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Oxidation of Hydrocarbons with Dioxygen via Peroxide Intermediates

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Abstract—Cyclohexane, cyclohexene, and α-pinene react with dioxygen in the liquid phase in the presence of catalysts based on platinum, heteropoly compounds (HPCs), metal-containing HPCs, and combinations of these components. In cyclohexane and α-pinene oxidations occurring by an autooxidation mechanism at 160–170 and 80–90°C, respectively, the catalysts serve to control free-radical processes. The simultaneous action of a Ru-containing phosphotungstate as a hydroperoxide decomposition catalyst and of a V-containing phosphotungstate as a scavenger of hydroxyl and alkoxyl radicals increases the cyclohexanol + cyclohexanone selectivity of cyclohexane oxidation without yielding a hydroperoxide. A Pt/C catalyst affords an increase in α-pinene conversion in a fixed time. In combination with ammonia or tetrahexylammonium chloride admixtures, it retards side reactions and raises the yield of verbenol and verbenone, which are the most valuable products. During cyclohexane, cyclohexene, and α-pinene oxidation with an O_2–H_2 mixture at room temperature, no free-radical chain reaction develops in the Pt–HPC system and reactive intermediates form and interact, involving the HPC, with hydrocarbons on the surface of the platinum catalyst. Analysis of reactivity and of the composition of substrate oxidation products suggests a mechanism for the conjugate oxidation of hydrocarbons in systems with various HPCs. In this mechanism, HPC composition determines, to a large extent, the nature of reactive intermediates, which may be peroxides or radicals bound to platinum or HPC. The properties of catalytic systems in oxidation with O_2–H_2 mixtures can be controlled by selecting an appropriate HPC as the modifying component.

Dioxygen, which is a readily available substance, is preferable to conventional oxygen-containing liquid-phase oxidizers such as hydrogen peroxide, alkyl hydroperoxides, and hypochlorites. Most of the latest achievements in selective catalytic oxidation of hydrocarbons in the liquid phase stem from progress in the low-temperature activation of dioxygen through partial reduction [1]. Formally, there are three possible mechanisms of reductive activation of oxygen [2]:

(1) Liquid-phase oxidation reactions, particularly conversion of unsaturated hydrocarbons, most often proceed by an autooxidation mechanism. Reaction is initiated by the formation of free radicals from the substrate. Dioxygen is activated through attachment to an alkyl radical with formation of a hydroperoxide. The hydroperoxide is then converted into an oxidation product, regenerating the radical.

(2) If the system contains a coreducer that is more readily oxidizable by oxygen into a peroxide than the substrate, then the overall process will be conjugate oxidation. The substrate will not be oxidized by dioxygen. It will react with the resulting peroxide by a homolytic or heterolytic mechanism.

(3) Enzymatic oxidations are regarded as a special class of conjugated reactions. The high selectivity of substrate conversion in these biochemical systems is due to transition-metal complexes, whose ligands participate in electron transfer and control the stereochemistry of the process. Biomimetic systems based on transition-metal complexes have not found any application as yet, because they do not afford a sufficiently high reaction rate and decompose rapidly because of the oxidation of the organic ligands.

Here, we consider simple catalytic systems that are not prone to irreversible oxidation, specifically, type 1 and 2 catalytic systems based on a heteropoly compound (HPC), platinum, or their combination. The oxidation of cyclohexane and cycloalkenes (cyclohexene and α-pinene) with dioxygen was studied under autooxidation and conjugate-oxidation conditions. The purpose of our study was to optimize the composition of active systems for highly selective conversion of the substrates into desired products. We introduced several components with specific catalytic properties into the system. Analysis of product composition as a function of catalyst composition for both types of catalytic sys-

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tem provided information concerning the chemism of the reactions in question.

The essence of many innovative ideas in liquid-phase oxidation of hydrocarbons is application of solid catalysts, either novel or analogous to known soluble catalysts [3–6]. Our study also dealt with heterogenized systems. Solid catalysts were used in autooxidation. Catalytic systems for conjugate oxidation were either mixtures of solid and soluble components or two-component solid supported catalysts.

EXPERIMENTAL

Synthesis and characterization of heteropoly acids and their tetrabutylammonium (Bu_4N) salts are reported in an earlier paper [7] and in articles cited therein.

The supported catalysts Bu_4N-PW_{11}/C, Bu_4N-$PW_{11}V$/C, Bu_4N-$PW_{11}Fe$/C, Bu_4N-$PW_{11}Cr$/C, Bu_4N-$PW_{11}Mn$/C, and Bu_4N-$PW_{11}Co$/C were prepared by impregnating the carbon support Sibunit (S_{sp} = 300 m^2/g) with an acetonitrile solution of the Bu_4N salt of $PW_{11}O_{39}^{7-}$, $PW_{11}VO_{40}^{4-}$, $PW_{11}M(H_2O)O_{39}^{4-}$ (M = Fe(III), Cr(III)), or $PW_{11}M(H_2O)O_{39}^{5-}$ (M = Mn(II), Co(II)). The solvent was removed in flowing air at room temperature, and the catalysts were dried at 100°C. The H_3PMo_{12}/C catalyst was prepared by impregnating Sibunit with an aqueous solution of $H_3PMo_{12}O_{40}$ followed by drying at 100°C. The HPC content of all samples was 20 wt %.

