=== **PEROXIDES-XI** ===

Reductive Dehydration of Alcohols: A Route to Alkanes

M. V. Tsodikov*, V. Ya. Kugel'*, F. A. Yandieva*, G. A. Kliger*, L. S. Glebov*, A. I. Mikaya*,
V. G. Zaikin*, E. V. Slivinskii*[†], N. A. Plate*, A. E. Gekhman**, and I. I. Moiseev**

* *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 117912 Russia*
** *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 117907 Russia*
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Abstract—The reductive dehydration of cyclic (C_5, C_6) and aliphatic (C_2–C_4) alcohols into polycycloalkanes and alkanes whose carbon skeleton has at least twice as many atoms as that of the original substrate is reported for the first time. This reaction takes place at 250–350°C and 7–50 atm in the presence of a polymetallic catalytic system based on an iron-containing fused catalyst or a hydrided iron- and titanium-containing intermetallide mixed with a small amount of Pt/Al_2O_3. The mechanism of this new reaction is discussed in terms of the mechanisms of known reactions of alcohols and aldehydes enlarging the carbon skeleton.

The annual world output of synthetic methanol is about 30 million tons. The total capacity of chemical and biochemical ethanol plants approaches 20 million tons per year. Millions of tons of C_3–C_5 fatty alcohols are annually produced from alkenes [1, 2].

Since Butlerov and Sabatier's times, alcohol chemistry has held a central position not only in catalysis science, but also in the industrial applications of catalysis.

Alcohol oxidation, oxidative dehydrogenation, and oxidative condensation into esters are widely used in industry to produce ethyl acetate, methyl formate, formaldehyde, and acetaldehyde [1]. Alcohol reduction to an alkane inheriting the chain length and geometry of the parent alkyl,

$$ROH + H_2 \longrightarrow R–H + H_2O$$
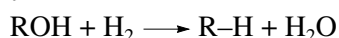
is employed in fine organic synthesis [3].

Acid-catalyzed ethanol dehydration,

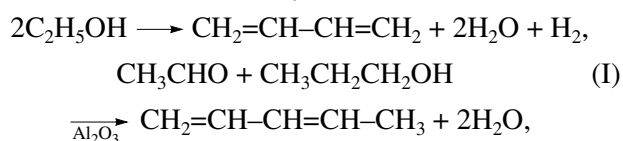$$C_2H_5OH \xrightarrow{H^+} CH_2=CH_2 + H_2O$$

was widespread in the production of alkenes (in particular, ethylene) before petrochemistry came into being. It still finds application in Brazil and other countries producing cheap ethanol by biomass fermentation [1].

The carbon chain can be lengthened by alcohol carbonylation [3],

$$CH_3OH + CO \xrightarrow[180°C, \; 10–20 \; atm]{Rh/CH_3I} CH_3COOH$$
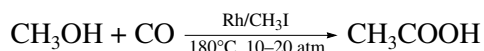
or by the diene synthesis methods suggested by Lebedev (1933) [4] and Ostromyslenskii (1915) [5],

$$2C_2H_5OH \longrightarrow CH_2=CH–CH=CH_2 + 2H_2O + H_2,$$

$$CH_3CHO + CH_3CH_2CH_2OH \qquad (I)$$

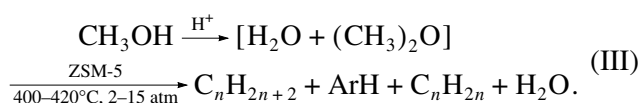$$\xrightarrow{Al_2O_3} CH_2=CH–CH=CH–CH_3 + 2H_2O,$$

which were industrially important until recently.

Another well-known reaction for lengthening the carbon chain is alcohol cross-condensation, discovered by Guerber in 1899 [6, 7]:

$$CH_3CH_2CH_2OH + CH_3OH$$
$$\xrightarrow[180–220°C]{Na^+ \; [Cat]} (CH_3)_2CHCH_2OH. \qquad (II)$$
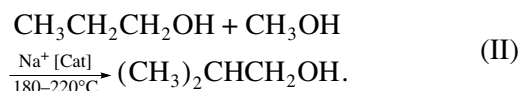
This reaction has gained attention as a synthetic route to precursors of high-quality additives for motor fuel [8, 9].

Mobil Co. has recently suggested a method for converting methanol into a mixture of hydrocarbons which boils near the final boiling point of motor fuel [1, 10]:

$$CH_3OH \xrightarrow{H^+} [H_2O + (CH_3)_2O]$$
$$\xrightarrow[400–420°C, \; 2–15 \; atm]{ZSM-5} C_nH_{2n+2} + ArH + C_nH_{2n} + H_2O. \qquad (III)$$

In 1986, New Zealand produced, by this method, 600000 tons of nitrogen- and sulfur-free motor fuel with an octane number of 95 [1].

Here, we report the reductive dehydration of alkanols yielding an alkane whose chain is at least twice as long as that of the parent alkanol:

$$2ROH + H_2 \longrightarrow R–R + 2H_2O.$$
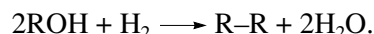
Since the early studies of the Fischer–Tropsch reaction, it has been known that, in the presence of a fused iron-based catalyst at atmospheric pressure, alcohol molecules not only fit into the growing hydrocarbon chain but, unlike alkenes, can also participate in the formation of an initial center of product synthesis [11–16].

It is interesting that, at elevated pressures of CO and H_2, when the molecules of these gases apparently can compete with alcohol molecules for a place in the coordination sphere of the active center, the alcohol can neither serve as an initiator nor fit into the growing chain [17–20].

[†] Deceased.

Table 1. Composition of magnetite for preparing PFRIC

Material	Composition, %									
	FeO	F_2O_3	Fe^0	Al_2O_3	CaO	K_2O	SiO_2	MgO	MnO_2	CuO
Natural magnetite	28.7	65.1	–	0.20	0.10	0.10	0.40	0.20	0.10	0.10

These facts prompted us to study alcohol conversion over a number of iron-containing catalysts in a reductive atmosphere.

In the first series of experiments, we tested promoted and unpromoted fused iron catalysts widely used in alcohol synthesis from CO and H_2 and in the Fischer–Tropsch synthesis. In subsequent experiments, the catalytic system was more complicated.

EXPERIMENTAL

Cyclopentanol, cyclohexanol, cyclopentanone, cyclohexanone, benzyl alcohol, benzaldehyde, ethanol, 2-methylpropanol-1, and 3-methylbutanol-1 (all analytical-grade) were used as received.

Alcohol reactions were studied in a laboratory-scale circulating-flow reactor with a fixed catalyst bed [21, 22] in a hydrogen atmosphere or, in the case of a hydrided intermetallide catalyst, in argon at 7–60 atm, 250–350°C, and a VHSV of 0.2 to 0.5 h^{-1}.

