ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 1, pp. 38–44. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © L.I. Kuznetsova, N.I. Kuznetsova, A.S. Lisitsyn, I.E. Beck, V.A. Likholobov, J.E. Ancel, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 1, pp. 44–50.

Liquid-Phase Oxidation of α-Pinene with Oxygen Catalyzed by Carbon-Supported Platinum Metals

L. I. Kuznetsova[a], N. I. Kuznetsova[a], A. S. Lisitsyn[a], I. E. Beck[a], V. A. Likholobov[b], and J. E. Ancel[c]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk, Russia*
[c] *ARCHEMIS, 24 Avenue Jean Jaurés, 69153 Decines Charpieu Cédex, France*
e-mail: livkuzn@catalysis.nsk.su

Received March 18, 2005

Abstract—The liquid-phase oxidation of α-pinene with oxygen at 70–90°C is studied in the presence of Pd, Pt, Ru, Rh, and Ir supported on carbon. The conversion of α-pinene and the selectivity of formation of the main reaction products, namely, verbenol (**1**), verbenone (**2**), and α-pinene oxide (**3**), depends on the nature of the metal, on its oxidation state and extent of dispersion, and on the admixtures introduced into the system. In the presence of the Pt catalysts and promoting admixtures of tetrahexylammonium chloride (Hex_4NCl), the selectivity of formation of the most valuable oxidation products (**1** + **2**) reaches 50% at an α-pinene conversion of 20–30%. The fraction of resinlike oxidation products decreases in the presence of the catalysts. The results obtained are discussed in the framework of the radical mechanism of α-pinene oxidation.

DOI: 10.1134/S0023158407010065

INTRODUCTION

The oxidation reactions of cyclic olefins, in particular, α-pinene, are of interest as a route for production of oxygen-containing compounds [1–13]. The most valuable oxidation products of α-pinene are verbenol and verbenone. The free-radical oxidation of α-pinene with oxygen at elevated temperatures occurs in the absence of a catalyst [1, 2]. Under the reaction conditions, the radical intermediates and primary oxidation products readily undergo various side transformations to form a complicated mixture with a high yield of by-products. The task of the studies on this subject was to achieve the highest possible selectivity of substrate conversion with respect to desired products using dioxygen as the oxidant. To increase the selectivity of formation of verbenol and verbenone, the steps of formation of intermediate hydroperoxide and its transformation into the products were proposed [3–5] to be carried out separately. Allylic oxidation products are usually formed with a low selectivity during the decomposition of intermediate hydroperoxides [1], and, therefore, reduction with sulfide or sulfite was used rather than standard disproportionation for the decomposition of hydroperoxide [3, 4]. This two-step process yielded verbenol (**1**), verbenon (**2**), α-pinene oxide (**3**), isomeric alcohol 3-pinen-2-ol (**4**), myrtenal (**5**), pinocarveol (**6**) (scheme), and a mixture of high-boiling resinlike products, which is typical of oxidation processes involving radicals. The ratio of the concentrations of **1**, **2**, and **3** among the volatiles was 12 : 7 : 10. The yield of the by-products decreases at a low α-pinene conversion to hydroperoxide followed by using hydrogen as the reducing agent in the presence of the Pd/C catalyst [5].

In other cases, the autooxidation is carried out by a standard method, without isolating the intermediate hydroperoxide, and the desired increase in the selectivity is achieved by the introduction of admixtures and/or catalysts. The addition of alkali was reported [6] to retard the oxidation of α-pinene with oxygen; however, the intensity of the side autooxidation processes decreases and the selectivity of verbenol and verbenone formation increases.

It is well known that variable-valence transition metal ions catalyze the decomposition of intermediate hydroperoxide, thus accelerating α-pinene oxidation. The effect of these ions on the amount and composition of the products depends on both the catalyst nature and reaction conditions: temperature, reaction time, the presence of solvent, and acidity of the medium [13–19]. In the typical example of α-pinene autooxidation catalyzed by the Co(II) complexes [19], products **1**, **2**, and **3** were formed in approximately equal amounts at the initial stages of the reaction; at high α-pinene conversions, no epoxide was detected among the products because it underwent secondary transformations.