Preparation of 5% Pt/C and 1% Pt/SiO_2 is described elsewhere [8]. To obtain 5% Ir/C and 5% Rh/C, Sibunit powder was impregnated with $IrCl_3$ and $RuCl_3$ solutions, respectively, dried at room temperature and then at 100°C, and reduced in flowing hydrogen at 400°C. Supported P–V–W and P–W–Ru catalysts were prepared from specially synthesized HPCs.

K-$PW_{11}V^{IV}$ was prepared by adding $VOSO_4 \cdot 2H_2O$ to a 0.02 M solution of $K_7PW_{11}O_{39}$ (pH 5) up to a V : PW_{11} molar ratio of 1 : 1. The solution was evaporated, and the resulting crystals were washed with water at 0°C and then with ethanol. The elemental composition of the product suggested the formula $K_5PW_{11}VO_{40} \cdot 9H_2O$. (Calculated (wt %): P, 0.99; W, 64.2; V, 1.62; K, 6.20; H_2O 5.16. Found (wt %): P, 0.95; W, 61.2; V, 1.50; K, 6.62; H_2O 5.34, SO_4^{2-}, <0.1). IR spectroscopic data indicated that the $PW_{11}V$ anion has a Keggin-type structure (P–O: absorption bands at 1090 and 1060 cm^{-1}; W=O: 965 cm^{-1}; W–O–W: 890 and 790 cm^{-1}).

The $Na_6HPW_8V_4O_{40} \cdot 15H_2O$ salt, which was obtained as described in [9] and was characterized in an earlier study [10], will be referred to as Na-PW_8V_4.

The compounds designated K-$PW_{11}V$ and K-$PW_{10}V_2$ were synthesized by neutralizing the acids $H_4PW_{11}VO_{40}$ and $H_5PW_{10}V_2O_{40}$ [11] to pH 4–6.

K-$(PW_9)_2W_2Ru_2$ was obtained by adding a ruthenium chloride solution in HCl with a Ru concentration of 7.5 mg/ml to a 0.02 M solution of $K_7PW_{11}O_{39}$ to an Ru : PW_{11} molar ratio of 0.8 : 1. The resulting solution (pH ~ 1) was filtered to remove the $H_3PW_{12}O_{40}$ precipitate, and the resulting complex was crystallized at room temperature. The elemental composition of the complex corresponded to the formula $K_{10}(PW_9O_{34})_2(WO_2)_2O[Ru(OH)]_2 \cdot 11KCl \cdot 36H_2O$. (Calculated (wt %): P, 0.886; W, 52.5; Ru, 2.89; K, 11.7; Cl, 5.58. Found (wt %): P, 0.860; W, 53.0; Ru, 3.42; K, 12.0; Cl, 5.20). IR spectroscopic data indicated that this compound is a ruthenium hydroxochloro complex of an unsaturated phosphotungstate of the $W_3(PW_9)_2$ family [12] (P–O: 1105, 1085, and 1035 cm^{-1}; W=O and W–O–W: 980, 945, 890, 775, and 705 cm^{-1}).

The supported catalysts K-$PW_{11}V^{IV}/SiO_2$, K-$PW_{11}V^{IV}$/C, Na-PW_8V_4/C, K-$PW_{11}V$/C, K-$PW_{10}V_2$/C, and K-$(PW_9)_2W_2Ru_2$/C were prepared by impregnating silica gel (S_{sp} = 260 m^2/g) or Sibunit with an HPC solution to an HPC content of 25 (for V-containing catalysts) or 14% (for Ru-containing catalysts). The solution was evaporated, and the solid was dried at 100°C.

V_2O_5/C was prepared by impregnating Sibunit with a hot NH_4VO_3 solution. The solution was evaporated, and the resulting powder was dried at 100°C and calcined in flowing He at 400°C.

To obtain 5% Pt-Na-PW_{11}/C, 5% Pt-Na-PW_{11}/C, and 5% Pt-Bu_4N-PW_{11}/C catalysts, 5% Pt/C was impregnated with an HPC solution in water or acetonitrile to an HPC content of 20% and then dried in air at room temperature.

Catalytic oxidation of cyclohexane was carried out in a mechanically stirred steel reactor at 150–170°C. The reactor, charged with a substrate and a catalyst, was sealed, purged with nitrogen, heated to a prescribed temperature, and filled with $N_2 : O_2 = 90 : 10$ gas mixture. After some time, stirring was stopped and the reactor was cooled. The resulting solution was treated with a mixture of bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane (Supelco) at 100°C and then was analyzed using a Kristall 2000m chromatograph with a flame ionization detector, a 30 m × 0.25 mm HP-5 column, and a stationary phase with a particle size of 0.25 μm.

The other oxidation reactions were carried out in a glass reactor fitted with purge valves and a gas burette [8]. GC analysis of their products was performed on the same chromatograph. For qualitative analysis, we used GC in combination with mass spectrometry. In the case of α-pinene oxidation with dioxygen, the resulting solution (1 ml) was diluted with acetonitrile to 20 ml and then chromatographed. This dilution was necessary to determine substrate conversion. Undecane was used as the internal standard in GC.