Reductive dehydration of cyclopentanol and cyclohexanol. These reactions were carried out in the presence of a fused iron-containing catalyst prepared by arc melting of natural magnetite (purchased from the Olenegorsk or Lebedinsk ore mill) with promoters (V_2O_5, BaO, Al_2O_3, Cr_2O_3, CuO; see Table 1) using water-cooled copper electrodes. The melting temperature of the oxide mixture was 1500–1600°C, and the melting time was 60–120 s. The resulting alloy was crushed and sieved to collect the 2- to 3-mm size fraction. The catalyst was preactivated with hydrogen at 450°C and 0.1–5 MPa for 10–12 h.

Reaction products were analyzed on LKhM-72, LKhM-80, and Biokhrom chromatographs and an LKB-2091 chromatomass spectrometer using packed and capillary columns [22].

Reductive dehydration of isobutanol, isoamyl alcohol, and ethanol. The conversions of these alcohols were carried out in the presence of a composite catalyst consisting of a small amount (10 wt %) of a commercial Pt/γ-Al_2O_3 catalyst [23] and a partially hydrided intermetallide of composition [TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$]H$_{0.36}$.

[TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$]H$_{0.36}$ was obtained by hydriding TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$ to [TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$]H$_2$ at 20°C and 10 MPa followed by partial dehydrogenation at 350°C [24].

The TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$ intermetallide was prepared by arc melting of the constituent metals on a water-cooled copper hearth using a tungsten nonconsumable electrode at the pilot plant of the All-Russia Institute of Light Alloys. The melting temperature was 2400–2600°C. The stock was prepared from sponge titanium (TG-100), low-carbon steel (Soviet Standard GOST 11036-75), iodide zirconium, and a molybdenum bar (MG-1) [25].

Just before being charged into the reactor, the intermetallide was crushed and sieved to collect the 2- to 3-mm size fraction. In the reactor, it was treated with hydrogen flowing at a rate of 5–10 l/h at 100–120°C for 10–14 h. Next, it was hydrided and then partially dehydrogenated.

Alcohol conversion products were analyzed on LKhM-80, LKhM-8M, and Biokhrom-1 chromatographs and a Kratos MS 25 RF chromatomass spectrometer using packed and capillary columns.

RESULTS

Cycloalkanols and Cycloalkanones

At 250–350°C and a hydrogen pressure of 0.1–1 MPa, cyclopentanol and cyclohexanol react with hydrogen, releasing water, to yield dicyclic and polycyclic hydrocarbons composed of the cycloalkyl (cycloalkenyl) rings of the starting alcohols. Among the products of cyclopentanol conversion catalyzed by the promoted fused reduced iron catalyst (PFRIC), we found hydrocarbons and their derivatives (Table 2).

Preliminary experiments demonstrated that the optimum conditions for the reductive dehydration of alcohols are P_{H_2} = 0.7 MPa, a hydrogen VHSV of 10^3 h^{-1}, an alcohol WHSV of 160–180 g h^{-1} kg$_{Cat}^{-1}$, and T = 205–270°C for cyclopentanone and 300–350°C for cyclohexanol. Cyclopentanol conversion data (Tables 2, 3) demonstrate that the best result is attained with the PFRIC promoted with a mixture of vanadium pentoxide (4.7%) and copper oxide (1%). Over this catalyst, cyclopentanol conversion exceeds 99.5% at a ~79% selectivity with respect to the sum of dicyclic, tricyclic, and tetracyclic hydrocarbons (products 3, 5, and 7 in Table 2).

Cyclohexanol dehydration at a conversion of ~99% yields 4–12% cyclohexylcyclohexane and up to 4% dicyclohexylcyclohexane (Scheme 1).

Thermodynamic calculations for the cyclohexanol + hydrogen reaction demonstrate that, at temperatures and reactant proportions favoring this reaction, the equilibrium mixture contains 10% cycloalkanones in spite of the presence of H_2. Since no noticeable

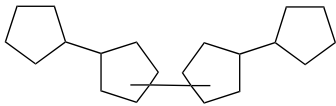**Table 2.** Most abundant products of the PFRIC-catalyzed conversion of cyclopentanol and cyclopentanone
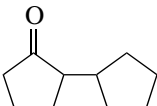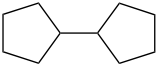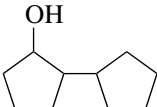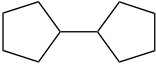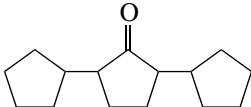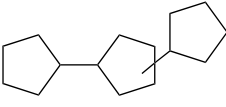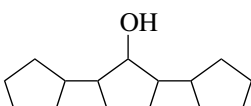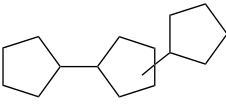
Product		Product	
(cyclopentane)	1	(tercyclopentyl)	7
(cyclopentene)	2	(cyclopentyl cyclopentanone, O)	8
(bicyclopentyl)	3	(cyclopentyl cyclopentanol, OH)	9
(bicyclopentyl with one C=C bond)	4	(2,5-dicyclopentylcyclopentanone, O)	10
(tercyclopentyl)	5	(2,5-dicyclopentylcyclopentanol, OH)	11
(tercyclopentyl with one C=C bond)	6		

Table 3. Results of the PFRIC-catalyzed synthesis of dicycloalkanes and polycycloalkanes from cyclopentanol and hydrogen

Experiment no.	PFRIC composition*, %	Alcohol conversion, %	Selectivity with respect to main products, %							
			1	2	3	4	5	6	7	8–11
1	Unpromoted	98	35	0	25	13	15	2	0	10
2	9% Al_2O_3	99.5	34	0	35	9	22	0	0	0
3**	4.7% V_2O_5	99.5	38	1	40	1	19	1	0	0
4	1% Al_2O_3 + 1.5% BaO	99.5	27	0	12	7	36	6	6	6
5***	3.1% Al_2O_3 + 2.2% CaO + 0.7% K_2O	96	23	0	13	13	6	1	4	41
6	3.8% BaO + 4.5% V_2O_5	99.5	35	3	23	5	31	1	0	2
7	4.7% V_2O_5 + 1% Cu	99.5	18	0	32	2	40	1	7	0

Note: $T = 250°C$; $P_{H_2} = 0.7$ MPa; hydrogen VHSV is 10^3 h^{-1}; alcohol WHSV is 160–180 g h^{-1} kg$_{Cat}^{-1}$.

* The composition data refer to unreduced materials; the balance is magnetite.