The oxidation of α-pinene with oxygen in the presence of the platinum and palladium catalysts (including those with cobalt and chromium admixtures) was described in [8, 9, 20]. The verbenol and verbenone selectivities reported in those publications are much higher than usually reported values. However, these data do not allow one to estimate their reliability, because they do not include the yields of all reaction products.

In the present work, we studied the oxidation of α-pinene with dioxygen without solvent in the presence of carbon-supported Pd, Pt, Ru, Rh, and Ir and analyzed the effect of the catalyst composition and some admixtures on the product yield. When estimating the selectivity of α-pinene transformation into verbenol and verbenone, special attention was given to factors decreasing the formation of high-boiling by-products under the oxidation conditions.

EXPERIMENTAL

Materials

α-Pinene (Aldrich) was distilled and stored in air at 5°C for no longer than one week. Other reagents were at least analytical grade. The mesoporous carbon support Sibunit^{TM} (S = 300 m^2/g) was used for catalyst preparation.

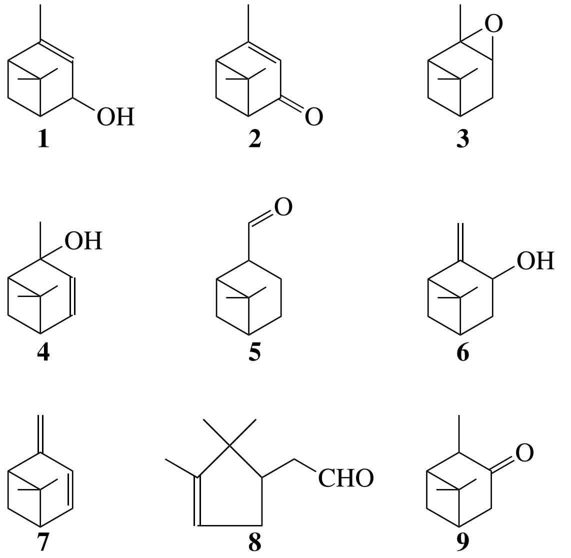
Preparation of Catalysts

Catalyst I (5% Pd/C) contained the supported Pd(II) hydroxocomplexes. The catalyst was prepared by the alkaline hydrolysis of H_2PdCl_4 in the presence of the carbon support (gradual addition of a saturated solution of sodium carbonate to pH 7). Palladium deposition was monitored using iodine–starch paper. The catalyst was separated from the solution, thoroughly washed with water, and dried in air. No reduction and heating of the sample was carried out prior to use.

Catalyst II (5% Pd/C) was also prepared using alkaline hydrolysis. After deposition, palladium was reduced with a solution of sodium formate and the sample was filtered, dried in vacuo for 6 h, and stored under argon.

Catalysts III and IV (5% Pt/C and 5% Pt/C) were prepared using an alkaline hydrolysis of H_2PtCl_6 in the presence of the carbon support followed by reduction with sodium formate. After reduction, the catalysts were stored in air. Catalysts **III** and **IV** were prepared with the variation of hydrolysis conditions (temperature and pH of the solution) and differed in the extent of dispersion of platinum. According to CO adsorption measurements, the dispersion was 0.45 for catalyst **III** and 0.70 for catalyst **IV**.

Catalysts 5% Ru/C, 5% Rh/C, and 5% Ir/C were prepared by the impregnation of the support with a solution of metal chloride. The samples were dried in air, heated at 100°C for 2 h, reduced in an H_2 flow at 400°C, and stored in air.



Scheme. Volatile products of α-pinene oxidation determined by gas chromatography.

Catalytic Experiments

α-Pinene (usually 1 ml), the catalyst, and the admixtures were placed in a temperature-controlled glass reactor (volume 30 ml) with a magnetic stirrer. The reactor was purged with oxygen or another reaction mixture and hermetically connected to a gas burette under atmospheric pressure. Gas absorption during the reaction was monitored by a change in the liquid volume in the burette.

After the end of an experiment, the reactor was cooled down, and the reaction solution was diluted with acetonitrile to 20 ml. For analysis by gas chromatography, a sample (0.2 ml) of the resulting solution was mixed with acetonitrile (1.8 ml) and undecane (1 μl) as the internal standard. Analysis was carried out on a Kristall 2000 instrument with a flame-ionization detector and DB-1701 capillary column (30 × 0.00053 m) in the temperature-programmed regime. Products were identified by the GC-MS method [21].