The substrates were cyclohexane (Ekros-1, analytical grade), cyclohexene (Aldrich), and α-pinene

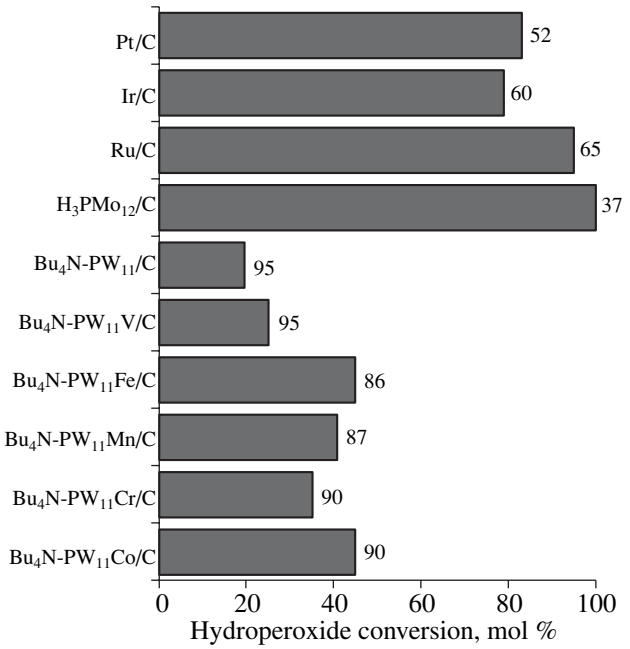


Fig. 1. Hydroperoxide conversion and cyclohexanol + cyclohexanone selectivity in the presence of the carbon-supported catalysts M/C (M = Pt, Ir, Ru) and HPC/C. Conditions: 25 ml of C_6H_{12}; 1000–1500 μmol of cyclohexyl hydroperoxide; 200 mg of catalyst; N_2, T = 70°C; reaction time, 1 h. The numbers are selectivity data for hydroperoxide conversion into cyclohexanol and cyclohexanone (%).

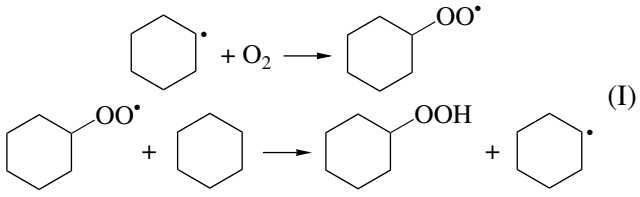
(Aldrich). The other chemicals were either reagent- or analytical-grade.

RESULTS AND DISCUSSION

Cyclohexane Oxidation with Dioxygen

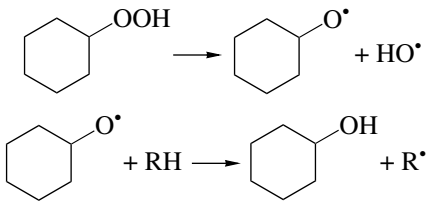
Cyclohexane oxidation into a cyclohexanol–cyclohexanone mixture is a step in the synthesis of adipic acid and caprolactam. The reaction between cyclohexane and oxygen proceeds by an autooxidation mechanism [2, 13].

A free-radical reaction is initiated through the decomposition of peroxides present as impurities in the hydrocarbon. The free-radical reaction involving dioxygen yields a hydroperoxide:



(I)

Cyclohexanol and cyclohexanone result from the thermal decomposition of this hydroperoxide:



(II)

The thermal decomposition of the peroxide is accompanied by chain branching, which increases the concentration of free radicals. This results in a higher oxidation rate and in a higher substrate conversion. At the same time, the free radicals, which are very active, react with intermediates and primary products, lowering the selectivity of oxidation with respect to the desired products. At a cyclohexane conversion of 4%, the cyclohexanol + cyclohexanone selectivity does not exceed 80%.

The catalysts and some admixtures act to increase the cyclohexanol + cyclohexanone selectivity at a given substrate conversion rather than to raise the oxidation rate (see, for example, [14–16]). A commercial-scale process conducted above 150°C in the presence of soluble cobalt salts [17] afforded a desired-product selectivity of 85% at a cyclohexane conversion of ~4%. This small gain in selectivity nevertheless makes the catalyzed reaction preferable and prompts researchers to develop more selective catalysts, especially heterogeneous ones.

We tested two types of catalyst, specifically, metal catalysts for peroxide decomposition and HPC-containing catalysts known as peroxide activators in various oxidation processes. In the latter case, a potassium or Bu_4N salt of a polyanion was added to the catalyst to obviate the dissolution of active components. These salts are tightly bound by the carbon surface and cannot be washed away by cyclohexane or water resulting from the reaction.

First, we tested the catalysts in cyclohexyl peroxide decomposition at a low temperature (Fig. 1) at which the hydroperoxide was fairly stable in the absence of a catalyst and did not decompose considerably within the measurement time. Bu_4N-PW_{11}/C increased the decomposition rate only slightly. In the presence of a phosphotungstate containing a first-row transition metal, hydroperoxide conversion into cyclohexanol and cyclohexanone proceeded at a moderate rate and with a high selectivity. By contrast, the polyacid H_3PMo_{12} caused a rapid and nonselective decomposition of the hydroperoxide.

Metal catalysts caused a nearly complete decomposition of the hydroperoxide. The cyclohexanol + cyclohexanone selectivity was low, as calculated from GC data. Furthermore, we observed the formation of insoluble compounds, which are undetectable by GC.

