MECHANISM OF THE CYCLIZATION OF NORMAL PENTA- AND HEXADIENES OVER IRON—MAGNESIUM OXIDE CATALYST

G. V. Isagulyants, K. M. Gitis,
M. I. Rozengart, K. Ya. Burshtein,
and V. F. Il'in

UDC 541.124:542.97:547.315

In [1, 2] the cyclization of piperylene over dehydrogenating oxide catalysts in a water vapor stream was considered, and a mechanism was proposed that involved intermediate pentadienyl and cyclopentenyl radicals. The present work is a study of n-pentene and penta- and hexadiene conversion in the presence of iron—magnesium oxide catalysts, and explains the effect of the number and location of the double bonds on the cyclization of unsaturated hydrocarbons and on the accompanying reactions.

EXPERIMENTAL

The tests were carried out in a flow apparatus with a quartz reactor holding 15 cm^3 of iron—magnesium oxide catalyst of 0.5-1.0 mm grain size at 525-630°C, space velocity of hydrocarbon feed 1 h^{-1}, and 1:10 dilution with water vapor. Analysis was carried out on an LKhM-8MD chromatograph with a flame-ionization detector, capillary steel columns (50 m long, 0.25 mm i.d.), and He carrier gas at 1 ml/min. Complete analysis of catalyzate was carried out on a column with Apiezon L at 140°C. Since the light hydrocarbons are poorly separated in this way, a second analysis was carried out on a triethylene glycol dibutyrate column at 25°C. This gave an efficient separation of the low-boiling products through benzene.

The starting hydrocarbons were purified by the distillation of the commercial products in a 100-theoretical-plate column. The purities were: 1,3-pentadiene (1,3-PD), 98%; 2,4-hexadiene (2,4-HD), 95%; 1,5-hexadiene (1,5-HD), 99%. 1-Pentene, obtained by pyrolysis of amyl acetate (from Ac_2O and primary $C_5H_{11}OH$), after fractional distillation contained no impurities. 1,4-Pentadiene (1,4-PD), obtained by the procedure of [3], was 97% pure.

DISCUSSION OF RESULTS

Table 1 shows that normal pentadienes and pentenes undergo 1,5-cyclization, dehydrogenation, decomposition, and condensation. The degree of cyclization of n-pentadienes is significantly greater than that of n-pentene. Thus, the overall yield of cyclopentadiene (CPD) and cyclopentene (CP) is 7 times greater from 1,3-PD and 10 times greater from 1,4-PD than from 1-pentene. The ratio of the CPD yield to the CP yield is practically the same from pentene as it is from pentadienes (6.5-6.8). This fact, as well as the noticeable increase

TABLE 1. Conversion of n-Pentenes and Pentadienes over Iron–Magnesium Oxide Catalyst [630°C, hydrocarbon feed rate 1 h^{-1}, hydrocarbon:H_2O 1:10 (molar)]

Starting hydrocarbon	Catalyzate yield, %	Catalyzate yield, %								Yield of cyclic products, %
		C_4H_6	C_5H_{10}	1,3-pentadiene trans	1,3-pentadiene cis	1,4-pentadiene	isoprene	cyclopentene	cyclopentadiene	
n-Pentenes	89,3	7,7	77,9	6,2	3,4	0,00	0,3	0,2	1,3	1,4
1,3-Pentadiene*	79,4	3,5	6,0	46,8	27,1	3,2	0,5	1,6	10,5	9,6
	72,3	4,0	4,0	48,3	27,8	3,4	0,5	1,8	10,5	9,0
1,4-Pentadiene*	92,7	2,6	0,9	10,6	6,0	62,8	0,1	2,0	13,5	14,6

*Up to 1% C_6-C_8 aromatic hydrocarbons, naphthalene, and azulene also obtained from pentadienes.

N. D. Zelinskii Institute of Organic Chemistry, Acacemy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2524-2529, November, 1981. Original article submitted April 7, 1981.