The concentrations of α-pinene, α-pinene oxide, and *trans*- and *cis*-verbenol and verbenone were determined from calibration plots, which were constructed using pure substances and undecane as the standard. The amounts of other products determined by gas chromatography were calculated from the total surface area of other peaks versus the surface area of the undecane peak (conversion factor 0.9).

RESULTS AND DISCUSSION

At 90°C α-pinene was oxidized with oxygen without a catalyst. In the presence of the carbon-supported platinum metals, the oxidation rate increased as can be seen from the amount of the products determined by

Table 1. Yield of products determined by gas chromatography (P-GC) and the selectivity of α-pinene oxidation with oxygen without a catalyst and in the presence of the 5% Pd/C samples

No.	Catalyst	T, °C	Time, h	Yield of P-GC, mmol				Selectivity, %		
				1	**2**	**3**	others	S	S_I	S_0
1	No catalyst	90	1	0.05	0.03	0.10	0.04	36	30	38
2	**I**	80	1.5	0.26	0.12	0.24	0.13	51	40	42
3	**I**	80	2.5	0.32	0.19	0.31	0.24	48	38	39
4	**II**	80	2	0.32	0.33	0.49	0.09	53	44	51
5	**II**	70	3	0.42	0.36	0.56	0.09	55	46	54

Note: S is the selectivity to **1** + **2** calculated from the sum of all products determined by gas chromatography, S_I is the selectivity to **1** + **2** calculated from α-pinene consumption, S_0 is the selectivity to oxygen consumption calculated by formula (1). Conditions: 6.3 mmol (entry 1) and 7.6 mmol (entries 2–5) of α-pinene, 50 mg of the catalyst, O_2, 1 h.

Table 2. Effect of modifying admixtures on the yield of P-GC and selectivity of α-pinene oxidation with oxygen in the presence of the 5% Pt/C catalyst (**III**)

No.	Catalyst	Admixture	Yield of P-GC, mmol				Selectivity, %		
			1	**2**	**3**	others	S	S_I	S_0
1	5% Pt/C, III	No	0.20	0.14	0.28	0.10	47	32	46
2	5% Pt/C, III	2 ml NH_3	0.19	0.11	0.21	0	59	55	62
3	5% Pt/C, III	10 mg Hex_4NCl	0.40	0.35	0.62	0.13	50	50	61
4	5% Pt/C, III (Na_2CO_3)	10 mg Hex_4NCl	0.33	0.23	0.42	0.07	53	43	42

Note: Conditions: 6.3 mmol of α-pinene, 50 mg of the catalyst, 90°C, O_2, 1 h.

gas chromatography (P-GC). The main volatile oxidation products were compounds **1**, **2**, and **3**. The other volatile oxidation products were formed in smaller amounts (at most 10%): compounds **5** and **6**, as well as verbenone (**7**), α-campholenic aldehyde (**8**), and pinocamphone (**9**) (scheme). The amount of hydroperoxides determined by iodometric titration of the solution after the reaction did not exceed 2% of the sum of P-GC.

The selectivity of the catalytic transformation of α-pinene into allylic oxidation products **1** and **2** was characterized by two quantities: the total amount of verbenol and verbenone divided to either the total yield of P-GC (S) or the fraction of reacted α-pinene (S_I). In addition, the selectivity of oxygen conversion to three main products of α-pinene oxidation (S_0) was determined as the ratio of the number of moles of oxygen consumed to the formation of products **1**, **2**, and **3** to the total amount of oxygen absorbed in the reaction (Eq. (1)). The results of determination of the yield of the main products of α-pinene oxidation in the presence of Pd and Pt catalysts **I**–**IV** and selectivity values are presented in Tables 1 and 2.

$$S_0 = \frac{0.5\ \text{mol}\ (\mathbf{1}) + 1.0\ \text{mol}\ (\mathbf{2}) + 0.5\ \text{mol}\ (\mathbf{3})}{n\ \text{mol}\ O_2} \times 100\%. \qquad (1)$$

In spite of the low conversion of α-pinene (~4%), the S and S_I values in the absence of a catalyst were 36 and 30% (Table 1, entry no. 1). Such a low selectivity of verbenol and verbenone formation is caused by a noticeable transformation of α-pinene into epoxide and other P-GC. When the reaction was carried out without a catalyst, we observed the low value S_0 = 38%, which corresponds to the consumption of oxygen to the formation of other P-GC and resinlike oxidation products along with compounds **1**, **2**, and **3**.

