CATALYTIC ACTIVITY OF THE PRODUCTS OF LOW-TEMPERATURE COCONDENSATION OF OLEFINS WITH THE VAPORS OF TRANSITION METALS

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A method which permits using metal vapors as synthetic reagents was developed in the last ten years [1]. The method of conducting the experiments consists of the evaporation of the metal and condensation of its vapors with the vapors of organic compounds on the walls of the reaction vessel cooled to 77°K. The intense development of the method was primarily due to its rich synthetic possibilities.

The study of the reaction of unsubstituted alkenes with metals demonstrated the presence of catalytic activity in the products of the combined condensation. Isolated observations of short-lived intermediate π-complexes of propene and butene with Ni in conditions of matrix isolation of the latter are described in the literature [2, 3]. It is understood that the decomposition of this type of compound can result in the products of a catalytic isomerization of olefins.

1-Hexene was selected as the matrix substance in the present study, and its transformations in the presence of condensed vapors of Cr, Mn, Fe, Co, Ni, and Pd were studied. The catalytic activity of these metals were evaluated with respect to 1-hexene in conditions of low-temperature vacuum cocondensation, and the stability of sols of the metals in the olefin and the possibility of the transformation of the organometallic compounds in the reaction of the metal vapors with the hexene were determined.

EXPERIMENTAL

The reaction of transition metals with hydrocarbons was conducted by the method of high-vacuum (10^{-5} mm Hg), low-temperature (77°K), combined condensation of the metal vapors and hydrocarbons according to the method described in detail in [4, 5]. The resistance method of evaporation was used for preparation of the metals in the vapor state. The rates of evaporation of the metal were 0.5 g/h, and the consumption of the hydrocarbon was 50 ml/h. The metal/hydrocarbon molar ratio in a typical experiment was 1:20. After thawing of the matrix, the cocondensate was siphoned from the reactor into a Schlenck vessel in an atmosphere of purified Ar. The cocondensate was a stable black suspension. The analysis of the suspension was conducted 10 min after thawing of the matrix began.

The study of the transformation of the starting 1-hexene in the suspension was conducted by taking samples and analyzing the products by gas chromatography: a 50 m × 0.25 mm capillary column containing triethylene glycol dibutyrate and a flame-ionization detector (FID) were used.

After elimination of the volatile products in the suspension at 20°C and 0.1 mm Hg, a solid sediment was obtained and treated with boiling hexane for 3 h. The metal black was filtered from the hexane extract, and viscous oily yellow products were obtained after its evaporation. The heavy hydrocarbons were analyzed by gas chromatography and chromato-mass spectrometry (CMS). Gas chromatography was conducted in a 50 m × 0.4 mm copper capillary column containing Apiezon L, with a FID, and temperature programming from 70 to 300°C at the rate of 4°C/min. The CMS analysis was conducted on an LKB-209 instrument with an ionizing electron energy of 70 eV using a column containing 5% SE-30 on Chromaton W. Elementary analysis was performed on the solid sediment before and after extraction with hexane.

DISCUSSION OF RESULTS

The gas chromatographic analysis of the suspension showed that it contained 2-hexane and 3-hexene in the cis and trans forms in addition to the starting 1-hexene. The products

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TABLE 1. Compositions of Isomeric Mixtures of Hexenes 20 h after Thawing of the Matrix

Isomer	Metal					Equilibrium composition [6]
	Cr	Mn	Ni	Co	Fe	
1-Hexene	0,6	0,5	1,5	6,8	0,9	0,95
trans-2-Hexene	62,0	62,3	61,0	59,6	65,7	51,20
cis-2-Hexene	20,6	20,8	22,3	18,0	23,9	15,25
3-Hexene (cis + trans)	16,8	16,4	15,2	15,6	9,5	32,60
cis/trans-2-Hexene	0,33	0,33	0,37	0,30	0,36	0,29

TABLE 2. Conversion of 1-Hexene, %

No. of expt.	Metal	Conversion time,* min			No. of expt.	Metal	Conversion time,* min		
		20	30	60			20	30	60
1	Cr	99,0	99,0	99,5	5	Fe	39,0	45,5	52,7
2	Mn	73,0	92,0	97,0	6	Pd	0	0	0
3	Ni	60,0	75,0	90,0	7	Cr†	16	25,8	59,2
4	Co	69,0	71,5	83,1	8	Cr†	0	0	0

*From the beginning of thawing of the mxtrix.

