Catalytic activity of the VIII Group metals in the hydrogenation and isomerization of α- and β-pinenes

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The kinetic regularities of the liquid-phase hydrogenation and isomerization of α- and β-pinenes over the Pd/C, Ru/C, Rh/C, Pt/C, and Ir/C catalysts were studied at temperatures ranging from 20 to 100 °C and at hydrogen pressures of 1—11 bar using *n*-octane as the solvent. The hydrogenation and isomerization of α- and β-pinenes occur simultaneously on the Ru/C, Rh/C, Pt/C, and Ir/C catalysts, and the reaction mixture contains the products of double bond hydrogenation, *viz.*, *cis*- and *trans*-pinanes. The Ru, Rh, and Pd metals have a higher catalytic activity in β-pinene isomerization than Ir and Pt. Among the VIII Group metals studied, the Pd-based catalyst has the highest catalytic activity in double bond isomerization of α- and β-pinenes. The general scheme of the mechanism of hydrogenation and isomerization of α- and β-pinenes on the Pd/C catalyst was proposed.

Key words: catalysts: Pd/C, Ru/C, Rh/C, Pt/C, Ir/C, β-pinene, α-pinene, isomerization, hydrogenation, *cis*-pinane, *trans*-pinane.

Pinene represents cheap and renewable feedstock for the synthesis of wide varieties of valuable chemicals: fragrances, vitamins, and pharmaceuticals. The major component of gum turpentine oil is α-pinene (~65%), and the β-pinene content usually does not exceeds 5%. At the same time, β-pinene is a valuable source for the fine organic synthesis. The most part of the produced β-pinene is transformed into nopol[1] (2-(2-hydroxyethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene) and polymeric resins.[2] Pyrolysis of β-pinene gives myrcene, which is an important intermediate for the synthesis of vitamins[3] A and E and some flavors and fragrances,[4,5] such as D-citronellol and L-menthol.

High demand for β-pinene cannot be provided by turpentine oil rectification and, therefore, large amounts of β-pinene are produced by the catalytic conversion of α-pinene (Scheme 1).

Various chemical methods for the synthesis of β-pinene from α-pinene are described in literature. In the presence of alkali metal hydrides, boranes, and organometallic compounds, the yields of β-pinene are 25%,[6] 50%,[7,8] and 92%,[9] respectively.

However, the chemical methods of α-pinene conversion into β-pinene have serious disadvantages: the multistep technology using expensive reagents and explosive compounds (boranes and organometallic compounds).

The main approach of the known catalytic methods is the formation of an equilibrium mixture of α- and β-pinenes during α-pinene isomerization followed by β-pinene separation on a high-efficient rectification column.[10] There are many various methods of α-pinene to β-pinene conversion described in literature including both the homogeneous acidic[11] and basic catalysts[12,13] and the heterogeneous alkali metal oxides,[14—17] as well as the metallic catalysts.[18,19]

The most promising and ecologically safe method seems to be α-pinene isomerization over heterogeneous catalysts based on Group VIII metals in the presence of hydrogen. However, several concurrent processes can take place under the catalytic isomerization conditions: α-pinene double bond isomerization to an equilibrium mixture of α- and β-pinenes, α-/β-pinene hydrogenation to *cis*- and *trans*-pinanes, hydrogenolysis of the four-membered pinene cycle to *p*-menthadienes, and dehydrogenation of α- and β-pinenes to *o*- and *p*-cymenes (see Scheme 1). The appearance of the corresponding by-products can considerably decrease the selectivity of β-pinene formation. The intensity of by-product formation depends on the nature of the catalyst active metal (Pd, Pt, Ru, Rh, Ir) and reaction conditions.

The aim of the present work is the study of the kinetic regularities of hydrogenation and isomerization of α- and β-pinenes on the Pd/C, Ru/C, Rh/C, Pt/C, and Ir/C catalysts.

Experimental

In the present work, a mixture of α- and β-pinenes obtained by the vacuum rectification of gum turpentine oil. The composition of the initial mixture is as follows: 80.1—97.6 mol.% of

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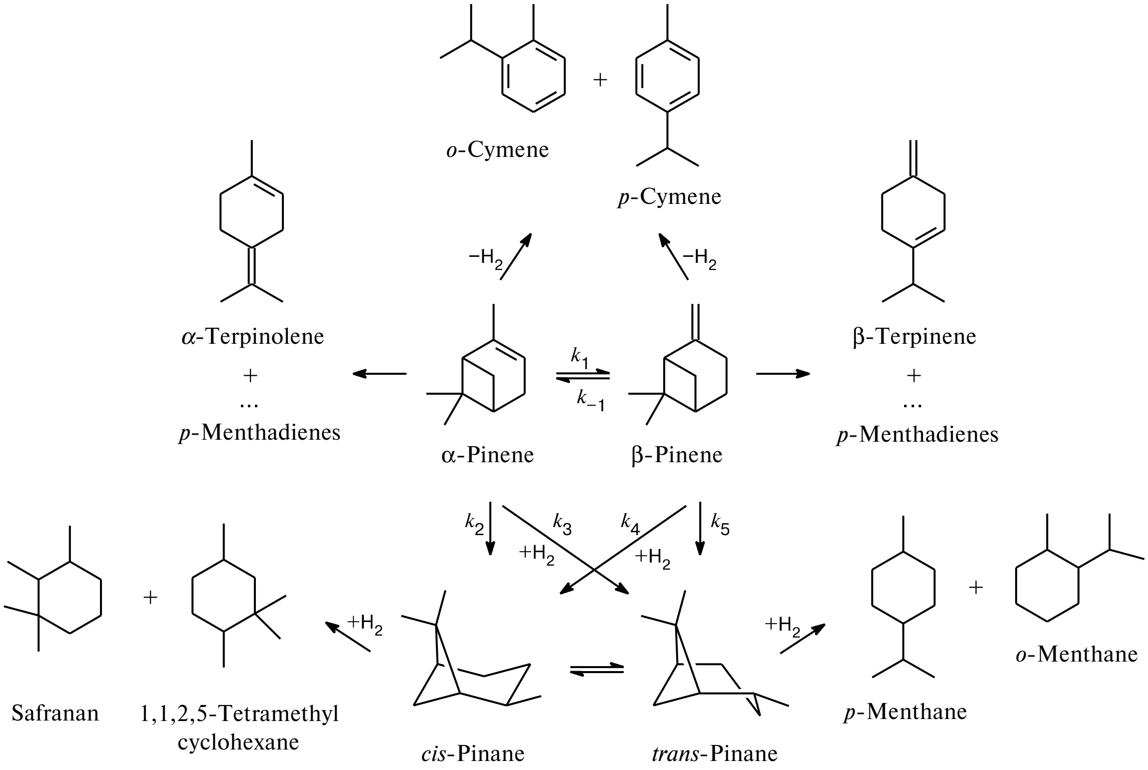
Scheme 1