When the reaction was carried out in the presence of the catalysts, the yield and distribution of the oxidation products changed substantially. According to the data in Table 1 (entry 2), in the reaction with catalyst **I**, which underwent no reductive treatment and contained Pd(II) hydroxide, the amount of the oxidation products was several times larger than that in an entry without a catalyst. Although the selectivity decreased sharply with an increase in the substrate conversion, which is characteristic of autooxidation reactions, the selectivity

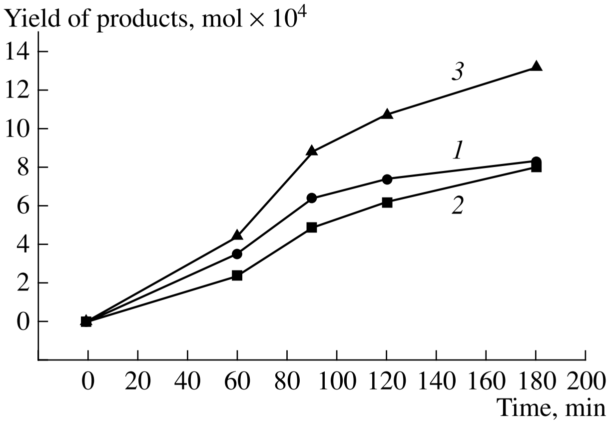


Fig. 1. Plots of the yield of (*1*) verbenol, (*2*) verbenone, and (*3*) α-pinene oxide vs. duration of α-pinene oxidation (6.3 mmol of α-pinene, 50 mg of 5% Pt/C, **III** + 10 mg of Hex_4NCl, 90°C, O_2).

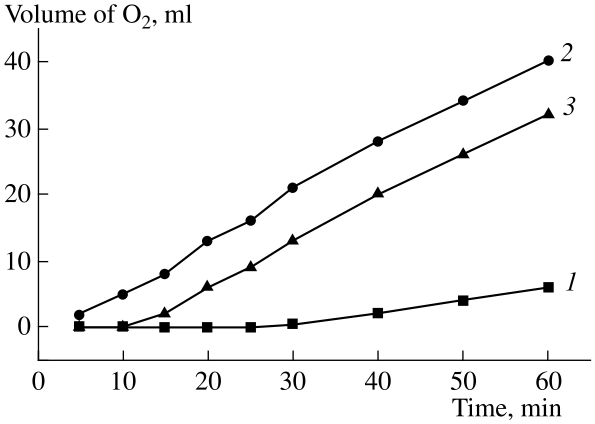


Fig. 2. Plots of the amount of absorbed oxygen vs. duration of α-pinene oxidation: (*1*) without a catalyst, (*2*) 10 mg of 5% Pt/C, **III** + 10 mg of Hex_4NCl, and (*3*) 50 mg of 5% Pt/C, **III** + 10 mg of Hex_4NCl (6.3 mmol of α-pinene, 90°C, O_2).

of formation of the allylic oxidation products in this entry was noticeably higher at 15% α-pinene conversion than that at a low conversion in the absence of a catalyst. In this case, the S_0 selectivity increased to 42%. A higher α-pinene conversion of 22%, achieved with longer reaction times, was accompanied by some decrease in S, S_I, and S_0 (Table 1, entry 3).

The initial catalyst used in entry nos. 2 and 3 contained only Pd(II). Palladium could be partially reduced in the reaction medium interacting with alkene. In the presence of catalyst **II** preliminarily reduced with hydrogen, both the yield of the main oxidation products (**1**, **2**, and **3**) and S, S_I, S_0 values increase at the same 20% α-pinene conversion (Table 1, entry 4). When the temperature was decreased by 10°C, a longer time was needed to achieve the same yield of the desired products (Table 1, entry 5); however, under these conditions, the S, S_I, and S_0 selectivities were higher than those in entry 4.