0568-5230/81/3011-2087$07.50

TABLE 2. Effect of Reaction Temperature on Composition of 1,5-Hexadiene Conversion Products [iron-magnesium catalyst; hydrocarbon feed rate 1 h^{-1}; hydrocarbon:water, 1:10 (molar); duration of test, 30 min]

Temp., °C	Catalyzate yield, %	Catalyzate composition, %											Yield, %	
		cracking products	hexenes	1,5-hexadiene	conjugated hexadienes	1,4-hexadiene	methylcyclopentadienes	methylcyclopentenes	cyclohexene	cyclohexadienes	benzene	unidentified	C_5 cyclic	C_6 cyclic
525	83,3	6,3	0,2	72,3	13,0	5,2	0,2	0,4	0,3	0,7	0,7	Tr.	0,5	1,5
550	84,7	4,6	0,2	75,2	7,6	5,2	0,4	1,0	0,9	1,8	2,0	1,0	1,1	4,0
575	64,7	4,7	0,4	66,7	11,6	4,8	0,7	1,0	1,1	2,3	5,9	1,4	1,1	6,0
	68,6	4,6	0,2	56,4	9,7	5,7	0,6	0,9	0,9	2,2	4,8	Tr.	1,0	5,3
600	53,4	3,9	1,1	51,3	10,7	3,6	1,3	1,4	1,7	3,0	19,7	0,8	1,5	13,0
630	27,5	6,3	0,9	41,7	3,7	2,3	2,2	2,1	2,2	4,6	30,5	0,8	1,2	10,2

TABLE 3. Effect of Reaction Temperature on Composition of 2,4-Hexadiene Conversion Products [iron-magnesium catalyst; hydrocarbon feed rate 1 h^{-1}; hydrocarbon:water, 1:10 (molar); duration of of test, 30 min]

Temp., °C	Catalyzate yield, %	Catalyzate composition, %												Yield, %	
		cracking products	1,3-pentadiene	n-hexenes	1,5-hexadiene	conjugated hexadienes	1,4-hexadiene	methylcyclopentadienes	methylcyclopentenes	cyclohexene	cyclohexadienes	benzene	unidentified	C_5 cyclic	C_6 cyclic
525	86,0	5,3	0,7	0,4	0,4	81,4	10,3	0,3	0,2	—	—	0,6	Tr.	0,4	0,5
550	90,7	3,9	1,1	0,5	0,9	81,9	9,2	0,7	0,4	Tr.	Tr.	1,2	0,08	1,0	1,1
575	81,9	3,1	2,5	1,0	2,1	75,2	7,4	2,2	0,5	0,1	2,6	2,9	Tr.	2,2	4,6
600	76,5	2,7	4,5	1,4	4,5	61,6	7,9	3,8	1,2	0,3	2,5	7,7	0,5	3,8	8,0
630	75,5	3,8	8,5	1,9	6,3	55,3	3,5	4,7	1,0	0,2	3,1	11,2	0,6	4,3	10,4

TABLE 4. Effect of Diluent on Composition of 1,5-Hexadiene Conversion Products [iron-magnesium catalyst, 500°C, hydrocarbon feed rate 1 h^{-1}, dilution 1:10 (molar), duration of test 30 min]

Diluent	Catalyzate yield, %	Catalyzate composition, %									Yield, %	
		cracking products	1,5-hexadiene	conjugated hexadienes	1,4-hexadiene	methylcyclopentadienes	methylcyclopentenes	cyclohexene	cyclohexadienes	benzene	C_5 cyclic	C_6 cyclic
Water vapor	84,7	4,6	75,2	7,6	5,2	0,4	1,0	0,9	1,9	2,0	1,2	4,1
Argon	53,6	5,9	60,9	12,1	5,7	0,6	1,7	0,7	3,0	9,3	1,2	7,0

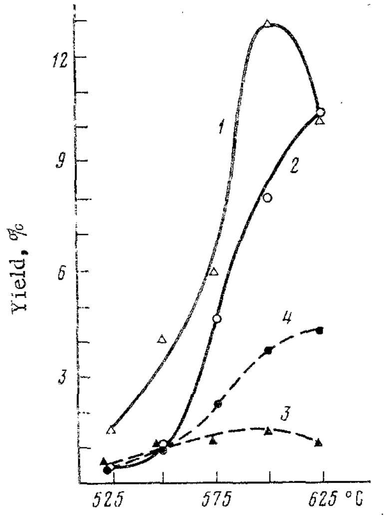

Fig. 1. Dependence of the yields of cyclic hydrocarbons from hexadienes on the temperature: 1) cyclohexadiene, benzene, and cyclohexene from 1,5-hexadiene; 2) the same, from 2,4-hexadiene; 3) methylcyclopentadiene and methylcyclopentenes from 1,5-hexadiene; 4) the same, from 2,4-hexadiene.