Unlike Ru/C, Ru ions in combination with a phosphotungstate led to selective hydroperoxide conversion into cyclohexanol and cyclohexanone (compare Fig. 1 and Table 1).

Table 1. Conversion of cyclohexyl hydroperoxide under the action of the K-$(PW_9)_2W_2Ru_2$/C catalyst

Catalyst weight, g	Initial hydroperoxide concentration, μmol/ml	Hydroperoxide conversion, mol %	Cyclohexanol + cyclohexanone selectivity, %
0.1	50	94.5	~100
0.1	80	94	95
0.1	160	92	90

Note: Conditions: 25 ml of C_6H_{12}; 1000–1500 μmol of cyclohexyl hydroperoxide; 100 mg of catalyst; N_2; T = 150°C; reaction time, 25 min.

Hydroperoxide decomposition in the presence of variable-valence metal ions (reaction (III)), unlike thermal decomposition (reaction (II)), does not cause chain branching:

$$\begin{aligned} &ROOH + M^{n+} \longrightarrow RO^{\bullet} + OH^{-} + M^{(n+1)+}, \\ &ROOH + M^{(n+1)+} \longrightarrow ROO^{\bullet} + H^{+} + M^{n+}. \end{aligned} \qquad \text{(III)}$$

Furthermore, the metal ions can serve as radical scavengers, thus diminishing radical concentration in the system:

$$RO^{\bullet} + M^{n+} \longrightarrow RO^{-} + M^{(n+1)+}. \qquad \text{(IV)}$$

Catalyzed hydroperoxide decomposition (reaction (III)) is characterized by a low concentration of free-radical intermediates and by a higher selectivity toward primary products.

Note that metal ions can also initiate the free-radical reaction. Since they perform diversified functions, they can only conditionally be regarded as catalysts.

The reaction between cyclohexane and dioxygen was conducted above 150°C. At this temperature, the hydroperoxide decomposes rapidly in the absence of any admixture. Introducing an admixture favoring rapid and selective hydroperoxide decomposition was expected to increase the selectivity of cyclohexane oxidation. Based on the data presented in Fig. 1 and Table 1, we selected the HPC containing Ru(IV) and Ru(III) ions and P–W–V HPCs for cyclohexane oxidation, since the former is very active in hydroperoxide decomposition and the latter combine moderate activity with high selectivity.

The primary products of cyclohexane oxidation are cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide. Secondary oxidation and the breaking of the carbon chain yield a variety of oxygenated products. In a noncatalytic run, we obtained a precipitate of adipic acid and insoluble resinous substances at high cyclohexane conversions. Therefore, GC analysis of the liquid probably gave an overestimated value of primary-product selectivity.

As is demonstrated in Table 2, oxidation in the presence of P–W–V HPC is more selective with respect to primary products than the noncatalytic reaction or the reaction catalyzed by vanadium oxide. In the presence of a P–W–V HPC catalyst, the formation of insoluble compounds was not observed, although we thoroughly searched the reactor contents for such compounds in each run.

At the early stages of the reaction, when cyclohexane conversion is low, the reaction mixture contains appreciable amounts of hydroperoxide (run 1 in Table 2). In the noncatalytic reaction in the absence of a stabilizer, only traces of the hydroperoxide remain when cyclohexane conversion is 3.4% (run 2). In the

Table 2. Results of cyclohexane oxidation with oxygen in the absence of a catalyst and in the presence of V-containing catalysts

Run no.	Catalyst	T, °C	Time, min	C_6H_{12} conversion, %	S*, %	HP**, %
1	No catalyst	170	15	1.5	86	46
2			30	3.4	83	0.3
3	V_2O_5/C	170	20	3.7	85	0
4	K-$PW_{11}V^{IV}$/C	170	25	3.5	89.7	24
5			30	5.1	85.3	9
6	K-$PW_{11}V^{IV}/SiO_2$	170	25	3.8	90	16
7	K-$PW_{11}V^{IV}/SiO_2$	160	25	0.4	91	50
8	Na-PW_8V_4/C	170	20	4.2	87.6	0
9	K-$PW_{10}V_2$/C	170	20	3.9	90.6	13
10	K-PW_{11}V/C	170	25	4.1	88	19
11	K-$(PW_9)_2W_2Ru_2$/C	170	20	3.8	84.2	0
12	K-$(PW_9)_2W_2Ru_2$/C	160	20	4.1	86.5	0

Note: Conditions: 25 ml of C_6H_{12}; 100 mg of catalyst; initial O_2 partial pressure, 1 atm.

* S is selectivity with respect to primary oxidation products as the molar ratio of cyclohexanol + cyclohexanone + hydroperoxide to the total product.