α- and β-pinenes, 4.2—13.5 mol.% Δ^3-carene (4,7,7-trimethylbicyclo[4.1.0]hept-3-ene), and low-boiling admixtures as the rest. The solvent was *n*-octane (Reakhim, Ural Chemicals Base, pure grade, technical conditions TU 6-09-3748-74).

The powdered carbon support Sibunit with the following texture characteristics was used:

S_{sp}/m^2 g^{-1} (based on Ar adsorption)	480
V_{pore}/cm^3 g^{-1} (based on moisture content)	0.7
D_{pore}/nm (based on N_2 adsorption)	30—35

Sibunit was preliminarily activated by the treatment with a 5% solution of HNO_3 at 100 °C for 4 h to change the composition and amount of oxygen-containing groups on the carbon material surface. The supported catalysts 0.9% Rh/C, 1.5% Ru/C, 1.0% Pt/C, 1.0% Pd/C, 4.0% Pd/C, and 1.0% Ir/C were prepared by the precipitation of the corresponding metal hydroxide on the carbon support according to previously described procedures.[20,21] The active component of the catalyst was reduced to the metal in a hydrogen flow at 90 °C for 3 h.

The pellet size of the Pd/C, Rh/C, Ru/C, Pt/C, and Ir/C catalysts was determined on a COULTER—COUNTER instrument (TA).

The chemical analysis of the active metal content was carried out by X-ray fluorescence spectrometry on a VRA-30 analyzer with the Cr anode in the X-ray tube.

Transmission electron microscopy (TEM) and high-resolution TEM were used to obtain information on the morphology and microstructure of the catalyst samples. The TEM data were obtained on JEM-100CX (JEOL, Japan, resolution at lines of 4.5 Å) and JEM2010 electron microscopes with the resolution at lines of 0.14 nm and an accelerating voltage of 200 kV.

A mixture of α- and β-pinenes was hydrogenated and isomerized in a stainless steel autoclave (0.15 L) equipped with an electromagnetic stirrer (800—1000 rpm), systems for gas preparation and dosage, a Sapfir-22M electric system of pressure conversion, and a system for sampling *in situ*. The kinetic features of isomerization and hydrogenation of a mixture of α- and β-pinenes were studied in the temperature region from 20 to 100 °C and a hydrogen pressure interval of 0.5—11.0 bar using *n*-octane as the solvent. The catalyst charge was varied in experiments from 5 to 75 mg. Prior to the reaction, the catalyst was activated with hydrogen at $p(H_2)$ = 4 bar and 90 °C for 1 h.

The conversion of β-pinene (K_β) was calculated by the formula

$$K_\beta = \frac{C_\beta(0) - C_\beta(t)}{C_\beta(0)} \cdot 100\%, \qquad (1)$$

where $C_\beta(0)$ corresponds to the initial concentration of β-pinene, and $C_\beta(t)$ is the current β-pinene concentration during time t.

The total yield of *cis*- and *trans*-pinanes (Y_{pinane}) was determined by the equation

$$Y_{pinane} = \frac{C_{cis}(t) + C_{trans}(t)}{C_\alpha(0) + C_\beta(0)} \cdot 100\%, \qquad (2)$$

where $C_{cis}(t)$ and $C_{trans}(t)$ are the current concentrations of *cis*- and *trans*-pinane in the reaction mixture; $C_\alpha(0)$ and $C_\beta(0)$ are the initial concentrations of α- and β-pinene in the initial mixture, respectively.

For the characterization of the catalyst activity, the initial rate of β-pinene transformation (W_i) was calculated by the linear regression as the slope ratio of the kinetic curve of the β-pinene concentration to the time axis.

The prepared samples of the reaction mixture were analyzed by GLC on a quartz capillary column (50 m×0.25 mm) with the Carbowax-20M phase. The elution time of the main components on the chromatograph at T = 120 °C: 16 min 10 s (α-pinene), 18 min 7 s (β-pinene), 17 min 45 s (*trans*-pinane), 18 min 20 s (*cis*-pinane), 17 min 33 s (α-terpinolene), and 19 min 32 s (Δ^3-carene).