** Commercial catalyst for ammonia synthesis (SA-1).

*** WHSV = 240 g h^{-1} kg$_{Cat}^{-1}$.

Reductive dehydration of cyclopentanol

$250°C$, $P_{H_2} = 0.7$ MPa, H_2 10^3 h^{-1}, 160–180 g h^{-1} kg^{-1}

35%   25%   13%   15%   2%

+ 10% alkanols and alkanones

UFRIC

OH

PFRIC (9%Al_2O_3)

34%   35%   9%   22%
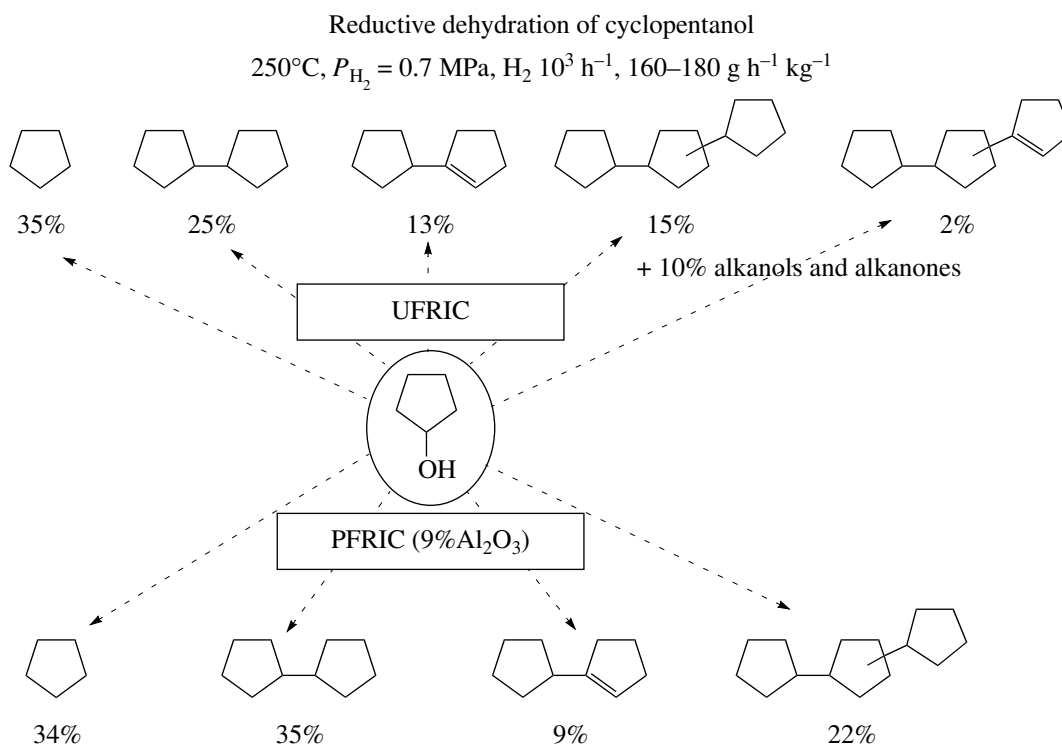
Scheme 1.

amounts of cycloalkanones are usually detected in the reaction product, it is likely that one of the routes from the alcohols to alkanes includes acid-catalyzed reactions involving cycloalkanones. Note that hydrocarbon formation from cycloalkanones in the presence of Ni/diatomaceous earth has also been reported in the literature [26].

Table 4. Results of the PFRIC-catalyzed synthesis of dicyclic and polycyclic hydrocarbons of the coupled-residue type from cyclopentanone and hydrogen

Experi-ment no.	PFRIC composition*, %	Ketone con-version, %	Selectivity with respect to main products, %					
			1	**3**	**4**	**5**	**7**	**8–11**
1	Unpromoted	99.5	18	7	6	6	5	48
2	9% Al_2O_3	99.5	30	35	8	22	0	13
3	4.7% V_2O_5	99.5	14	29	8	42	0	5
4	1% Al_2O_3 + 1.5 BaO	99.5	10	14	10	36	8	12
5**	3.8% BaO + 4.5% V_2O_5	99.5	19	30	5	33	0	13
6	3.1% Al_2O_3 + 2.2% CaO + 0.7% K_2O	98	18	7	6	6	5	48
7	4.7% V_2O_5 + 0.5% CuO	99.5	5	42	2	46	5	0
8	4.7% V_2O_5 + 1% CuO	99.5	7	35	3	50	4	1
9	4.7% V_2O_5 + 2% CuO	99.5	5	40	2	47	6	0
10	4.7% V_2O_5 + 2.5% CuO	99.5	6	3	4	48	6	0
11***	6% V_2O_5 + 2% CuO	99.5	5	41	2	46	6	0

Note: $T = 250°C$; $P_{H_2} = 0.8$ MPa; ketone WHSV is 160 g h^{-1} kg_{Cat}^{-1}.

  * The composition data refer to unreduced materials; the balance is magnetite.

 ** Commercial catalyst for ammonia synthesis (SA-1).

*** WHSV = 240 g h^{-1} kg_{Cat}^{-1}.

Table 5. Results of the PFRIC-catalyzed synthesis of dicyclic and tricyclic hydrocarbons of the coupled-residue type from cyclohexanone and hydrogen

Experiment no.	PFRIC composition*, %	T, °C	Ketone conversion, %	Selectivity with respect to main products**, %											
				12	13	14	15	16	17	18	19	20	21	22	23
1	4.7% V_2O_5	300	99.5	20	29	18	24	0	0	7	0	2	0	0	0
2	4.7% V_2O_5	350	99.5	25	34	9	19	5	3	5	0	0	0	0	0
3	4.7% V_2O_5 + 1% CuO	300	99.5	23	22	17	29	0	0	9	0	0	0	0	0
4	3.1% Al_2O_3 + 2.2% CaO + 0.7% K_2O	300	93	20	6	1	13	13	1	2	3	24	5	2	4

Note: P_{H_2} = 0.8–1 MPa; ketone WHSV is 160 g h^{-1} kg$_{Cat}^{-1}$.

  * The composition data refer to unreduced materials; the balance is magnetite.

  ** Product designation: **12**, cyclohexane; **13**, cyclohexene; **14**, benzene; **15**, cyclohexylcyclohexane; **16**, the same with one C=C bond; **17**, phenylcyclohexane; **18**, dicyclohexylcyclohexane; **19**, the same with one C=C bond; **20**, cyclohexanol; **21**, cyclohexylcyclohexanone; **22**, cyclohexylcyclohexanol; **23**, dicyclohexylcyclohexanone.

In view of this, we studied the reactions of cyclopentanone and cyclohexanone with hydrogen over PFRICs of varied composition under conditions optimal for the formation of a mixture of dicyclic and polycyclic hydrocarbons (Tables 4, 5).