In the presence of the preliminarily reduced (and stored in air) platinum catalyst 5% Pt/C (**III**), the selectivity of α-pinene oxidation was not high (Table 2, entry no. 1). A substantial promoting effect of some admixtures was observed. For instance, after ammonia was added to the reaction volume in a ratio of $Pt/NH_3 = 1 : 6$ (mol/mol), the selectivity of verbenol and verbenone formation increased to ~60%, other P-GC were absent, and the intensity of resin formation decreased, because the S_0 selectivity increased to 62% (Table 2, entry 2). An admixture of tetrahexylammonium chloride (Hex_4NCl) dissolved in α-pinene in the ratio Pt/Cl = 1 : 2 (mol/mol) resulted in an increase in the selectivity of oxidation (Table 2, entry 3) at a higher α-pinene conversion of 24%. The preliminary impregnation of the Pt catalyst with a solution of Na_2CO_3 (pH 11) followed by drying worsened its properties (Table 2, entry no. 4). On this catalyst α-pinene oxidation was accompanied by more rapid resin formation even in the presence of Hex_4NCl, due to which S_0 was the same as that on the initial catalyst in the absence of promoting admixtures. The most characteristic features of α-pinene oxidation were determined in the presence of catalysts **III** and **IV** (5% Pt/C) with a Hex_4NCl admixture.

The accumulation curves of the main reaction products were S-like (Fig. 1). Since oxygen is absorbed in the presence of the catalyst, the induction period is substantially shortened (compare curves *1* and *2* in Fig. 2). When the catalyst weight is increased from 10 to 50 mg, the volume of absorbed oxygen decreases (compare curves *2* and *3* in Fig. 2) and the S_0 selectivity increases from 46 to 61%. Correspondingly, the amount of P-GC increases (compare entry nos. 1 and 2 in Table 3) and the S selectivity of formation of the allylic oxidation products increases from 39 to 50% (Table 3, entry nos. 1, 2). These results show clearly that the presence of the catalyst decreases the rate of side oxidation processes due to which nonvolatile resinlike substances are formed.

When the oxygen concentration was halved (gas mixture $O_2/N_2 = 1 : 1$), the yield of the main products decreased proportionally without noticeable changes in selectivity (Table 3, entry no. 3).

The state of the platinum catalyst exerted a substantial effect on α-pinene oxidation. For the catalyst repeatedly reduced with hydrogen prior to the experiment, the yield of P-GC remained unchanged and the amount of nonvolatile products decreased noticeably. As a result, S_0 on the repeatedly reduced catalyst reached 80% (Table 3, entry 4).

The change in the catalytic properties depending on the dispersion of platinum was monitored for two 5% Pt/C samples. In the presence of sample **IV** in which platinum was more dispersed ($d = 0.7$) compared to sample **III** ($d = 0.45$) used earlier, the yield of P-GC was twofold lower (Table 3, entries 3, 5). An unusual

Table 3. Yield of P-GC and the selectivity of α-pinene oxidation with oxygen in the presence of the Pt catalysts with the Hex_4NCl admixture (10 mg)

No.	Catalyst	Composition of gas mixture	Yield of P-GC, mmol				Selectivity, %	
			1	**2**	**3**	others	S	S_0
1	10 mg, **III**	O_2	0.29	0.27	0.75	0.11	39	46
2	50 mg, **III**	O_2	0.40	0.35	0.62	0.13	50	61
3	50 mg, **III**	$O_2/N_2 = 1:1$	0.20	0.16	0.32	0.03	51	58
4	50 mg, **III**, reduced with H_2	$O_2/N_2 = 1:1$	0.16	0.15	0.28	0.06	48	80
5	50 mg, **IV**	$O_2/N_2 = 1:1$	0.11	0.09	0.13	0.02	57	64

Note: Conditions: 6.3 mmol of α-pinene, 90°C, O_2, 1 h.

