe(acac)$_3$], M	T, °C	t, min	$10^2 Q$, mol/mol Fe	10^3[Fe(acac)$_3$], M	T, °C	t, min	$10^2 Q$, mol/mol Fe
1	14	240	1.6	1	30	51	1.6
1	20	100	—	10	20	40	0.5
1	20	135	0.4	10	20	70	0.8
1	20	255	1.0	10	20	95	0.9
1	20	280	2.8	10	20	240	1.0

*Solvent—benzene; pressure 640 mmHg; $[CH_4] = 1.93 \times 10^{-2}$ M; $[C_2H_2] = 0.6 \times 10^{-2}$ M; Al/Fe = 4.

In the absence of methane or acetylene, propane is not formed, while the replacement of methane by deuteromethane, results in the detection of deuteropropene in the reaction products. It was noted above that, after the hydrolysis of the catalytic system treated with tetradeuteromethane, trideuteromethane is formed in small amounts ($CD_3H/Fe = 2.2 \times 10^{-4}$).[53] This fact shows that the fraction of the active centres responsible for the addition of methane to acetylene, relative to the total amount of iron in the system, is small. This is evidently the reason for the observed low yield of propene relative to the initial amount of the catalyst.

Enikolopov presented for the first time the results of studies on reactions involving the addition of methane to unsaturated hydrocarbons (ethylene and acetylene) in the 1979 Medvedev lectures. This fundamentally new reaction of paraffinic hydrocarbons aroused much interest not only in our country but also abroad. Studies on the activation of alkanes by non-platinum metal complexes are being vigorously prosecuted in many laboratories at the present time.

The formation of propene in the H_2–CH_4–C_2H_4–C_2H_2 mixture in the presence of a catalytic system based on nickel(II) stearate, naphthenate, and naphthenehydroxamate, deposited on the surface of nickel hydroxide, in combination with triethylaluminium or di-isobutylaluminium hydride has also been reported by Noskova and co-workers[60,61]. In the presence of these catalysts it is possible to obtain propene in higher yields. However, unfortunately, owing to the complexity of the system proposed in these investigations, the role of methane in the formation of the propene molecule has not so far been unambiguously established. The situation is also complicated by the fact that the formation of a small amount of propene in the system is observed also in the absence of methane, apparently as a result of the metathesis of ethylene. Despite this, the above studies merit special attention, since there is no doubt about the activation of methane in these systems.

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Analysis of the literature data on the catalytic activation of alkanes indicates a vigorous development of the chemistry of saturated hydrocarbons. In the presence of 3*d* transition metal complexes, a fundamentally new type of reactions of methane, namely addition reactions, has been discovered. By adding methane to unsaturated hydrocarbons (in particular to acetylene), it is possible to obtain the most important petroleum processing products from a non-petroleum raw material—natural gas. The possibility of the practical application of this process arises owing to the development of highly active catalysts, which make it possible to increase sharply the yield of the product (for example, propene) per unit mass of the catalyst. We believe that, under the conditions of the vigorous development of the research in this field, the practical application of the available results is a matter for the near future.

The possibility, in principle, of achieving the hydromethylation of various compounds with the aid of methane leads to new ways of synthesising various organic compounds using the side products from the processing of petroleum, natural gas, and coal. The range of thermodynamically feasible reactions involving methane is fairly wide. These reactions include, for example, the hydromethylation of allene, leading to the formation of butenes, the formation of ethyl methyl ketone from methane, carbon monoxide, and ethylene (analogously to the hydroformylation reaction), the synthesis of acetaldehyde from methane and carbon monoxide at elevated pressures, and many others. The search for the selective catalysts of these and other most important reactions of alkanes (oxidation, chlorination, dehydrogenation, etc.) is being actively prosecuted in various countries[22–31,40–47,60–70]. One must note that studies of Soviet investigators have played a leading role in the catalytic activation of alkanes; these investigations have already significantly enriched the chemistry of alkanes.

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