The reaction products were identified by MS-LC on a VG-7070 instrument (quartz capillary column (30 m×0.2 mm) with the Silicone SE-30 phase).

Results and Discussion

Study of the catalyst structure. To study the effect of the metal nature on the catalytic activity in the hydrogenation and isomerization of a mixture of α- and β-pinenes, we prepared the catalyst samples on the carbon support Sibunite containing various Platinum Group metals. According to the granulometric analysis data, the carbon support has a narrow particle size distribution (5—50 μm) with a predominant particle size of 45 μm. To determine whether the reaction occurs in the internal-diffusion or kinetic regime, we prepared the catalyst samples with the particle size <1 μm, whose mean particle size was 0.1 μm. It was shown that with a decrease in the particle size of the 4% Pd/C catalyst by ~10^2 times the initial rate of β-pinene transformation increases insignificantly from 2.15 to 3.79 mol (L g s)$^{-1}$ at the temperature 30 °C and under a hydrogen pressure of 11 bar. These data indicate that under the experimental conditions the hydrogenation and isomerization of a mixture of α- and β-pinenes occur in the kinetic region, which allows the correct determination of the kinetic parameters to be performed on the basis of the obtained experimental data.

According to the transmission electron microscopy data, the Sibunite surface of all supported catalysts contains uniformly distributed metal particles ~2 nm in size regardless of the active metal (Pd, Pt, Rh, Ir, Ru). With an increase in the palladium amount from 1 to 4 wt.%, the mean particle size of the supported metal increases to 3.5 nm, whereas a uniform distribution of the metal on the support surface is retained. It is most likely that the metal particles in the catalysts obtained are easily accessible to reactant molecules, and the mass transfer processes should not impede pinene isomerization and hydrogenation.

Kinetic regularities of isomerization and hydrogenation of α- and β-pinenes. The hydrogenation and isomerization of α- and β-pinenes were carried out in the temperature range 25 to 100 °C and at hydrogen pressures of 0.5—11.0 bar on the Pd/C, Ru/C, Rh/C, Pt/C, and Ir/C catalysts using *n*-octane as the solvent. To determine the kinetic regularities of the reversible isomerization of β-pinene into α-pinene, we chose a mixture containing α- and β-pinene in the ratio α : β = 35.0 : 65.0, which differed from the thermodynamically equilibrium composition. According to published data,[22] the thermodynamically equilibrium composition at 20 °C corresponds to the isomer ratio α : β = 99.1 : 0.9. The typical curves of the reaction product composition as a function of the reaction time are shown in Fig. 1 for the Ir/C catalyst at 60 °C and under a hydrogen pressure of 6.3 bar. According to the chromatographic data, on the 1% Ir/C, 1.5% Ru/C, 0.9% Rh/C, and 1% Pt/C catalysts a mixture of α- and β-pinenes is simultaneously isomerized and hydrogenated to form *cis*- and *trans*-pinanes. No formation of by-products of the four-membered pinane cycle opening was observed. The total yield of *cis*- and *trans*-pinanes increases with an increase in the β-pinene conversion (Fig. 2). The different patterns of dependence of the com-

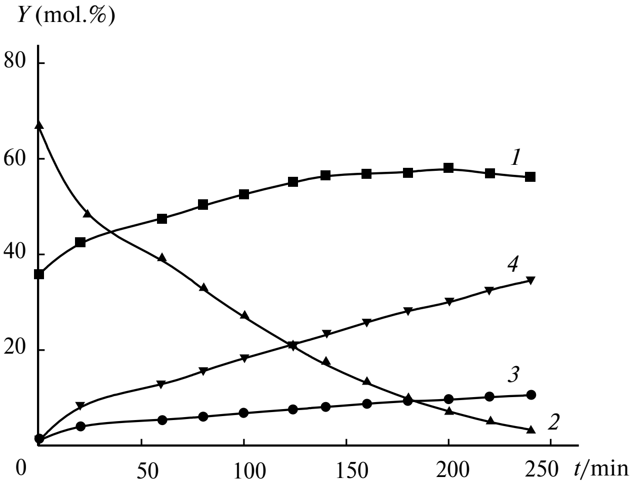


Fig. 1. Kinetic curves of isomerization and hydrogenation of a mixture of α- and β-pinenes on the 1% Ir/C catalyst: α-pinene (*1*), β-pinene (*2*), *trans*-pinane (*3*), *cis*-pinane (*4*). *Y* is the content of the products. Reaction conditions: $p(H_2)$ = 6.3 bar, T = 60 °C, [α-pinene+β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 40 mg.

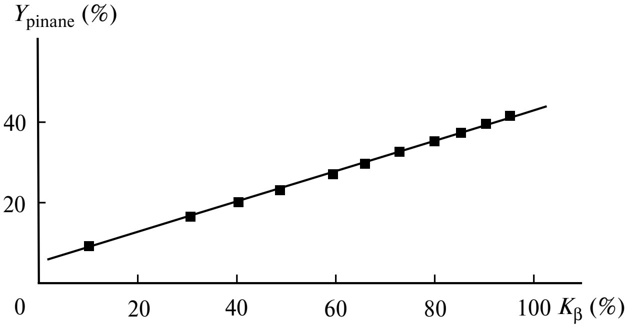


Fig. 2. Dependence of the total yield of *cis*- and *trans*-pinane (*Y*) on the β-pinene conversion ($C_β$) on the 1% Ir/C catalyst. Reaction conditions: $p(H_2)$ = 6.3 bar, T = 60 °C, [α-pinene + + β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 40 mg.