Table 4. Yield of P-GC and the selectivity of α-pinene oxidation in the presence of the Ru, Ir, and Rh catalysts

No.	Catalyst	Conversion of α-pinene	Yield of P-GC, mmol				Selectivity, %	
			1	**2**	**3**	others	S	S_0
1	5% Ru/C	29	0.30	0.31	0.43	0.12	53	37
2	5% Ir/C	44	0.34	0.44	0.62	0.16	49	56
3	5% Rh/C	52	0.34	0.40	0.56	0.14	51	36

Note: Conditions: 6.3 mmol of α-pinene, 50 mg of catalyst + 10 mg of Hex_4NCl, 90°C, O_2, 1 h.

effect of dispersion was observed previously for some liquid-phase systems [22]. The effect is related to specific features of the porous structure of the carbon support and indicates that only part of the platinum surface is involved in catalysis. Fine metallic particles in narrow pores are inaccessible for reactants.

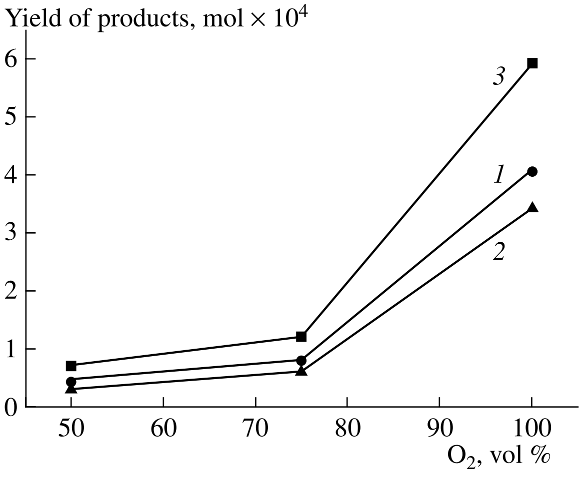


Fig. 3. Effect of the composition of the gas mixture (% O_2 in a mixture with H_2) on the yield of (*1*) verbenol, (*2*) verbenone, and (*3*) α-pinene oxide formed upon α-pinene oxidation (6.3 mmol of α-pinene, 50 mg of 5% Pt/C, **III** + 10 mg of Hex_4NCl, 90°C, O_2).

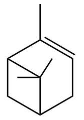
Almost equal amounts of products **1**, **2**, and **3** and, correspondingly, close values of the S selectivity of α-pinene transformation into the allylic oxidation products were obtained in entries with samples containing other platinum group metals (Table 4). These values differ slightly from the corresponding characteristics for the platinum catalyst. However, the α-pinene conversion on going from Ru, Ir, and Rh increased to ~50% and, correspondingly, the S_I selectivity decreased to ≤30%. The S_0 selectivity, which characterizes the intensity of side oxidation processes, is higher for carbon-supported Pt than that for Ru and Rh (Table 4).

The results presented showed that the α-pinene oxidation process can substantially be improved compared to the noncatalytic process choosing the composition of the catalytic system and the state of the platinum metal. Platinum catalyst **III** repeatedly reduced before the experiment was the most active and selective for the formation of volatile oxidation products **1**–**3**. The selectivity of formation of the allylic oxidation products increased in the presence of platinum catalyst **III** with an admixture of ammonium or tetrahexylammonium chloride.

As mentioned above, hydrogen can reduce hydroperoxides. The oxidation of α-pinene became slower upon the addition of hydrogen together with oxygen into the reaction gas composition, and the inhibition effect became stronger with an increase in the partial hydrogen pressure (Fig. 3).

In the presence of hydrogen, products **1**–**3** were accumulated simultaneously in the initial reaction period. The ratio of concentrations of these compounds in the initial reaction step (Fig. 4) remained the same as in the absence of H_2 (Table 3, entry no. 5). After a considerable portion of α-pinene was oxidized, verbenol accumulation decreased and, further, only verbenone was accumulated. The epoxide amount in the solution decreased beginning from a certain time (Fig. 4), indicating its involvement in the secondary reactions leading to the formation of nonvolatile compounds.