The data presented in Table 4 suggest that using V_2O_5 and CuO as promoters somewhat raises the total yield of dicyclic, tricyclic, and tetracyclic hydrocarbons. Varying the proportions of these promoters has only a slight effect on the total yield of the reductive dehydration products. In the case of cyclohexanone, the total yield of the products whose molecules contain at least 12 carbon atoms—cyclohexylcyclohexane, dicyclohexylcyclohexane, cyclohexylcyclohexene, phenylcyclohexane, cyclohexylcyclohexanone, cyclohexylcyclohexanol, and dicyclohexylcyclohexanone—ranges between 30 and 60%, depending on the promoter (Table 5).

Furthermore, it is clear from the data listed in Table 3 that introducing Al_2O_3, an acidic promoter, into an unpromoted fused reduced iron catalyst (UFRIC) produces only a slight effect on the outcome of cyclopentanol conversion (see also Scheme 1).
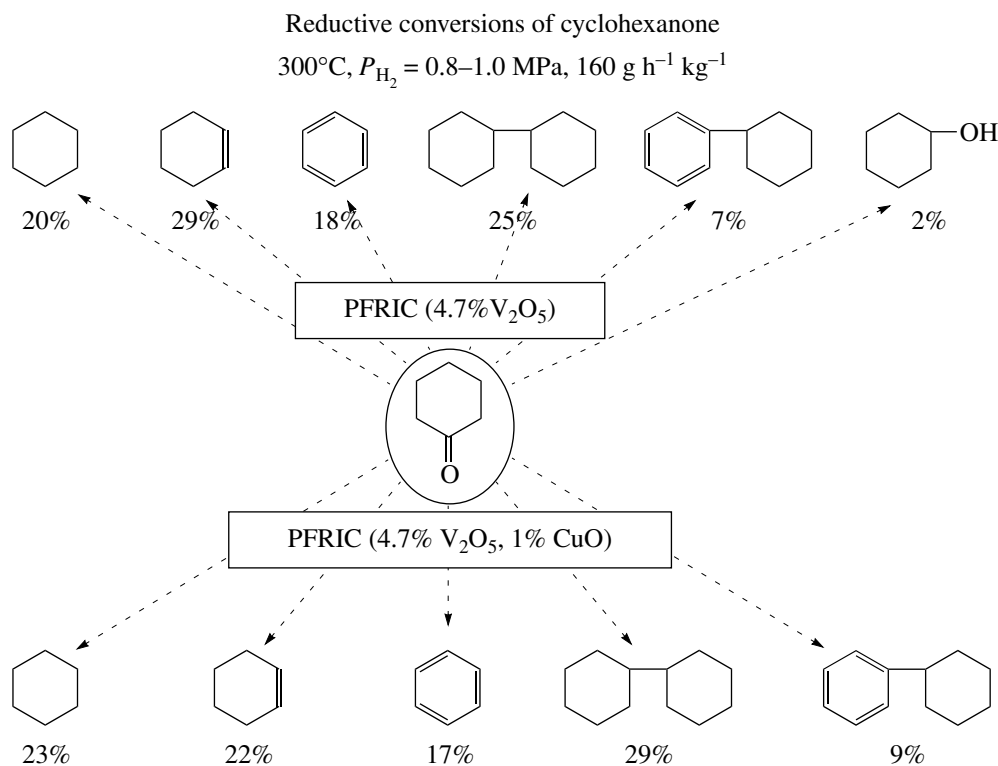

Reductive conversions of cyclohexanone

300°C, P_{H_2} = 0.8–1.0 MPa, 160 g h^{-1} kg^{-1}

Scheme 2.

Table 6. Results of the PFRIC-catalyzed conversion of benzaldehyde and related compounds in the presence of hydrogen (hydrogen VHSV, 10^3 h^{-1})

Experi- ment no.	Reactant, %	T, °C	Conver- sion, %	Reactant WHSV, g h^{-1} per liter of catalyst	Selectivity*, %							
					24	25	26	27	28	29	30	31
1	PhCHO	220	72	240	0	60	32	6	0.6	–	1	0.4
2	PhCHO	250	97	240	1.5	82	15	0.1	0.1	–	0.1	0.5
3	PhCH$_2$OH	250	96	520	0.1	57	29	0.1	0.5	12	–	0.8
4	(PhCH$_2$)$_2$O	220	38	120	0	93	5	0.1	0	1	0.1	–
5**	PhCHO	220	47	210	0	65	4	0.1	0	–	31	0
6	PhCH–CPh $\vert$ $\Vert$ OH O	220	95	90	0	0.1	97	0	2	0	0	0

* Product designation: **24**, PhH; **25**, PhCH$_3$; **26**, (PhCH$_2$)$_2$; **27**, PhCh=CHPh; **28**, PhCH$_2$CH(Ph)CH$_2$Ph; **29**, PhCHO; **30**, PhCH$_2$OH; **31**, (PhCH$_2$)$_2$O.

** Experiment involving D$_2$O.

Cyclohexanone conversion, like cyclopentanol conversion, does not depend strongly on the nature of the promoter (Scheme 2).

Analysis of the data listed in Tables 3–5 shows that, at a given catalyst composition, hydrocarbon yields do not change considerably in passing from cycloalkanols to cycloalkanones. This finding suggests that cycloalkanol conversion into dicycloalkanes or polycycloalkanes can proceed via alcohol dehydration to a ketone as an intermediate step. One can also assume, with equally good reason, that the cycloalkanone-to-hydrocarbon conversion proceeds via substrate reduction to cyclohexanol.

Benzyl Alcohol and Benzaldehyde

As distinct from cycloalkanone and cycloalkanol molecules, benzaldehyde and benzyl alcohol molecules do not have hydrogen atoms in the α-position with respect to the functional group. In view of this, these substrates cannot undergo aldol condensation or crotonization, unlike the cycloalkanones considered in the previous section. At the same time, benzaldehyde can be reduced in the presence of an iron catalyst [27, 28] and tungsten sulfide at 280–330°C, and a hydrogen pressure of 10 MPa.

In the presence of conventional metathesis catalysts (WCl$_6$/BuLi, WCl$_6$/LiAlH$_4$, WCl$_6$/sec-BuLi [29, 30]), benzaldehyde converts into cis- and trans-stilbenes, which are possible precursors of dibenzene. Unlike those catalytic systems, PFRIC does not catalyze olefin metathesis.

Experiments demonstrated that both benzaldehyde and benzyl alcohol in a hydrogen atmosphere at $P_{\text{H}_2} =$ 0.1 atm and 200–250°C, in the presence of PFRIC containing ~4.7% V$_2$O$_5$ as a promoter, gives products with coupled aralkyl residues. These products are dominated by 1,2-diphenylethane and contain some trans-stilbenes and even hexaphenylpropane (no cis-stilbenes were detected; see Table 6).