†Dilute matrix: molar ratios in combined condensation Cr:1-hexene - 1:100.

Control experiment: combined condensation of Cr and hexene with subsequent addition of 1-hexene to the suspension.

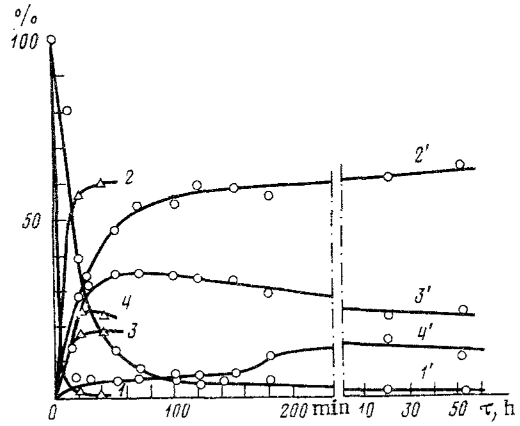


Fig. 1. Change in the isomeric composition of the hexenes in chromium—1-hexene (1-4) and nickel—1-hexene (1'-4') suspensions at 293°K: 1, 1') 1-hexene; 2, 2') trans-2-hexene; 3, 3') cis-2-hexene; 4, 4') trans- and cis-3-hexene.

of isomerization accumulated in the suspension in time, and the composition of the mixture of isomers approached the equilibrium concentration (Table 1).

The transition metals studied exhibit different catalytic activity in the reaction of isomerization of the starting 1-hexene (Table 2) and can be placed in the following order with respect to the decrease in the activity: Cr > Mn > Ni ≈ Co > Fe. Palladium was inert in this process. The catalytic activity of Cr and Mn was so high that it was not possible to follow the kinetics of isomerization in detail. The kinetic curves of the isomerization of 1-hexene for Ni and Cr are shown in Fig. 1.

The nature of the kinetic curves indicates that the catalytic reaction primarily takes place in thawing of the matrix and not during cocondensation. Extrapolation of the kinetic curves to the zero time showed that isomerization does not occur in the solid matrix of the cocondensate.

However, the catalytic transformations of the starting hexene are not exhausted by positional and cis-, trans-isomerization alone. This is indicated by the presence of oily

TABLE 3. Oligomerization of 1-Hexene

Metal	Oligomer in the solid segment of the suspension, wt. %	Metal	Oligomer in the solid segment of the suspension, wt. %
Cr	55.2	Co	19,3
Mn	39,9	Fe	16,4
Ni	20,5	Pd	0

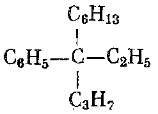
organic products obtained from the hexane extract of the solid sediment of the suspension and the exothermic effect observed immediately on thawing of the matrix. Actually, the gas chromatographic analysis of the extract revealed the presence of a set of products of the oligomerization of 1-hexene.

Cr and Co cause the formation of the di- and trimers of hexene, the di-, tri-, and tetramers are primarily formed on Mn, and the tetra-, penta-, and hexamers of hexene are chiefly formed on Fe.

The CMS study suggests that the oligomers of hexene have the structure of branched olefins. A smooth decrease in the intensities of the peaks of the ions up to molecular ions of low intensity takes place in all cases. Two groups of peaks are observed for the oligomers obtained in the reaction of Cr with 1-hexene: C_{12} dimers and C_{18} trimers. The low-intensity molecular ions $C_{12}H_{24}^+$ (168) and $C_{18}H_{36}^+$ (252) correspond to them. In the region of low values, the mass spectra are identical: $C_4H_9^+$ (57), $C_5H_{11}^+$ (71), $C_6H_{11}^+$ (83), and $C_7H_{13}^+$ (97). In some cases, there are maxima corresponding to the elimination of the $C_4H_9^+$ and $C_7H_{13}^+$ ions from the starting molecular ion on the smoothly diminishing curve of the ion intensities; this corresponds to the presence of substituents in the hydrocarbon backbone. All of these data indicate the presence of oligomers with a branched structure in the samples analyzed.