The effect of platinum metals in α-pinene oxidation at a rather high temperature (70–90°C) both in pure O_2 and using an O_2/H_2 mixture can be explained in the framework of the autooxidation mechanism. The reaction is initiated on the metallic catalyst surface by hydrogen atom abstraction from the secondary carbon atom in the allylic position (step (I)) to form the radical

$R^\bullet =$ 

Hydroperoxide is formed in the presence of oxygen (steps (II) and (III)) and undergoes subsequent transformations. Since the catalyst affects the ratio of concentrations of the reaction products, it is unambiguous that it is involved in subsequent transformations of intermediate active species.

$$RH \xrightarrow{Pt/C} R^\bullet, \quad (I)$$

$$R^\bullet + O_2 \longrightarrow ROO^\bullet, \quad (II)$$

$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet, \quad (III)$$

$$ROO^\bullet + RH \longrightarrow \text{epoxide} + ROH, \quad (IV)$$

$$2ROO^\bullet \longrightarrow ROH + R{=}O + O_2, \quad (V)$$

$$2ROOH \xrightarrow{Pt/C} RO^\bullet + ROO^\bullet + H_2O, \quad (VI)$$

$$RO^\bullet + RH \longrightarrow ROH + R^\bullet, \quad (VII)$$

$$ROH \xrightarrow{Pt/C,\ O_2} R{=}O + H_2O. \quad (VIII)$$

Three routes of conversion of intermediate hydroperoxide into the primary reaction products are possible: (1) thermal decomposition, (2) decomposition involving the catalyst, and (3) electrophilic interaction with α-pinene.

Thermal decomposition is a chain branched process including not only α-pinene transformation but also the interaction of the primary oxidation products with free-radical intermediates. As a result, large amounts of by-products are accumulated along with verbenol and verbenone [4], so that the noncatalytic process is characterized by low S and S_0 values. In the noncatalytic process in the initial reaction period, the fractions of the allylic oxidation products (**1** + **2**) and epoxide (**3**) are approximately equal according to Eq. (IV); reaction (V) slightly contributes to the formation of the products. In the presence of the Pt catalyst under conditions of rapid hydroperoxide decomposition (step (VI)), the fraction of verbenol resulting from reaction (VII) increases, and verbenol is partially oxidized to verbenone (step (VIII)). In fact, according to the data in Tables 1–4, the (verbenol+verbenone)/epoxide ratio in the catalytic systems varied from 1.1 : 1 to 1.6 : 1, whereas it was substantially lower (0.8 : 1) in the absence of the catalyst.

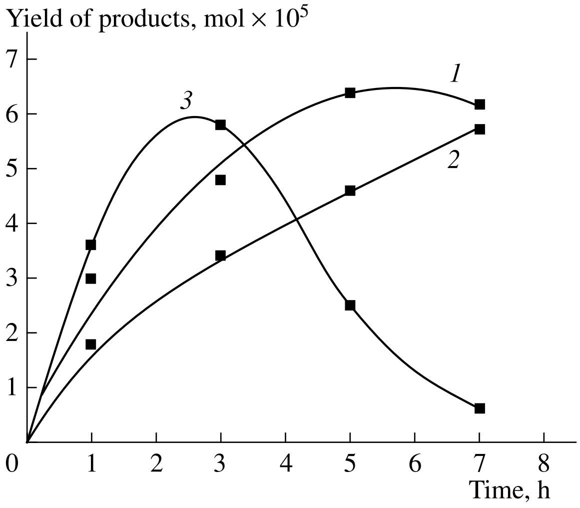


Fig. 4. Plots of the yield of (*1*) verbenol, (*2*) verbenone, and (*3*) α-pinene oxide in the presence of an O_2/H_2 mixture vs. duration of α-pinene oxidation (6.3 mmol of α-pinene, 50 mg of 5%Pt/C, **IV** + 10 mg of Hex_4NCl, 90°C, O_2/H_2 = 1 : 1 (vol/vol)).

For olefin oxidation in the coordination sphere of the platinum metal complexes, ketones are formed due to the electrophilic oxygen atom transfer from hydroperoxide to olefin [23]. In our systems no predominant formation of verbenone was observed compared to other products: verbenol and epoxide. Thus, in the presence of the catalysts containing platinum metals, the electrophilic oxidation of α-pinene occurs under the action of the $ROO^\bullet$ radicals (step (IV)) in the same way as in the presence of compounds of other transition metals [19]. A distinction of our systems is the possibility to control the state of the platinum metal surface by preliminary reduction with hydrogen and by the addition of admixtures (NH_3, Hex_4NCl). As a result, in α-pinene oxidation the supported metallic catalyst suppresses side reactions of resin formation.