It is demonstrated by Scheme 3 that the product mixtures resulting from the benzaldehyde and benzyl alcohol conversions have similar percentage compositions.
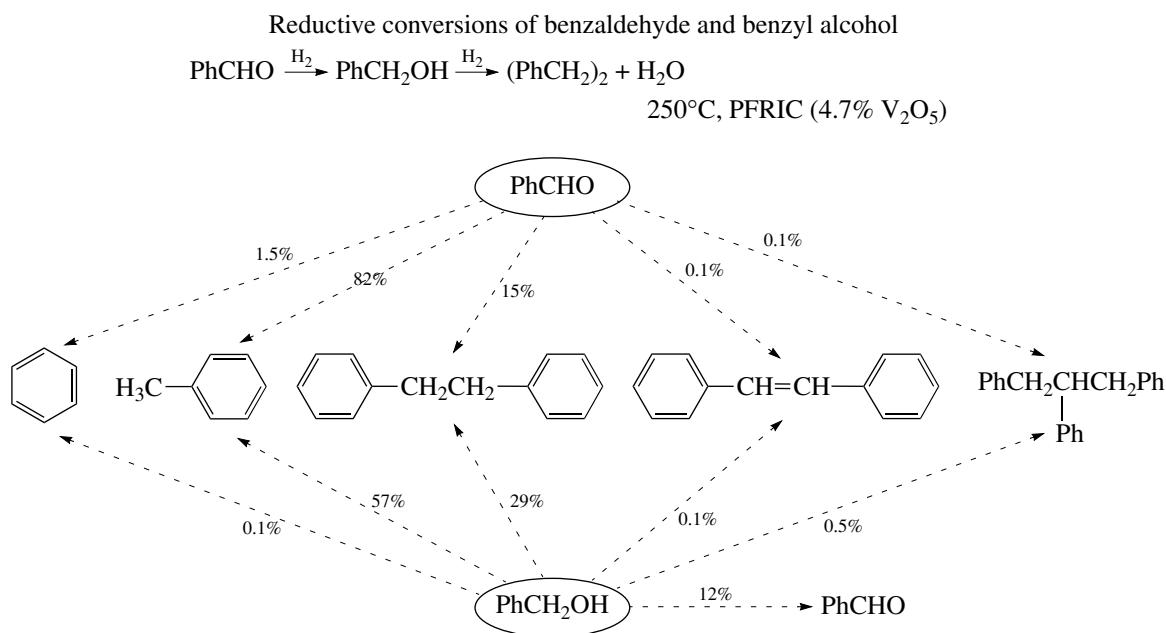
3-Methylbutanol-1

It follows from the above results that, apart from undergoing PFRIC-catalyzed reductive dehydration, cyclohexanols and benzyl alcohol convert into alkanes with the same carbon backbone:

$$C_nH_{2n-1}OH + H_2 \longrightarrow C_nH_{2n+2} + H_2O,$$
$$C_6H_5CH_2OH + H_2 \longrightarrow C_6H_5CH_3 + H_2O. \tag{IV}$$
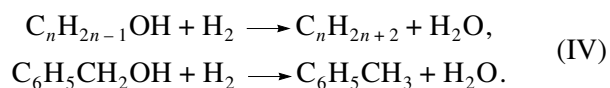
In the case of $C_nH_{2n+1}OH$ alkanols, alcohol reduction dominates under conditions as in the reductive dehydration of cycloalkanols. This reaction can be suppressed by using a composite catalyst containing the hydrided intermetallide [TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$]H$_{0.36}$ [24] apart from a small amount of Pt/γ-Al$_2$O$_3$, a well-known hydrogenation catalyst. The hydride serves as a catalyst and a source of hydrogen at the same time.

With the supported platinum catalyst, the yield of C_{10} isoalkanes does not exceed 2.5%. In the presence of [TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$]H$_{0.36}$ without Pt/γ-Al$_2$O$_3$, it is about 3.2%. With the Pt/γ-Al$_2$O$_3$ + [TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$]H$_{0.36}$ catalyst, it is above 10% (Table 7).

Reductive conversions of benzaldehyde and benzyl alcohol

$$PhCHO \xrightarrow{H_2} PhCH_2OH \xrightarrow{H_2} (PhCH_2)_2 + H_2O$$

250°C, PFRIC (4.7% V_2O_5)

Scheme 3.

The lowest yield of gaseous products, mainly C_5 alkanes, is observed with $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$. In the reactions catalyzed by $Pt/\gamma-Al_2O_3$ and the $Pt/\gamma-Al_2O_3$ + $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ mixture, the yield of gaseous products is higher by a factor of about 1.5. The yield of liquid products in the intermetallide catalyzed reaction is markedly higher than the yield in reactions catalyzed by the supported platinum and mixed catalysts.

The liquid fractions obtained with the intermetallide and mixed catalysts differ markedly in composition. Clearly, no less than 30% of the alcohol that does not undergo reduction by reaction (IV) is converted by the reductive dehydration mechanism, in which two alkyl radicals of the alcohol join to form 2,7-dimethyloctane:
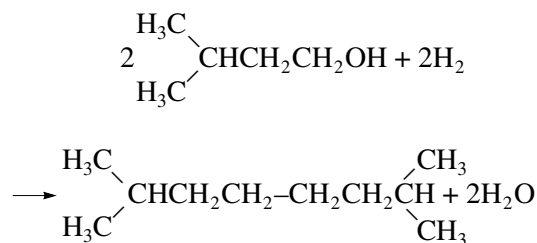
The main product, dimethyloctane, is accompanied by other isoalkanes, including methylpentanes, dimethylpentanes, dimethylhexanes, dimethylheptanes, and hexamethyldecanes. This is evidence of hydrocarbon cracking occurring as a side reaction under the rather severe conditions of the main reaction.

2-Methylpropanol-1

The hydrocarbon fraction resulting from 2-methylpropanol-1 conversion over the $Pt/\gamma-Al_2O_3$ + $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_{0.36}$ catalyst contains at least 60 wt % C_8 hydrocarbons. It is clear from the data presented in Tables 7 and 8 that the yield of gaseous products in this reaction is several times lower than that in isoamyl alcohol conversion. The yield of liquid products increases noticeably on passing from 3-methylbutanol-1 to 2-methylpropanol-1. The hydrocarbon fraction resulting from this reaction is dominated by products with coupled alkyl groups (Figs. 1, 2), as in the case of 3-methylbutanol-1.

Alkane formation in this system is accompanied by aromatization, as indicated by the presence of xylenes.