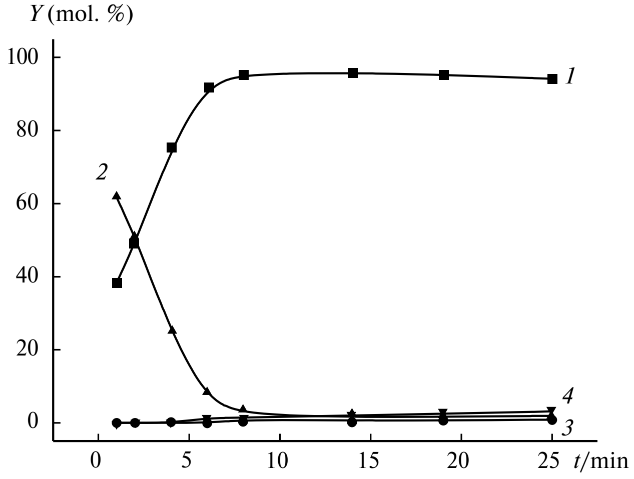


Fig. 3. Kinetic curves of isomerization and hydrogenation of a mixture of α- and β-pinenes on the 4% Pd/C catalyst: α-pinene (*1*), β-pinene (*2*), *trans*-pinane (*3*), and *cis*-pinane (*4*). Reaction conditions: $p(H_2)$ = 11 bar, T = 30 °C, [α-pinene + + β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 10 mg.

position of hydroisomerization of a mixture of α- and β-pinenes on the reaction time were obtained for the 4% Pd/C catalyst (Fig. 3). It was found that only the isomerization of α- and β-pinenes took place before the β-pinene conversion of ~95% was achieved. The isomerization gives a mixture of α- and β-pinenes with the composition close to the thermodynamically equilibrium mixture, and no hydrogenation products are observed. According to the published data,[23] the Gibbs energy of α-pinene is lower than that of β-pinene, whose cyclic system with the exocyclic double bond is highly strained due to the loss of one degree of freedom of internal rotation of the methyl group. A small difference in the Gibbs energy between two isomers favors the transformation of β-pinene into α-pinene, which agrees with the obtained experimental data.

The dependence of β-pinene isomerization to α-pinene on the β-pinene concentration on the Pd/C catalyst in the logarithmic coordinates is linear, and the slope ratio of this straight line is unity and in accord with the first-order reaction with respect to the β-pinene concentration.

The isomerization of α-pinene on the 4% Pd/C catalyst (m = 5 mg) at 100 °C and under a hydrogen pressure of 11 bar affords β-pinene in a yield of 2.86±0.14 mol.%, and no hydrogenation products are observed. The obtained value for the β-pinene yield is comparable with the published data[10] for the formation of β-pinene by α-pinene isomerization on the Pd/α-Al_2O_3 catalyst under a hydrogen atmosphere. Thus, the Pd/C catalyst is a promising system for the synthesis of β-pinene by α-pinene isomerization under a hydrogen pressure.

For the description of the concentration profiles of the components that are present in the reaction we proposed the simple kinetic model (the reaction rate constants are given in Scheme 1) based on the assumption that the isomerization and hydrogenation of a mixture of α- and β-pinenes on the Platinum Group metals to *cis*- and *trans*-pinanes took place concurrently.

The system of kinetic equations in the proposed model has the form

$$\frac{dC_\alpha(t)}{dt} = -[k_1 C_{H_2}^{n_{iso}}(t) + k_2 C_{H_2}^{n_{hydr}}(t) + k_3 C_{H_2}^{n_{hydr}}(t)]C_\alpha(t) + k_{-1} C_{H_2}^{n_{iso}}(t) C_\beta(t), \tag{3}$$

$$\frac{dC_\beta(t)}{dt} = -[k_{-1} C_{H_2}^{n_{iso}}(t) + k_4 C_{H_2}^{n_{hydr}}(t) + k_5 C_{H_2}^{n_{hydr}}(t)]C_\beta(t) + k_1 C_{H_2}^{n_{iso}}(t) C_\alpha(t), \tag{4}$$

$$\frac{dC_{cis}(t)}{dt} = [k_2 C_\alpha(t) + k_4 C_\beta(t)] C_{H_2}^{n_{hydr}}(t), \tag{5}$$

$$\frac{dC_{trans}(t)}{dt} = [k_3 C_\alpha(t) + k_5 C_\beta(t)] C_{H_2}^{n_{hydr}}(t), \tag{6}$$

where $C_{H_2}(t)$, $C_\alpha(t)$, $C_\beta(t)$, $C_{cis}(t)$, and $C_{trans}(t)$ are the current concentrations of hydrogen, α-pinene, β-pinene, *cis*-pinane, and *trans*-pinane, respectively; n_{iso} and n_{hydr} are the reaction rate orders of isomerization and hydrogenation of α- and β-pinenes with respect to hydrogen. The hydrogen—substrate ratio is high and, hence, the change in the hydrogen concentration in the course of the reaction can be neglected and the apparent reaction rate constants (k_i'), including the constant concentration of hydrogen in the reaction mixture, can be introduced

$$k_i' = k_i C_{H_2}. \tag{7}$$

The k_1, k_{-1}, k_2', k_3', k_4', and k_5' parameters from the system of kinetic equations of the reaction rate were optimized by the search for the minimal sum of the squared differences between the experimental and calculated values. The minimum was obtained by Newton method for the system of nonlinear differential equations.[24] As shown in Fig. 4, the calculated kinetic curves of isomerization and hydrogenation of a mixture of α- and β-pinenes agree well with the experimental kinetic curves. The apparent rate constants in the proposed model calculated for all the catalysts based on the Group VIII metals are listed in Table 1. The highest ratio of the isomerization/hydrogenation rate constants was obtained for the Pd/C catalyst, the medium ratio was obtained for Rh/C, and Pt/C is characterized by a very low ratio.