ACKNOWLEDGMENTS

The authors are grateful to L.M. Pokrovskii for identification of reaction products by the GC-MS method.

This work was supported by the ARCHEMIS Co. and the Foundation of the President of the Russian Federation (grant. no. NSh-2287.2003.3).

REFERENCES

1. Rubailo, V.L. and Maslov, S.A., *Zhidkofaznoe okislenie nenasyshchennykh soedinenii* (Liquid-Phase Oxidation of Unsaturated Compounds), Moscow: Khimiya, 1989.
2. Patlasov, V.P., Savinykh, V.I., Kushnir, S.R., and Lukoyanov, V.P., *Izv. Vyssh. Uchebn. Zaved., Lesn. Zh.*, 1999, no. 5, p. 74.
3. US Patent 2911442, 1959.
4. Moore, R.N., Golumbic, C., and Fisher, G.S., *J. Am. Chem. Soc.*, 1956, vol. 78, no. 6, p. 1173.
5. Ancel, J.E., Maksimchuk, N.V., Simakova, I.L., and Semikolenov, V.A., *Appl. Catal., A*, 2004, vol. 272, no. 1, p. 109.
6. Encinar, J.M. and Beltran, F.J., *J. Chem. Technol. Biotechnol.*, 1994, vol. 61, no. 4, p. 395.
7. USSR Patent 816 393, *Byull. Izobret.*, 1981, no. 11.
8. CS Patent 270180, 1991.
9. CS Patent 270181, 1991.
10. Murphy, E.E., Mallat, T., and Baiker, A., *Catal. Today*, 2000, vol. 57, nos. 1–2, p. 115.
11. Suh, Y.-W., Kim, N.-K., Ahn, W.-S., and Rhee, H.-K., *J. Mol. Catal. A: Chem.*, 2003, vol. 198, nos. 1–2, p. 309.
12. Da Silva, M.J., Robles-Dutenhefner, P., Menini, L., and Gusevskaja, E.V., *J. Mol. Catal. A: Chem.*, 2003, vol. 201, nos. 1–2, p. 71.
13. Weber, L., Grosche, M., and Hennig, H., *J. Mol. Catal.*, 1993, vol. 78, no. 1, p. L9.
14. Rothenberg, G., Yatziv, Y., and Sasson, Y., *Tetrahedron*, 1998, vol. 54, p. 593.
15. de Fatima, M., Gomez, T., and Antunes, O.A.C., *J. Mol. Catal. A: Chem.*, 1997, vol. 121, nos. 2–3, p. 145.
16. Tissa, J., Sawant, D.P., Gopinath, C.S., and Halligudi, S.B., *J. Mol. Catal. A: Chem.*, 2002, vol. 184, nos. 1–2, p. 289.
17. Lajunen, M.K., Maunula, T., and Koskinen, A.M.P., *Tetrahedron*, 2000, vol. 56, no. 41, p. 8167.
18. Lajunen, M.K., *J. Mol. Catal. A: Chem.*, 2001, vol. 169, nos. 1–2, p. 33.
19. Lajunen, M.K., Myllykoski, M., and Asikkala, J., *J. Mol. Catal. A: Chem.*, 2003, vol. 198, nos. 1–2, p. 223.
20. Hronec, M., Cvengrosova, Z., Tuleja, J., and Ilavsky, J., in *New Developments in Selective Oxidation*, Centi, G. and Trifiro, F., Eds., Bologna: Univ. of Bologna, 1989, p. D4.
21. Kuznetsova, N.I., Kuznetsova, L.I., Kirillova, N.V., Pokrovskii, L.M., Detusheva, L.G., Ansel', Zh., and Likholobov, V.A., *Izv. Akad. Nauk, Ser. Khim.*, 2003, no. 7, p. 1462 [*Russ. Chem. Bull.* (Engl. transl.), vol. 52, p. 1544].
22. Okhlopkova, L.B., Lisitsyn, A.S., Likholobov, V.A., Gurrat, M., and Boehm, H.P., *Appl. Catal., A*, 2000, vol. 204, no. 2, p. 229.
23. Di Furia, F. and Modena, G., *Pure Appl. Chem.*, 1982, vol. 54, no. 10, p. 1853.