Ethanol. Alcohol conversion appeared to be sensitive to replacement of argon with CO_2. While argon
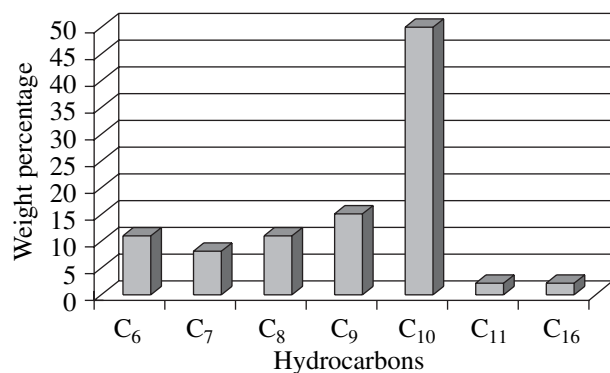
Fig. 1. Composition of the hydrocarbon fraction resulting from reductive dehydration of 3-methylbutanol-1 in argon in the presence of the $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ + Pt/Al_2O_3 catalyst.

Table 7. Results of 3-methylbutanol-1 conversion on various catalytic systems

Catalyst	$Pt/\gamma\text{-}Al_2O_3^a$	$TiFe_{0.95}Zr_{0.03}Mo_{0.02}^b$	$TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ + $Pt/\gamma\text{-}Al_2O_3^b$
Conversion, %	69.7	43.8	79.6
Yield of gaseous products per alcohol converted, wt %, including:	51.9	31.05	64.6
CO	0.1	–	10.7
CO_2	8.8	–	5.0
ΣC_1–C_5	43.0^c	31.05^d	48.8^e
Yield of liquid products per alcohol converted, wt %, including:	47.9	68.95	35.4
Hydrocarbons ($i + n$):			
C_6 (methylpentanes)	–	–	2.2
C_7 (dimethylpentanes)	–	–	1.7
C_8 (methylheptanes)	9.9	6.16	2.2
C_9 (methyloctanes)	1.5	–	3.1
C_{10} (dimethyloctanes)	2.5	3.2	10.2^f
C_{11} (methyldecanes)	–	–	0.5
C_{16} (tetramethyldecanes)	–	–	0.5
Oxygen-containing compounds:			
C_5 (dimethylpropanal)	12.3	–	–
C_5 (3-methylbutanal)	–	31.12	–
C_5 (methylbutanal)	–	–	1.4
R–O–R (diisoamyl ether)	1.0	7.77	0.5
R–COO–R (isoamyl valerate)	6.3	7.4	1.9
Unidentified condensation products	8.5	6.04	6.6
Water	5.9	7.26	4.7

Note: T = 350°C; P = 50 atm; alcohol WHSV, 0.3–0.6 h^{-1}.
[a] Ar : H^2 = 1 : 1 atmosphere.
[b] Ar atmosphere.
[c] C_5 = 85%. [d] C_5 = 86.5%.
[e] C_5 = 75%.
[f] Up to 65% 2,5-dimethyloctane.

apparently acts only to raise the alcohol coverage of the catalyst surface under the reaction conditions (50 atm, 350°C), the role of carbon dioxide is likely to be more complex. The composite catalyst can reduce CO_2 to CO [21].

Carbon monoxide resulting from this reaction may not only affect the properties of the active centers but also react with the alcohol or reaction intermediates. This is indicated by the fact that the reaction products obtained in CO_2 and Ar atmospheres differ in composition (Table 9).

DISCUSSION

Expected primary products of alcohol conversions in the presence of metal catalysts are aldehydes and

Table 8. Results of 2-methylpropanol-1 conversion in an argon atmosphere in the presence of the $TiFe_{0.095}Zr_{0.03}Mo_{0.02}$ + Pt/γ-Al_2O_3 catalyst

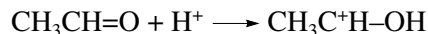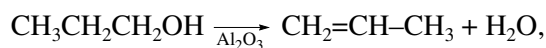|	
2-Methylpropanol-1 conversion, %	67
Yield of gaseous products per alcohol converted, wt %,	12
including:	
CO_2	4.3
ΣC_1–C_4	7.7
Yield of liquid products per alcohol converted, wt %,	88
including:	
Hydrocarbons (*i*- + *n*-):	
C_7 (dimethylpentanes)	5.8
C_8 (methylheptanes)	38.5*
C_{10} (dimethyloctanes)	3.3
C_{17} (heptamethyldecanes)	6.3
C_{18} (octamethyldecanes)	4.1
Arenes:	
xylenes	3.7
Oxygen-containing compounds:	
C_4 (2-methylpropanal)	6.5
R–COO–R (isobutyl isobutyrrate)	0.5
Unidentified condensation products	4
Water	11.8

Note: T = 350°C; alcohol WHSV, 0.3–0.6 h^{-1}.
* Up to 73% 2,5-dimethylhexane.

ketones, which result from alcohol dehydrogenation. As is noted above, rough estimation shows that up to 10% of the alcohol can be dehydrogenated to a carbonyl compound even at P_{H_2} = 1 MPa. The acid centers
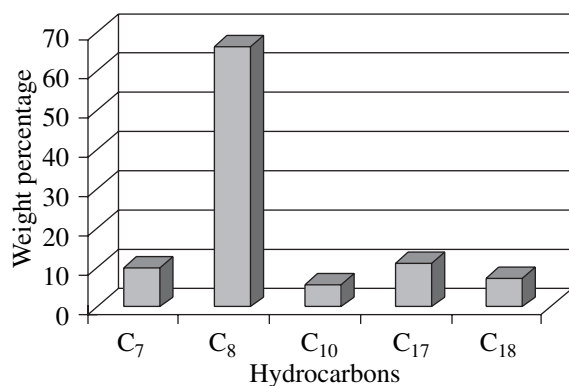
Fig. 2. Makeup of the C_{6+} hydrocarbon fraction resulting from reductive dehydration of 2-methylpropanol-1 in argon in the presence of the $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ + Pt/Al_2O_3 catalyst.

of the catalyst can cause a crotonization-like condensation of the resulting ketones and aldehydes. It is possible that the Ostromyslenskii reaction (I) [5] proceeds via alcohol dehydration followed by the reaction between the resulting olefin and the protonated aldehyde:

$$CH_3CH_2CH_2OH \xrightarrow{Al_2O_3} CH_2=CH–CH_3 + H_2O,$$

$$CH_3CH=O + H^+ \longrightarrow CH_3C^+H–OH$$

$$\xrightarrow{CH_3CH=CH_2} CH_3C^+H–CH_2–CHOH–CH_3,$$

$$CH_3C^+H–CH_2–CHOH–CH_3$$

$$\xrightarrow{-H^+, -H_2O} CH_3CH=CH–CH=CH_2$$
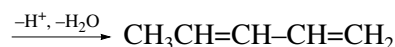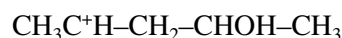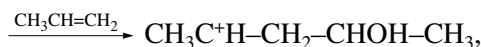
Likewise, cyclohexanol might be expected to form a enol, enone, diene, etc., as intermediates by reactions like
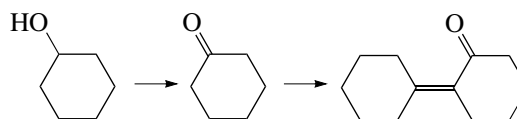
The hydrogenolysis of all these intermediates would eventually yield dicyclohexyl. This mechanism could explain the formation of the variety of hydrocarbons we detected in the reaction product. It is this mechanism that was suggested for dicyclohexyl formation from cyclohexanone in the presence of an Ni/diatomaceous earth catalyst at 250–300°C and atmospheric pressure [26]. The acidic support used in our experiments could accelerate cyclohexanone condensation into a enone. However, this hypothesis is disproved by the following facts:

(1) The amount of acidic promoters in the cycloalkanol and cyclohexanone conversions was small. Moreover, introducing basic components (BaO, CaO, K_2O), which reduced the acidity of the catalyst, exerted no significant effect on the activity of the catalyst (Table 4, experiment 6; Table 5, experiment 4).

(2) Although aldol condensation is impossible for benzaldehyde, the conversion products of benzaldehyde and benzyl alcohol contain considerable amounts of 1,2-diphenylethane (Table 6, experiments 1–3). The presence of this compound could be explained by the intermediate formation of benzoin, which can almost stoichiometrically reduce to 1,2-diphenylethane under conditions still milder than those required for benzaldehyde or benzyl alcohol (Table 6, experiment 6). However, benzoin condensation is possible only in the presence of a strong base such as CN^- or a carbanion [30]. The catalysts examined apparently have no such anionic centers. Mechanisms assuming that the same catalyst may act as either a strong acid or a strong base seem quite unlikely.
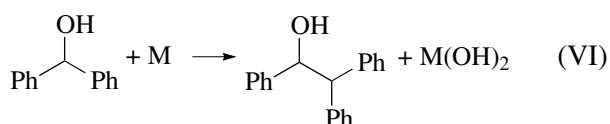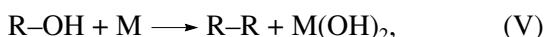
(3) In the case of 2-methylpropanol-1, acid-catalyzed aldehyde condensation would be expected to yield 2,2,4-trimethylpentane, which is thermodynamically very stable. In fact, the C_8 fraction resulting from

2- methylpropanol-1 conversion is dominated by dimethylhexanes.

The above facts are difficult to reconcile with mechanisms which assume the domination of alcohol dehydration and the conversion of carbonyl compounds under the action of the catalysts as strong acids or strong bases.

There are stoichiometric reactions between an alcohol and a compound of low-valence Ti or Nb that couple two alkyl residues together [31].

Likewise, lanthanum metal in the presence of trimethylchlorosilane and catalytic amounts of iodine reacts with aliphatic alcohols and arylalkanols [32]:

$$R\text{–}OH + M \longrightarrow R\text{–}R + M(OH)_2, \qquad (V)$$

$$\underset{Ph \quad Ph}{\overset{OH}{|}} + M \longrightarrow \underset{Ph \quad \underset{Ph}{|}}{\overset{OH}{|}} Ph + M(OH)_2 \qquad (VI)$$

One would assume that the metal catalyst in our experiments serves as a one-electron reducer regenerable by oxygen. However, to make an ultimate conclusion as to this reaction mechanism, it is necessary to collect additional data for the reaction kinetics and for the rates of the hypothetical steps, including oxide and hydroxide reduction in the reductive dehydration of cycloalkanols and other alcohols. Furthermore, the formation of products composed of three or four alkyl residues, as is the case with ethanol, is hardly describable in terms of a scheme including reactions (IV) and (V).

Another mechanism is possible for the conversion of alcohols into hydrocarbons. In its first step, the alcohol or the carbonyl compound would undergo oxidative addition to the M–M bond. The process involving an alcohol would give an intermediate with neighboring alkyl and hydroxyl groups:

$$M\text{–}M + R\text{–}CH_2\text{–}OH \longrightarrow \underset{M \cdots\cdots M}{\overset{CH_2R \quad OH}{|\qquad\ |}}$$
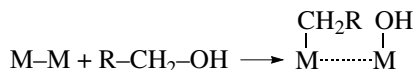
Note that the alkyl derivative of the metal (M–CH$_2$–R) may participate in the reduction of the alcohol to an alkane with the same number of carbon atoms—a side reaction.

The reductive elimination of two R–CH$_2$– groups would result in R–CH$_2$–CH$_2$–R. However, for completion of the catalytic cycle, it would be necessary to reduce, with hydrogen, the MOH groups that would have formed on the catalyst surface. As is noted above, the assumption of the reduction of iron and titanium hydroxides and other catalyst components needs kinetic confirmation.

Table 9. Results of ethanol conversion on the TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$ + Pt/γ-Al$_2$O$_3$ catalyst

	Ar	CO$_2$
Ethanol conversion, %	87.3	84
Yield of gaseous products per alcohol converted, wt %, including:	18.6	20.1
CO	3.4	5
CO$_2$	2.3	5.2
ΣC$_1$–C$_4$	12.9	9.9
Yield of liquid products, wt %, including:	81.4	79.9
Hydrocarbons (*i*- + *n*-):		
C$_5$ (pentanes)	3.4	–
C$_6$ (hexane, hexenes, methylpentenes)	–	22.3*
C$_7$ (heptane, heptenes, methylhexenes)	8	3**
C$_8$ (methylheptenes, octane, octenes)	–	8*
C$_9$ (methyloctane, nonane)	–	4
C$_{10}$ (dimethyloctanes)	21.6***	–
C$_{10-11}$ (methyldecanes, undecene)	–	5
C$_{22}$ (dimethyleicosane)	4.6	–
C$_{6-7}$ (cyclohexane, methylcyclohexane)	–	3
alkylbenzenes	4.6	3
Oxygen-containing compounds:		
Et$_2$O		3.3
EtOAc	7.2	1.7
diethoxyethane	2.3	1.6
methylbtanone	–	–
ethoxybutane	1.7	4
hexyl acetate	3.4	–
ethyl isobutyrate	4.6	–
heptanone	1.2	–
hexanal	3.6	0.4
ethylbutyric acid	–	1.5
methyl propionate	–	1.7
ethyl hexanoate	–	1.5
dimethyl hexanoate	–	1.7
nonanone	–	0.2
Unidentified products	1.4	2
Water	13.8	12

Note: T = 350°C; P = 50 atm; alcohol WHSV, 0.3–0.6 h^{-1}.

   * Up to 50% branched hydrocarbons.