Effect of the hydrogen pressure. When the H_2 pressure in the reaction increases from 1 to 11 bar at 60 °C, the initial rate of β-pinene transformation increases 3—4 times (Table 2) for all the catalysts studied, except for Pd/C, in the presence of which the reaction rate increases by a

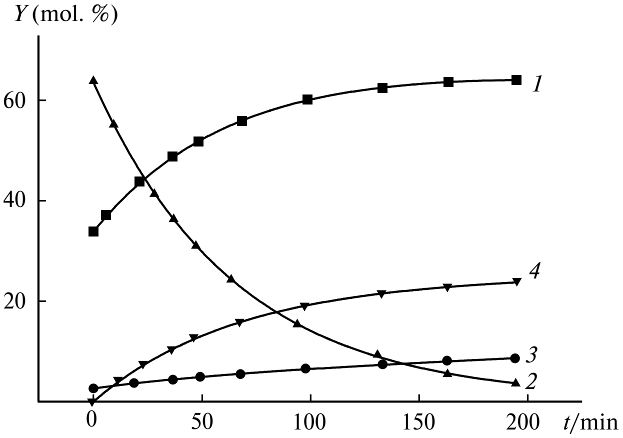


Fig. 4. Kinetic curves of isomerization and hydrogenation of a mixture of α- and β-pinenes on the 0.9% Rh/C catalyst: α-pinene (*1*), β-pinene (*2*), *trans*-pinane (*3*), and *cis*-pinane (*4*). Y is the content of the products. Solid lines are calculation, and points are experiment. Reaction conditions: $p(H_2)$ = 6.3 bar, T = 80 °C, [α-pinene+β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 6 mg.

Table 1. Calculated values of the apparent reaction rate constants*

k_i/s^{-1}	Pd/C	Pt/C	Rh/C	Ru/C	Ir/C
k_1	1.79	$3.18 \cdot 10^{-1}$	2.39	$1.3 \cdot 10^{-2}$	$1.87 \cdot 10^{-2}$
k_{-1}	$9.69 \cdot 10^{1}$	$1.72 \cdot 10^{1}$	$1.29 \cdot 10^{2}$	$7.21 \cdot 10^{-1}$	$9.83 \cdot 10^{-1}$
k_2'	4.16	2.27	4.43	$2.33 \cdot 10^{-1}$	$4.07 \cdot 10^{-2}$
k_3'	5.81	$2.72 \cdot 10^{-1}$	1.92	$3.89 \cdot 10^{-4}$	$5.77 \cdot 10^{-3}$
k_4'	8.03	$1.65 \cdot 10^{1}$	$5.57 \cdot 10^{1}$	$5.88 \cdot 10^{-1}$	$4.95 \cdot 10^{-1}$
k_5'	6.08	6.47	3.32	$1.94 \cdot 10^{-1}$	$5.51 \cdot 10^{-2}$

* Reaction conditions: $p(H_2)$ = 1 bar, T = 60 °C, [α-pinene+β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 10—75 mg.

factor of ~16. At the 70% β-pinene conversion for various metals, the total yield of the hydrogenation products (*cis*- and *trans*-pinanes) demonstrates different dependences on the hydrogen pressure. With an increase in the hydrogen pressure from 1 to 11 bar for the Rh/C and Ir/C catalysts, the total yield of pinane nearly doubled, whereas for the Pt/C and Ru/C catalysts the total yield of pinane remains almost unchanged, being ~40%. This indicates the low isomerizing ability of Pt and Ru under low hydrogen pressure and is caused, most likely, by the high energy of the bond of chemisorbed hydrogen with the metal surface. The activation energy of hydrogen chemisorption[25] (E_{ads}) at the {111} face for Pd is 3.1 kJ mol^{-1}, and that for Pt it is 44.8 kJ mol^{-1}.

When the hydrogen pressure decreases to 0.5 bar, an induction period appears in the curves of the dependence of the product composition on the reaction time. This possibly indicates that H_2 is slowly dissolved in the reaction mixture and the catalyst surface is saturated with hydrogen. In the absence of hydrogen in the system, the rates of isomerization and hydrogenation of a mixture of α- and β-pinenes are low. It is most likely that the isomerization and hydrogenation of the double bond of a pinene molecule require the participation of hydrogen, which is adsorbed on the Platinum Group metal surface.

Under the H_2 pressure equal to 11 bar, the isomerization rate exceeds that of pinene hydrogenation by an order of magnitude, which makes it possible to carry out the isomerization with high selectivity. The logarithmic dependence of β-pinene isomerization on the hydrogen pressure for the Pd/C catalyst is presented in Fig. 5. The slope ratio of this straight line corresponds to the observed reaction order with respect to hydrogen $n(p(H_2)) = 0.51 \pm 0.05$. According to literature data, if the observed reaction order of isomerization of the double bond of alkene with respect to hydrogen is 0.5, the rate-determining step is the addition of chemisorbed hydrogen to alkene.[26,27] For other metals (Pt, Rh, Ru, and Ir) the dependence of the β-pinene transformation rate on the hydrogen pressure is complicated and requires further investigation.