With respect to the activity in the oligomerization reaction, the metals are in the following order: Cr > Mn > Ni ≈ Co ≈ Fe (Table 3).

In addition to the processes of isomerization and oligomerization, the reaction of low-temperature dehydrocyclization of 1-hexene also takes place to a small degree in the experimental conditions. The CMS analysis of the extract of the solid sediment of a suspension of Cr in 1-hexene revealed the intense molecular ion $C_{18}H_{30}^+$ (246) = P^+. The ion $C_7H_7^+$ (91), characteristic of alkyl aromatic compounds, is very intense. A set of five ions (105, 119, 133, 147, 164) follow this ion, corresponding to branching into six carbon atoms at the α C atom. The ion $[P - C_6H_{13}]^+$ (161), corresponding to cleavage of the hexyl substituent from the α C atom, is the most intense ion in the mass spectrum. The ions $[P - C_3H_7]^+$ (203) and $[P - C_2H_5]^+$ (217) are very pronounced. These data suggest the presence of the following structure in the products of the alkyl aromatic derivative:



$$C_6H_5{-}\overset{\displaystyle C_6H_{13}}{\underset{\displaystyle C_3H_7}{C}}{-}C_2H_5$$

It is known that the aromatization reaction is thermodynamically allowed at a temperature of 300°C and higher [7]. It is still difficult to draw a conclusion as to whether aromatic compounds are formed during cocondensation or in subsequent transformations.

The products of oligomerization of hexene accumulate on the surface of the highly dispersed metal particles. Even after long treatment of the solid residue of the suspension with boiling hexane, the particles contain a significant number of the products of deep oligomerization and polymerization (Table 4). These products apparently form a loose coating on the surface of the highly dispersed metal particles. The high stability of the thawed condensate as a colloidal system could be due to the presence of this lyophilic coating. For example, we note that a suspension of metallic Cr in 1-hexene prepared by high-vacuum, low-temperature cocondensation is stable for more than 6 months.

If saturated hydrocarbons, particularly n-hexane, are used as the matrix, it is not possible to obtain a stable colloidal solution. This is due to the fact that n-hexane does not undergo catalytic transformations, does not react with the transition metal in the conditions of the method, and the surface of the metal particles in this case is lyophobic, which is also responsible for the rapid coagulation of the suspension.

TABLE 4. Elementary Analysis of the Solid Sediment of the Suspension

Metal	C, %		H, %		C/H	
	a*	b*	a	b	a	b
Cr	47,6	32,8	7,6	5,5	6,3	6,0
Mn	34,4	17,9	5,5	3,1	6,2	5,8
Ni	18,4	17,9	2,1	3,1	8,8	5,8
Co	16,3	13,3	3,0	2,6	5,4	5,1
Fe	13,9	4,0	2,5	0,5	5,6	8,0
Cr†	6,4	–	1,2	–	5,3	–
Pd	17,1	–	2,4	–	7,1	–

*a) Before extraction; b) after extraction with boiling hexane.
†Control experiment (cf. Table 2).

The looseness of the layer of the oligomers of hexene on the surface of the metal particles indicates their rapid oxidation in the presence of even traces of O_2. An almost instantaneous change in the color and coagulation of the suspension is observed when the thawed condensate comes in contact with air. The high activity of the particles in the suspension with respect to O_2 is confirmed by the pyrophoric nature of the powders obtained in evacuation of the liquid phase from the suspension. The tentative size of the metal particles in the suspension is ∿50 Å according to x-ray analysis. This value corresponds to the data in the literature [8]. Matrix isolation and a preparative cryochemical method previously showed that an extremely short-lived π-complex is formed in the cocondensation of vapors of transition metals and olefins, and the starting metal and isomerized olefin are formed on its decomposition.

There is no stable point of view concerning the nature of the intermediate π-complex: according to [9], a π-allyl complex is formed, but according to [3] and [10], the π-complex is of an olefin nature. These concepts apply to the experiments discussed.