in cyclic hydrocarbon yield with C=C bond accumulation in the molecule, may be explained by the fact that under these conditions five-membered rings are formed from pentadienes, but not from pentenes. The overall CPD and CP content of the catalyzate and their yield from 1,4-PD are greater than from 1,3-PD. It also follows from Table 1 that the isomerization of 1,4-PD to 1,3-PD is faster than the reverse reaction; this conforms with the thermodynamic equilibrium calculated from the data of [4]. It should also be noticed that the hydrogenation* of 1,3-PD over iron-magnesium oxide is about four times more intensive than that of 1,4-PD. Also noticeable is the significantly lower yield of catalyzate from 1,3-PD than from 1,4-PD. This difference is apparently caused by the greater propensity of 1,3-PD for polymerization and condensation.

Aside from the reactions analogous to those observed for the pentadienes, the hexadienes (HD) also undergo aromatization. The catalyzates contain (Tables 2 and 3) hydrocarbons with both five-membered rings [methylcyclopentenes (MCP) and methylcyclopentadienes (MCPD)] and six-membered rings [benzene, cyclohexene (CH), cyclohexadiene (CHD)], and many products of isomerization, hydrogenation, decomposition, and condensation.

From a comparison of Table 4 and the data of [5], it follows that this catalyst has significantly less isomerization activity than one on an Al_2O_3 support. Water vapor further reduces its isomerization and cracking activities (see Table 4). All this enables us to estimate the reactivity of the dienes as the least distorted by isomerization.

At any one temperature the yield of liquid catalyzate from 1,5-HD was less than from 2,4-HD, and the yield of decomposition products is greater (see Tables 2 and 3); this is undoubtedly related to the ease of rupture of the middle β,β-C—C bond in the 1,5-HD, which is the weakest: $\mathrm{C{=}C{-}C\vdots C{-}C{=}C}$. Nevertheless, the total yield of benzene, CHD, and CH is greater from 1,5-HD than from 2,4-HD (see Fig. 1). At 525°C and 550°C the total yield of MCP and MCPD is practically the same for both dienes, but at 575°C and higher, not only the yield but the C_5 cyclic content of the catalyzate of 2,4-HD are higher.

The HD also differ somewhat in the selectivity of cyclic hydrocarbon formation. With 1,5-HD the total yield of benzene, CHD, and CH is higher than that of MCPD and MCP. With 2,4-D at 525 and 550°C the yields of hydrocarbons with six-membered and five-membered rings are the same, but at higher temperatures the yield of benzene and higher C_6 cyclics is higher than that of C_5 cyclics (see Fig. 1). The increasing proportion of aromatization with increasing temperature is typical of both HD. There is a noticeable difference in 1,3-PD formation from the hexadienes. In 2,4-HD catalyzate, the 1,3-PD content increases with temperature and reaches 8.5% at 630°C, whereas the 1,5-HD catalyzate contains only traces at all temperatures.

Our results enable us to make some proposals concerning the mechanism of aliphatic diene

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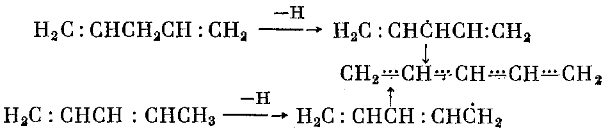
*Hydrogenation occurs because of H_2 that is formed in the dehydrocyclization of pentadienes, and possibly in the reaction of H_2O with hydrocarbons and coke.

cyclization. According to Table 1, unconjugated pentadiene cyclizes more easily than conjugated. This is apparently explainable by the fact that the energy for detaching the allyl hydrogen (E_d) from the secondary carbon in 1,4-PD is less than from the primary carbon in 1,3-PD; consequently, the intermediate radical is more easily formed from 1,4-PD:



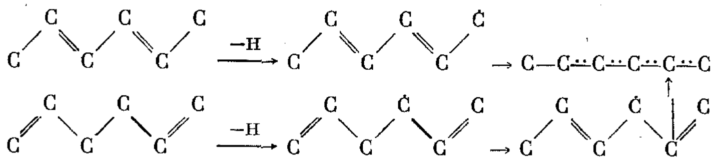
$$H_2C:CHCH_2CH:CH_2 \xrightarrow{-H} H_2C:CH\dot{C}HCH:CH_2 \quad (1)$$