Effect of the reaction temperature. We carried out a series of experiments on the effect of the reaction temperature on the reaction rate of isomerization and hydrogenation of a mixture of α- and β-pinenes in the presence of the Pd/C, Rh/C, Pt/C, Ru/C, and Ir/C catalysts. The results of the studies are given in Table 3. With an increase

Table 2. Effect of the hydrogen pressure on the initial rate of β-pinene conversion W_i (mol (L g s)$^{-1}$) and the total yield of *cis*- and *trans*-pinanes (Y_{pinane}) on various catalysts*

Catalyst	1.0 bar		3.0 bar		6.3 bar		11 bar	
	W_i	Y_{pinane} (%)	W_i	Y_{pinane} (%)	W_i	Y_{pinane} (%)	W_i	Y_{pinane} (%)
Pd/C	2.36	0.0	$1.05 \cdot 10^{1}$	0.0	$2.09 \cdot 10^{1}$	0.0	$3.79 \cdot 10^{1}$	0.0
Pt/C	$1.82 \cdot 10^{-1}$	36.9	$2.21 \cdot 10^{-2}$	30.3	$2.58 \cdot 10^{-1}$	33.3	$3.78 \cdot 10^{-1}$	38.8
Rh/C	1.22	18.9	1.42	27.5	7.93	30.2	4.62	33.3
Ru/C	$6.61 \cdot 10^{-2}$	42.7	$9.05 \cdot 10^{-2}$	45.9	$2.25 \cdot 10^{-1}$	46.4	$1.82 \cdot 10^{-1}$	44.4
Ir/C	$1.19 \cdot 10^{-1}$	23.3	$5.15 \cdot 10^{-1}$	27.8	$7.83 \cdot 10^{-2}$	32.2	3.25	40.5

* Reaction conditions: $p(H_2)$ = 1—11 bar, T = 60 °C, [α-pinene+β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 5—75 mg. Y_{pinane} (%) was calculated at the 70% conversion of β-pinene.

Table 3. Effect of the reaction temperature on the initial rate of β-pinene conversion W_i (mol (L g s)$^{-1}$) and the total yield of *cis*- and *trans*-pinanes (Y_{pinane}) on various catalysts*

Catalyst	25 °C		40 °C		60 °C		80 °C	
	W_i	Y_{pinane} (%)	W_i	Y_{pinane} (%)	W_i	Y_{pinane} (%)	W_i	Y_{pinane} (%)
Pd/C	1.79	0.0	8.85	0.0	$2.09 \cdot 10^{1}$	0.0	$2.82 \cdot 10^{1}$	0.0
Pt/C	$1.59 \cdot 10^{-1}$	46.1	—	—	$2.58 \cdot 10^{-1}$	33.3	$3.60 \cdot 10^{-1}$	20.5
Rh/C	$7.13 \cdot 10^{-1}$	50.5	2.93	60.9	7.93	30.2	7.34	24.3
Ru/C	$2.81 \cdot 10^{-2}$	14.2	$1.40 \cdot 10^{-1}$	26.6	$2.25 \cdot 10^{-1}$	46.4	$8.73 \cdot 10^{-1}$	49.2
Ir/C	$9.37 \cdot 10^{-3}$	16.1	$1.16 \cdot 10^{-2}$	21.2	$7.78 \cdot 10^{-2}$	32.2	$1.02 \cdot 10^{-1}$	18.5

* Reaction conditions: $p(H_2)$ = 6.3 bar, T = 25—80 °C, [α-pinene+β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 5—75 mg. Y_{pinane} (%) was calculated at the 70% conversion of β-pinene.

in the reaction temperature from 25 to 80 °C, the initial rate of β-pinene transformation for the Pd/C, Rh/C, and Ir/C catalysts increases ~10—15 times, for the Ru/C catalyst it increases 30 times, whereas for Pt/C the initial rate doubles.

The apparent rate constants for the reversible isomerization of α- and β-pinene on the Pd/C catalyst are presented in Table 4. The apparent rate of β-pinene isomerization to α-pinene increases with temperature. The temperature dependence in the Arrhenius coordinates is linear (Fig. 6). The estimated value of the apparent activation energy ($E_a{}^*{}_{iso}$ = 25.7±9.0 kJ mol^{-1}) is lower than that for α-pinene hydrogenation[28] ($E_a{}^*{}_{hydr}$ = 37.5 kJ mol^{-1}) on the 4% Pd/C catalyst. Based on the data obtained ($E_a{}^*{}_{iso} < E_a{}^*{}_{hydr}$), we can suggest the most probable mechanism of isomerization through the formation of adsorbed semihydrogenated alkyl intermediates[26] on the palladium surface.

An increase in the reaction temperature to 150 °C increases the contribution of side reactions, such as the hydrogenolysis of the four-membered cycle of α- and β-pinene producing tetramethylcyclohexanes and cymenes and the hydrogenation of the double bond to form pinane *cis*- and *trans*-isomers (see Scheme 1) that decrease the yield of the target product.