** HP is the percentage of hydroperoxide in the primary products.

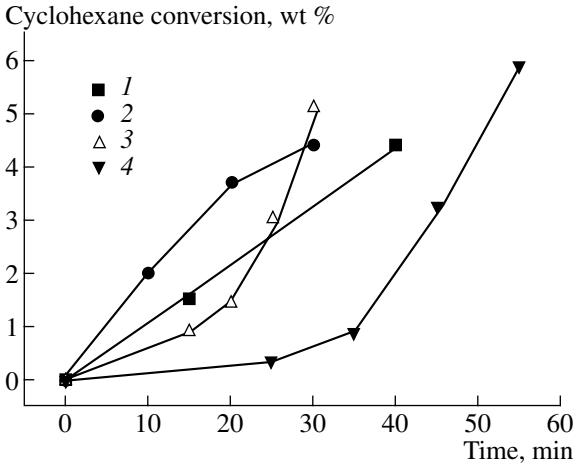


Fig. 2. Cyclohexane conversion vs. cyclohexane/oxygen contact time: (*1*) no catalyst, (*2*) V_2O_5/C, and (*3*, *4*) K-$W_{11}V^{IV}$/C. Conditions: 25 ml of C_6H_{12}; 100 mg of catalyst; O_2 partial pressure, 1 atm; T = (*1–3*) 170 and (*4*) 160°C.

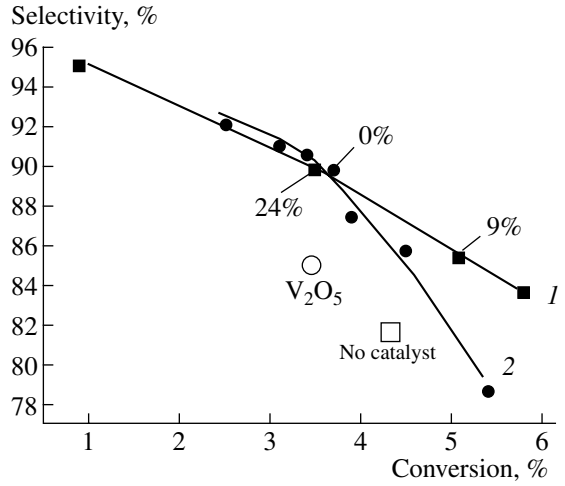


Fig. 3. Cyclohexanol + cyclohexanone + hydroperoxide selectivity vs. cyclohexane conversion for the catalysts (*1*) K-$PW_{11}V$/C and (*2*) (K-$PW_{11}V$ + K-$PW_{11}Ru$)/C. Conditions: 25 ml of C_6H_{12}; 100 mg of catalyst; initial O_2 partial pressure, 1 atm; T = 170°C. The numbers are hydroperoxide content data for products.

presence of a P–W–V catalyst, cyclohexane conversion is the same and it is reached in 20–25 min at 170°C. At the same time, there is some hydroperoxide in the reaction mixture at a high cyclohexane conversion. For example, 9% of the hydroperoxide persists at a cyclohexane conversion of about 5% (run 5).

Autooxidation typically has an induction period. In the conversion-versus-time curves for the reactions in the absence of any catalyst and in the presence of V_2O_5, the induction period was not pronounced (Fig. 2). By contrast, in the presence of K-$PW_{11}V^{IV}$/C, we observed a well-pronounced induction period, which was particularly long at 160°C. Hydroperoxide stabilization is apparently due to the interaction between the HPC and intermediate free radicals (probably, hydroxyl and alkoxyl ones) according to reaction (IV). Hydroperoxide formation is slowed down to a lesser extent, because the HPC does not bind alkyl radicals responsible for this process.

The process involving Na-PW_8V_4/C differs in the amount of hydroperoxide formed from the processes involving other P–W–V HPC catalysts (Table 2), because these catalysts differ in the oxidation state of vanadium during the reaction. No matter what its initial state, vanadium in K-$PW_{11}V^{IV}$, K$PW_{11}V$, and K$PW_{10}V_2$ is mainly in the V^{IV} state during the reaction, while V^{IV} in Na-PW_8V_4 is rapidly oxidized by dioxygen [10]. It is because of V^{IV}/V^{V} transition occurring readily that the peroxide decomposes more rapidly on the Na-PW_8V_4/C catalyst than on the other P–W–V HPC catalysts.

In all examples given in Table 2, the free-radical oxidation controlled by a P–W–V HPC is characterized by a high primary-product selectivity. The selectivity of the reaction is as high as 90% at cyclohexane conversions up to 3.5–4.0%. At higher conversions, the selectivity is lower. Anyway, it was higher in the presence of P–W–V catalysts than in the noncatalytic process or in the process involving V_2O_5.

A drawback of the most selective catalysts—K-$PW_{11}V^{IV}$/C, K-$PW_{11}V^{IV}/SiO_2$, K-$PW_{10}V_2$/C, and K-$PW_{11}V$/C (Table 2)—is that hydroperoxide is incompletely converted even at a high cyclohexane conversion. It is necessary to add a component that will cause selective hydroperoxide decomposition. We used a ruthenium-containing HPC of composition K-$(PW_9)_2W_2Ru_2$ for this purpose.

Owing to the high activity of ruthenium in hydroperoxide decomposition, the free-radical process in the reaction involving dioxygen is more rapid in the presence of the ruthenium catalyst than in the presence of the vanadium catalyst (see runs 7 and 12 in Table 2, which were conducted at a lower temperature). The Ru-containing catalyst is not as selective as its vanadium counterparts of similar composition. The ruthenium catalyst is advantageous in that there is no hydroperoxide in the system even at a low cyclohexane conversion.

To ensure high selectivity together with complete hydroperoxide decomposition, we used a two-component catalyst: the V-containing component served as a radical scavenger, and the Ru-containing component catalyzed hydroperoxide decomposition. In the presence of the specimen with V : Ru = 1 : 1, reaction selectivity is up to 90% at a cyclohexane conversion of 3.5%. When cyclohexane conversion is 3%, the solution contains only traces of hydroperoxide. At conversions above 4%, reaction selectivity is lower in the presence

of the two-component catalyst than in the presence of K-$PW_{11}V^{IV}$ (see the lower portion of curve 2 in Fig. 3).