$$CH_2 \cdots CH \cdots CH \cdots CH \cdots CH_2$$

$$H_2C:CHCH:CHCH_3 \xrightarrow{-H} H_2C:CHCH:CH\dot{C}H_2 \quad (2)$$

If it is assumed that in reactions (1) and (2) the same product — a pentadienyl radical with a delocalized electron — is obtained, then the difference in E_d of the two pentadienes is determined by the difference in the heats of formation of the starting hydrocarbons, which according to [4] is 6.5 kcal/mole. Since according to [6] for 1,4-PD E_d = 80 kcal/mole, then for piperylene it is 86 kcal/mole, which coincides with E_d for propylene. This analysis of E_d values permits us to propose that the energy for detaching an allyl hydrocarbon is affected by the degree of substitution at that carbon atom and by the number of nearby double bonds. The effect of more distant bonds on E_d is less than the inherent experimental error (±2 kcal/mole) in present determinations of bond energy.

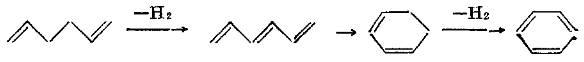
In the case of the HD, only 2,4-HD can form an alkyl-substituted pentadienyl radical; 1,5-HD or the respective hexadienyl radical must first isomerize:



(3)

(4)

Therefore, the C_5 cyclic yield is less from 1,5-HD than from 2,4-HD (see Fig. 1). At the same time, the 1,5-HD structure is favorable for aromatization, i.e., for the formation of hexatriene, which, as is known [7], is easily converted over a dehydrogenating catalyst to cyclohexadiene and then to benzene:



(5)

Thanks to these two favoring circumstances, of the two hexadienes, specifically 1,5-HD is selectively converted to hexatriene, and consequently to C_6 cyclic products.

Thus, if it is assumed that over a dehydrogenating catalyst C_5 cyclic hydrocarbons are obtained from dienes through radicals, while C_6 are obtained through trienes, then the data of the present work are well explained by, and fully confirm, the concepts developed in [2, 7] concerning the mechanism of diene cyclization over oxide catalysts.

The authors are grateful to Yu. N. Bubnov for providing the sample of 1,4-pentadiene.

CONCLUSIONS

1. In the reaction of 1-pentene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, and 2,4-hexadiene over iron-magnesium oxide catalyst, the yield of cyclic products increases with the number of double bonds in the starting hydrocarbon, and with the lower energy of the allyl hydrogen.

2. Over an iron-magnesium catalyst, the yield of C_5 cyclic products from hexadienes increases with the probability of pentadienyl radical formation, while the yield of C_6 cyclic products increases with the ease of dehydrogenation of diene to triene.

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HYDROGENATION OF CARBON DIOXIDE ON HYDRIDES OF INTERMETALLIDES

A. L. Lapidus, I. A. Bruk,
V. V. Mal'tsev, A. F. Ivanovskii,
and V. V. Lunin

UDC 542.941.7:546.264-31

The hydrogenation of oxides of carbon for the purpose of preparing a synthetic substitute for natural gas is practically very important [1]. The process of reducing CO and CO_2 is studied mostly by using supported Ni catalysts [2], on which CO also disproportionates to form coke. At high temperatures this reaction competes with methanation. The catalysts are easily poisoned by sulfur- and nitrogen-containing compounds [2].

Hydrides of intermetallides are stable to carbonization and to poisoning by sulfur-containing substances owing to constant heterophase exchange of hydrogen with the body of the hydride [3]. They are active and selective in the synthesis of methane from CO and H_2 [4]. We investigated the composition of products of hydrogenation of CO_2 on hydrides of the intermetallides Zr—Ni, Zr—Co, Hf—Ni, and Hf—Co, the component metals being present in the atomic ratio 1:1.

EXPERIMENTAL

The catalysts were prepared by the method of [5]. The experimental procedures and methods of analysis of the gaseous products are given in [4]. The duration of each experiment was 3 h. The mixture $CO_2:H_2 = 1:3.8\text{-}4.0$ (vol.) was used for the experiments.

When calculating equilibrium concentrations, we took into account only independent reactions, selecting for this the following:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (1)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

The Kjaer equations [6] were used in the calculations.

DISCUSSION OF RESULTS

The maximum CO_2 conversion is observed at 350°C in the presence of Zr—Ni and Zr—Co hydrides and at 450°C in that of Hf—Ni and Hf—Co hydrides (Table 1).

When comparing experimental results with equilibrium compositions calculated from

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2529-2531, November, 1981. Original article submitted December 19, 1980.

0568-5230/81/3011-2091$07.50