The mechanism of the catalytic action of highly dispersed metals was not specially studied in the present article. However, all of the experimental data obtained do not contradict the data in the literature on the π-complex mechanism of isomerization of α-olefins [11]. Our attempts to isolate an intermediate π-allyl or π-olefin complex or to characterize it were unsuccessful. Nevertheless, it is possible to state with sufficient probability that a molecule of the olefin coordinated with the metal is part of the active site. By analogy with [12], we hypothesize that the π-complexes of olefins with metals are not random, but are highly mobile systems in which the rapid mutual transformation of the π-olefin complex and the π-allyl metal hydride takes place. This is in agreement with the findings of the control experiment (cf. Table 2, experiment 8). It was found that Cr, which exhibited the maximum catalytic activity in our experiments, is totally inert in n-hexane: no products of the reaction were detected. The presence of a polymeric material in the powders after extraction with hexane is also not excluded. The hypothesis on the polymeric reaction in the powders is based on the data in [11] which indicate that the π-allyl complexes of transition metals cause polymerization of monoolefins. In particular, it is known that triallylchromium polymerizes ethylene in soft conditions with the formation of polyethylene with a high molecular weight [13]. According to Table 3, it is possible to assume that the π-hexenyl derivative of Cr is the most active catalyst of the polymerization of hexene.

CONCLUSIONS

1. The reaction of 1-hexene with vapors of Cr, Mn, Fe, Co, and Ni in the conditions of the method of high-vacuum, low-temperature cocondensation results in the formation of a suspension which is stable in an atmosphere of argon.

2. When the cocondensate is thawed, the starting 1-hexene undergoes catalytic transformations with the formation of products of positional and cis-, trans-isomerization, oligomerization, and dehydrocyclization.

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REACTION OF 3α-HYDROXY-4β-CHLOROCARANE WITH POCl$_3$

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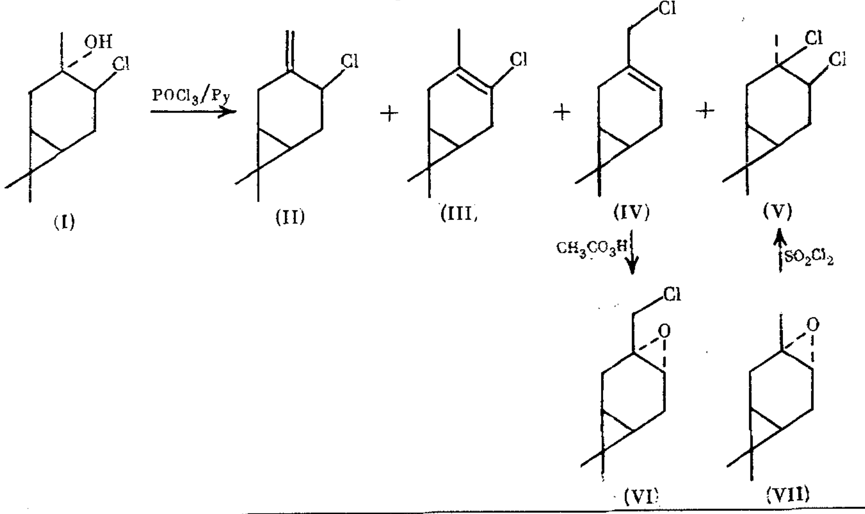
Continuing our investigation of the three-dimensional structure and stereochemistry of epoxidation of epimeric 4-chloro-3(10)-carenes [1], we report here the possibility of synthesizing 4β-chloro-3(10)-carene (II) by dehydration of the trans-chlorohydrin (I). It is known [2, 3] that monoethers of α- and β-cis-3,4-caranediols form mainly ethers of epimeric 3(10)-caren-4-ols when treated with POCl$_3$. The monoacetate of trans-3,4-caranediol, together with the ether of 3(10)-caren-4-ol under the same conditions, gives an unsaturated ether of noncarane structure, but information regarding elimination of 3α,4β-caranediols is absent.

Reaction of I with POCl$_3$ in pyridine gives a complex mixture of substances which, in addition to II, contains 4-chloro-3-carene (III), 10-chloro-3-carene (IV), 3β,4β-dichlorocarane (V), and hydrocarbons of unknown composition. The structure of II, formed as the basic product of dehydration of I, follows from spectroscopic data. In the IR spectrum,



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