  ** Up to 40% branched hydrocarbons.

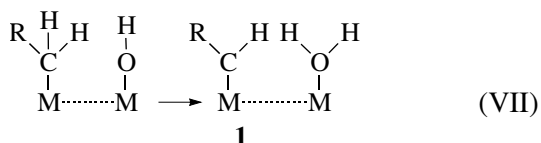*** Up to 90% branched hydrocarbons.

Table 10. Thermodynamics of free methylene formation*

$$CH_{4(g)} \longrightarrow CH_{2(g)} + H_{2(g)}$$

$\Delta H^0_{298} = 111.28$ kcal/mol

$\Delta G^0_{298} = 101.4$ kcal/mol

$$CH_3F_{(g)} \longrightarrow CH_{2(g)} + HF_{(g)}$$

$\Delta H^0_{298} = 87.7$ kcal/mol

$\Delta G^0_{298} = 79.52$ kcal/mol

$$CH_3OH_{(g)} \longrightarrow CH_{2(g)} + H_2O_{(g)}$$

$\Delta H^0_{298} = 83.65$ kcal/mol

$\Delta G^0_{298} = 73.39$ kcal/mol

$$CO_{(g)} + 2H_{2(g)} \longrightarrow CH_{2(g)} + H_2O_{(g)}$$

$\Delta H^0_{298} = 62.02$ kcal/mol

$\Delta G^0_{298} = 66.2$ kcal/mol

$$1/2C_2H_{4(g)} \longrightarrow CH_{2(g)}$$

$\Delta H^0_{298} = 80.85$ kcal/mol

$\Delta G^0_{298} = 74.77$ kcal/mol

* Estimated from data presented in [34, 35].

It is not impossible that the alkyl R–CH$_2$ is capable of donating one of the hydrogen atoms of its CH$_2$ group to a neighboring hydroxyl:

$$
\begin{matrix}
R & H & H & H & & R & H & H & H \\
 & \backslash | & & / & & & \backslash & & / \\
 & C & & O & \longrightarrow & & C & & O \\
 & | & & | & & & & & \\
 & M \cdots\cdots M & & & & M \cdots\cdots M & & \\
\end{matrix}
\qquad \text{(VII)}
$$

1

The carbene complex **1** forming in this step could be a source of both hydrocarbons with the same number of carbon atoms as in the original alcohol R–CH$_3$ and alkanes with a larger number of carbon atoms. The hypothesis of the formation of carbenes as hydrates, adducts with dimethyl ether, etc., was put forward by Olah and Molnar [31] to explain the mechanism of

reaction (II). Scheme (VI) was suggested to explain the formation of *trans*-stilbene by the reaction between benzyl alcohol and a Pd/Mo cluster [33]. Thermodynamic analysis using data from Table 10 demonstrates that the Gibbs energy of formation of free methylene in methanol decomposition is comparable with that in synthesis gas conversion and is somewhat lower than that in ethylene dissociation (Table 10) [34, 35].

Simultaneous acid–base (aldol condensation) and redox (hydrogenation and dehydrogenation) reactions are conventionally considered to explain the Guerber reaction, which takes place at 150–220°C in the liquid phase (solutions of NaOCH$_3$, a strong base, in absolute alcohols) in the presence of Raney copper or a kindred catalyst [8, 9]. Obviously [8], such strong bases make
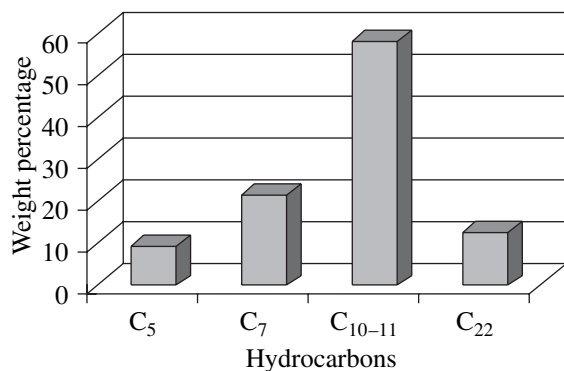
Fig. 3. Makeup of the C$_{4+}$ hydrocarbon fraction resulting from reductive dehydration of ethanol in argon in the presence of the TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$ + Pt/Al$_2$O$_3$ catalyst.
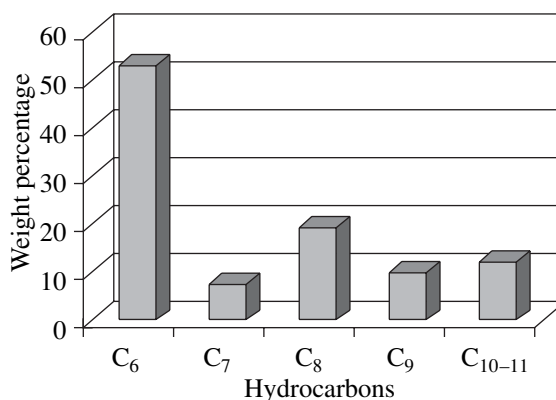
Fig. 4. Makeup of the C$_{5+}$ hydrocarbon fraction resulting from reductive dehydration of ethanol in CO$_2$ in the presence of the TiFe$_{0.95}$Zr$_{0.03}$Mo$_{0.02}$ + Pt/Al$_2$O$_3$ catalyst.

very probable the aldol condensation of the aldehydes that have resulted from alcohol dehydrogenation.

However, it was found that adding propanal to a methanol–propanol mixture lowers the isobutanol yield.

Another fact in conflict with the conventional mechanism of the Guerber reaction is the very high isobutanol formation selectivity of this reaction. The intermediate formation of propanol and the cross-condensation of this alcohol with formaldehyde would lead to 2-methyl-3-hydroxypropanal and, eventually, 2-methylpropanediol. In fact, neither these products nor formaldehyde is likely to form.

One enigmatic aspect of the Guerber reaction is the appearance of a methyl group at the β-carbon in the case of a long-chain alcohol.

To account for this fact, Carlini *et. al.* [8] have assumed that coordinated methylene ligands take part in this reaction as intermediates.

Clearly, under experimental conditions, including high temperatures above 250°C, all of the mechanisms examined can compete and, moreover, a variety of side reactions, for example, hydrocarbon cracking and isomerization, can take place.

Note that the $Pt/\gamma\text{-}Al_2O_3$ + hydrided intermetallide catalyst is capable of effecting a number of other unusual reactions. The conversion products of not only ethanol but also its higher homologues contain esters and acids (Tables 7–9), whose formation in a reductive atmosphere is rather surprising.

CONCLUSION

This paper presents the first report on the conversion of cycloalkanols and methanol homologues into alkanes. Apart from being of theoretical importance, this reaction is expected to find application as a route from renewable natural resources and alkanes (including motor fuel components), considering that alcohols result from the fermentation of any kind of biomass. At present, we are working at improving the catalytic systems and gaining a deeper insight into the mechanism of catalysis.

ACKNOWLEDGMENTS

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