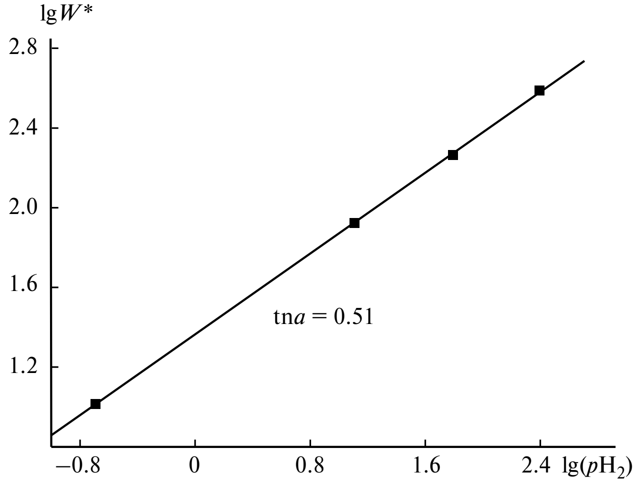


Fig. 5. Effect of the hydrogen pressure on the isomerization rate of β-pinene to α-pinene on the 4% Pd/C catalyst. Reaction conditions: $p(H_2)$ = 1—11 bar, T = 60 °C, [α-pinene+β-pinene]$_0$ = 0.40 mol L^{-1}, m_{cat} = 10 mg.

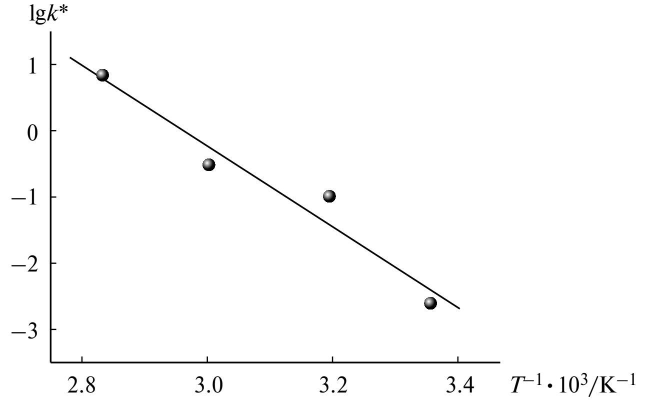


Fig. 6. Effect of the reaction temperature on the apparent rate constant of β-pinene isomerization to α-pinene on the 4% Pd/C catalyst in the Arrhenius coordinates. Reaction conditions: $p(H_2)$ = 6.3 bar, T = 25—80 °C, [α-pinene+β-pinene]$_0$ = = 0.40 mol L^{-1}, m_{cat} = 10 mg.

At the 70% conversion of β-pinene, with an increase in the reaction temperature the total yield of pinanes decreases for the Pt/C and Rh/C catalysts, increases for the Ru/C catalyst, and remains almost unchanged for the Pd/C and Ir/C catalysts.

Table 4. Effect of the reaction temperature on the apparent rate constants of α- and β-pinene isomerization on the 4% Pd/C catalyst

T/°C	k_1	k_{-1}
	s^{-1}	
20	0.030±0.002	2.33±0.4
30	0.046±0.003	4.78±0.5
40	0.080±0.007	5.47±0.9
50	0.087±0.009	5.39±1.2

Comparison of the catalytic activity of various group VIII metals in the isomerization and hydrogenation of α- and β-pinenes. The difference in the catalytic activity of the platinum metals in the isomerization and hydrogenation of the pinene double bond can be explained by the difference in the electronic properties of the Group VIII metals and mechanisms of adsorption of olefin and hydrogen on the metal surface.

The studies performed showed that the isomerization rate of α- and β-pinenes correlates with the activation energy of hydrogen adsorption on the metal surface. The Pd/C catalyst is most active in the isomerization of the double bond in a pinene molecule. For the Pd surface the activation energy of hydrogen chemisorption on the {111} face is lowest, being[25] 3.1 kJ mol^{-1}. The other catalytic systems Rh/C, Pt/C, Ru/C, and Ir/C exhibit considerable activity in the hydrogenation of α- and β-pinene (see Tables 2 and 3).

Based on the obtained experimental data, the orders of decreasing activity for the metal in β-pinene isomerization to α-pinene are

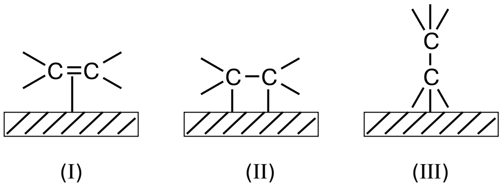
25 °C: Ir < Ru < Pt <Rh < Pd,

80 °C: Ir < Pt < Ru < Rh < Pd,

which agree with the known literature data[29] for the isomerization of the double bond of olefins on the Platinum Group metals.

A probable reason for differences in the catalytic activity of the platinum metals in double bond isomerization can be different mechanisms of olefin adsorption on the metal surface. According to the data of IR spectroscopy,[30] alkenes adsorbed on the surface of Platinum Group metals can exist in at least three forms: π-bonded (I), di-σ-bonded (II), and ethylidine (III) species (Scheme 2). For example, the study of adsorption of butenes[31] showed that π-allylic particles predominate on the surface of the {111} face. These particles were shown[32] to be primary intermediates in the hydrogenation and migration of the double bond.

Scheme 2



The kinetic data obtained by us for the isomerization and hydrogenation of a mixture of α- and β-pinenes on the Pd/C catalyst are consistent with the known mechanism proposed[33] for the isomerization and hydrogenation of the double bond of *n*-butenes on the Pd/C, Rh/C, and Pt/C catalysts. The mechanism includes the semihydrogenated alkyl intermediates adsorbed on the surface. However, further studies are required to propose probable mechanisms of isomerization and hydrogenation of a mixture of α- and β-pinenes on the catalysts based on other Group VIII metals (Pt, Rh, Ru, and Ir).