These results demonstrate that the selectivity of the autocatalytic oxidation of cyclohexane can be well controlled by adding components capable of accelerating hydroperoxide decomposition and of controlling the concentration of intermediate free radicals in the system.

α-Pinene Oxidation with Dioxygen

The oxidation of cyclic olefins is a source of a variety of oxygen-containing products [18–23]. Many cyclic olefins are rapidly oxidized by dioxygen below their boiling points in the absence of a catalyst. Autooxidation reactions typically suffer from low selectivity. Because cyclic olefins are very reactive, the problem of increasing the selectivity of their conversion into desired products is particularly challenging.

α-Pinene autooxidation yields three main primary oxidation products: verbenol and verbenone result from the decomposition of the intermediate hydroperoxide, and an epoxide results from the electrophilic attack of the hydroperoxide on the double bond of the olefin (see reaction (V)).

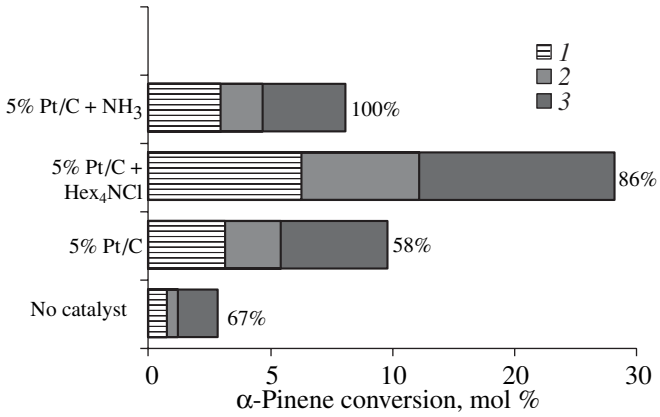
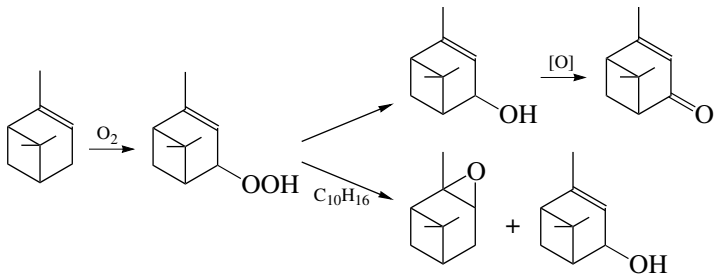


Fig. 4. Effect of catalyst composition on α-pinene conversion into primary oxidation products: (*1*) verbenol, (*2*) verbenone, and (*3*) epoxide. Conditions: 6.3 mmol of α-pinene; 50 mg of catalyst; O_2; 10 mg of Hex_4NCl or 4% NH_3 in the gas phase as an extra component; T = 90°C; reaction time, 1 h. The numbers are selectivity data for α-pinene conversion into primary oxidation products.

The first two compounds are the most valuable of the products.



(V)

Secondary oxidation, isomerization, the breaking of the C_4 ring, and polymerization give by-products. As a consequence, the verbenol + verbenone selectivity does not exceed 40% at an α-pinene conversion of 25% [24, 25].

Compounds of variable-valence metals (Co, Cr, Fe, and Cu) accelerate the rate of hydroperoxide conversion into primary products, thereby increasing the selectivity of α-pinene oxidation [22]. Furthermore, a catalyst may favor one of the hydroperoxide conversion pathways, leading either to the epoxide or to the allyl derivatives.

In the reaction between α-pinene and dioxygen, the platinum catalyst, either alone or in combination with promoters, accelerates the free-radical process, shortening the induction period. As a result, an increased olefin conversion is attained in a fixed time (Fig. 4). The Pt/C catalyst in the presence of ammonia or tetrahexylammonium chloride (Hex_4NCl) affords both an increase in conversion and a markedly higher primary-product selectivity: no by-products are found in the ammonia-containing system. The molar ratio of the epoxide to the allyl derivatives is 0.8 in the noncatalytic reaction, 1.2 in the presence of the platinum catalyst, and 1.4 in the presence of the platinum catalyst and NH_3 or Hex_4NCl (Fig. 4). Obviously, the catalyst in these systems acts primarily to activate the conversion of the hydroperoxide into verbenol and verbenone. With 5% Pt/C, α-pinene conversion reaches 30 mol % in 1.5 h. However, the overall primary-product selectivity is decreased at this time, probably because of the secondary conversion of the products.

Next, we studied how the proportions of the main oxidation products depend on reaction conditions. The accumulation rate of primary oxidation products in the Pt/C + Hex_4NCl system decreases in going from 90°C to room temperature (Fig. 5), while the verbenol : verbenone : epoxide ratio is 0.7 : 0.7 : 1.0 throughout the temperature range 55–90°C. As the temperature is further lowered to 25°C, the epoxide gradually becomes the main product, because alkene epoxidation with peroxides typically occurs at low temperatures.

Diluting the dioxygen with an inert gas causes a proportional decrease in the amount of products and does not affect the verbenol : verbenone : epoxide ratio. In

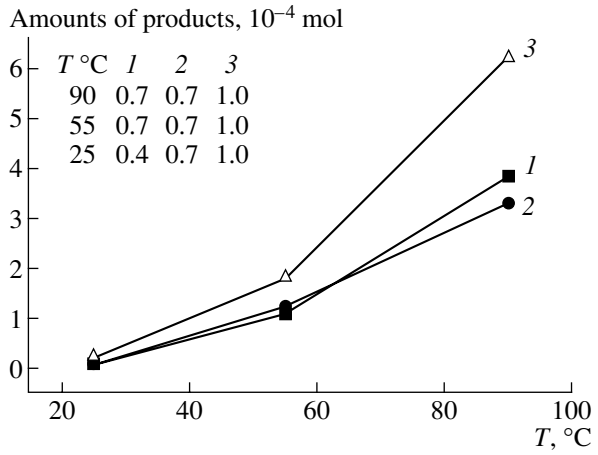


Fig. 5. (*1*) Verbenol, (*2*) verbenone, and (*3*) epoxide yields as a function of temperature for α-pinene oxidation on 5% Pt/C. Conditions: 6.3 mmol of α-pinene; 50 mg of catalyst; 10 mg of Hex_4NCl; O_2; reaction time, 1 h.

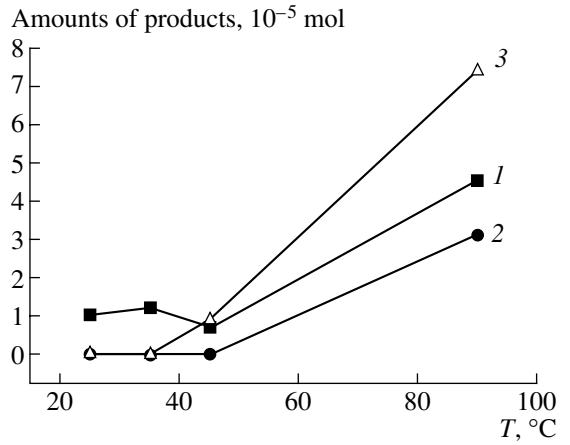


Fig. 6. (*1*) Verbenol, (*2*) verbenone, and (*3*) epoxide yields as a function of temperature for α-pinene oxidation on 5% Pt/C in the presence of H_2. Conditions: 6.3 mmol of α-pinene; 50 mg of catalyst; 10 mg of Hex_4NCl, $O_2 : H_2 = 1 : 1$; reaction time, 1 h.

the case of oxidation with an oxygen–hydrogen (1 : 1) mixture at a high temperature, the amount of products is smaller by one order of magnitude (compare the amounts of verbenol, verbenone, and epoxide at 90°C in Figs. 5 and 6). In the presence of the platinum catalyst, hydrogen reduces the peroxide and, probably, intermediate radicals, thus suppressing the chain reaction to a considerable extent. In spite of the lower oxidation rate, the verbenol : verbenone : epoxide ratio under these conditions is the same as in the oxidation with pure dioxygen. This suggests that the free-radical mechanism persists in the presence of hydrogen.

A quite different situation is observed between 20 and 40°C. Even at a temperature as low as 20°C, α-pinene oxidation in the presence of hydrogen yields verbenol alone. Apparently, hydrogen completely suppresses autooxidation and the reaction mechanism observed at room temperature in the presence of hydrogen is based on the reductive activation of oxygen with hydrogen on the platinum catalyst without hydroperoxide formation. Such reactions typically occur at low temperatures.

Cyclohexane Oxidation with an Oxygen–Hydrogen Mixture

In autooxidation reactions, dioxygen is activated by reaction with an alkyl radical (reaction (I)); therefore, the concentration of free radicals must be constant or increase with time for a chain reaction to be possible. A sufficiently high concentration of free radicals is maintained at $T > 150$°C in cyclohexane oxidation and at $T = 70$–90°C in α-pinene oxidation. At these temperatures, substrate oxidation is rapid and a considerable conversion is reached in one or a few hours. In conjugate oxidation reactions, reductive activation of dioxygen by a coreducer such as dihydrogen is possible at a low (room) temperature. This process yields an oxidizer belonging to the class of atomic oxygen donors such as hydrogen peroxide [26]. This peroxide can be used in hydrocarbon oxidation:

$$\begin{aligned} O_2 + H_2 &= H_2O_2, \\ RH + H_2O_2 &= ROH + H_2O. \end{aligned} \qquad \text{(VI)}$$

Hydrocarbon oxidation with an O_2–H_2 mixture requires two-component catalysts based on transition metals. In such systems, the key stage of the formation of active oxygen is transfer of two electrons accompanying dioxygen adsorption onto the metal surface:

$$[M^0] + O_2 \longrightarrow [M^{2+}(O_2)^{2-}]. \qquad \text{(VII)}$$

A second (modifying) component is necessary for substrate oxidation, and the behavior of the catalytic system depends considerably on this component.

The liquid-phase oxidation of cyclohexane was conducted at atmospheric pressure and a temperature of 35°C. The catalytic system included 1% Pt/SiO_2 or 5% Pt/C powder suspended in a C_6H_{12}–CH_3CN mixture and an HPC dissolved in an organic medium. In the absence of an HPC, the platinum catalysts rapidly convert the O_2–H_2 mixture into H_2O without yielding organic products. HPCs modify the platinum catalysts so that gas sorption is reduced and cyclohexane oxidation takes place [27, 28].