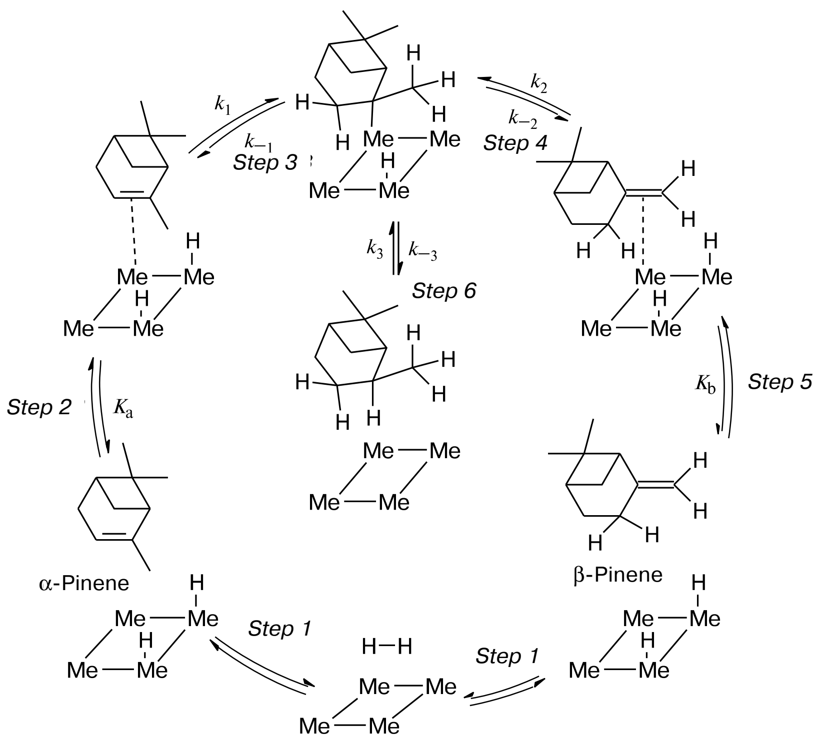
Scheme of the mechanism of hydrogenation and isomerization of α- and β-pinene on the Pd/C catalyst. The formation of hydride species on the metal surface is necessary for steps leading to the migration and hydrogenation of the double bond of olefins on the Platinum Group metals.[34] The source of chemisorbed hydrogen can be external hydrogen and hydrogen obtained by the β-elimination of the alkyl intermediate adsorbed on the metal surface. We found that in the absence of hydrogen the rate of isomerization and hydrogenation of a mixture of α- and β-pinenes on the Group VIII metals was low. This indicates no formation of the η^3-allylic intermediate, which is necessary for the reaction to occur, *via* the mechanism of intramolecular hydrogen transfer promoted by the palladium adsorption sites.

The assumed scheme of the mechanism of isomerization and hydrogenation of α- and β-pinene (migration of the C=C double bond) on the Pd/C catalyst includes the following steps (Scheme 3): step *1*, chemisorption of H_2 molecules on the palladium surface; steps *2* and *5*, α- and β-pinene molecules are reversibly adsorbed on the metal surface with the formation of intermediates π-bonded with the surface metal atoms; step *3*, insertion of the activated C=C double bond between the metal—hydrogen bond affords the σ-bonded pinanyl intermediate; step *4*, β-elimination of the hydrogen atom from the chemisorbed σ-pinanyl intermediate results in the formation of the π-complex with the surface palladium atom; step *6*, insertion of the second hydrogen atom at the metal—carbon bond in the σ-pinanyl complex followed by the desorption of *cis*- or *trans*-pinane results in the formation of a vacancy on the catalyst surface.

The multiple reiteration of the steps of addition and elimination of hydrogen results in the establishment of equilibrium between the pinene α- and β-isomers.

Thus, the liquid-phase hydrogenation and isomerization of α- and β-pinenes was conduced on the Pd/C, Ru/C, Rh/C, Pt/C, and Ir/C catalysts in the temperature interval 25 to 100 °C and at hydrogen pressures of 0.5—11 bar. It was shown that among the studied catalysts the Pd/C catalyst has the highest catalytic activity and selectivity in α-pinene isomerization to β-pinene. The maximum yield of β-pinene upon the isomerization of α-pinene at $T = 100$ °C and under the hydrogen pressure $p(H_2) = 11$ bar is 2.8 mol.%, which is close to the thermodynamically equilibrium value. It was found that the rate of β-pinene isomerization to α-pinene has the first order with respect to β-pinene and the order equal to 0.5 with respect to

Scheme 3



hydrogen. The apparent activation energy of β-pinene isomerization to α-pinene on the Pd/C catalyst was found to be 25.7 kJ mol^{-1}. The mechanism was proposed for the isomerization and hydrogenation of a mixture of α- and β-pinenes on the Pd/C catalyst under a hydrogen atmosphere.

It was found that pinene isomerization and hydrogenation occur simultaneously in the presence of the Ru/C, Rh/C, Pt/C, and Ir/C catalysts, and the reaction mixture contains the products of α- and β-pinene hydrogenation: *cis*-pinane and *trans*-pinane. The obtained rows of activity of the Group VIII metals in the isomerization of the double bond of a pinene molecule are consistent with literature data. It was shown that the metals of the second row (Ru, Rh, Pd) are highly active in β-pinene isomerization, whereas the metals of the third row (Ir, Pt) are insignificantly active. These distinctions can be due to the difference in the mechanism of interaction of α- and β-pinenes and hydrogen with the metal surface.

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