In the presence of platinum and an HPC, cyclohexane is oxidized into cyclohexanol and cyclohexanone, whose ratio varies between 10 and 50, depending on catalyst composition. Another product is hydroperoxide, whose amount does not exceed 10% of the total amount of the main products. The activity of catalytic system in cyclohexane oxidation depends on HPC composition, as is demonstrated in Figs. 7 and 8. Earlier, we found that oxidation reactions involving an O_2–H_2 mix-

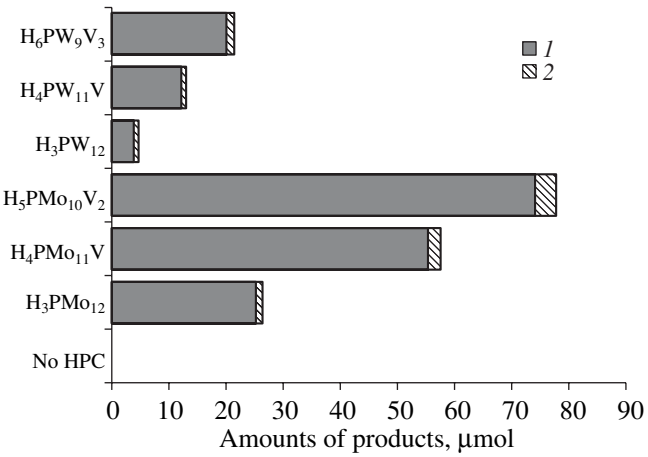


Fig. 7. Proportions of (*1*) cyclohexanol and (*2*) cyclohexanone in the product of cyclohexane oxidation in the presence of various HPCs. Conditions: 55 mg of 1% Pt/SiO_2; 1 ml of CH_3CN; 950 μmol of C_6H_{12}; 8 mg of HPC; T = 35°C; $O_2 : H_2 = 1 : 2$; reaction time, 1 h.

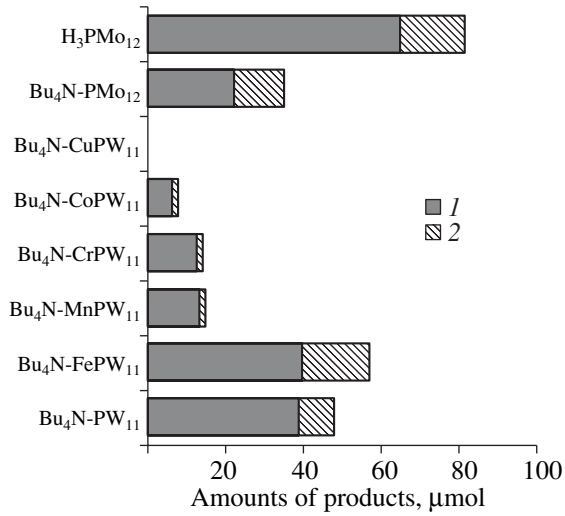


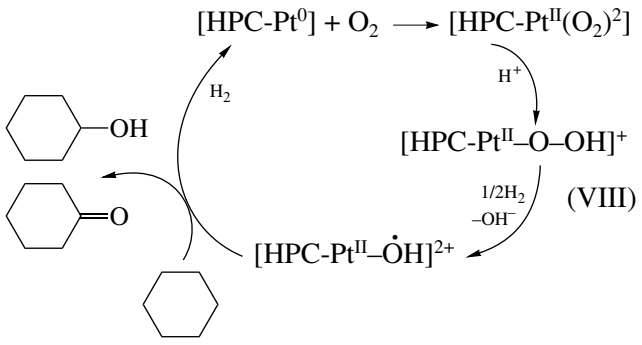
Fig. 8. Proportions of (*1*) cyclohexanol and (*2*) cyclohexanone in the product of cyclohexane oxidation in the presence of various HPCs. The liquid mixture contains 10 mg of 5% Pt/C, 1 ml of CH_3CN, 950 μmol of C_6H_{12}, and 10 mg of HPC. T = 35°C; $O_2 : H_2 = 1 : 2$; reaction time, 1 h.

ture occur only on modified metal surfaces [29]. We believe that the high activity of the Pt–HPC systems is due to the sorption of polyanions on metallic platinum [27].

Thus, HPCs of various compositions exert their modifying effect through adsorption on the platinum surface. The HPC–platinum interaction is as effective as the complexation of Pd(II) aqua complexes by $PW_{11}O_{39}^{7-}$ anions in solution [30]. Both the strongest capacity for Pd(II) coordination and the strongest modifying effect on the platinum surface were observed for the lacunar anion PW_{11} rather than for the structurally saturated anion PW_{12} (compare the activities of the PW_{12} and PW_{11} systems in Figs. 7 and 8).

Adsorption facilitates electron transfer from platinum to the oxygen molecule with the formation of a peroxo complex and then Pt(II) peroxide. Further reduction of the peroxide species located on Pt(II) results in hydroxyl radicals, which are intermediates typical of alkene peroxidation [31].

The sequence of conversions suggested is described by the following scheme:



The role of the HPC in scheme (VIII) is limited to bringing platinum to an electronic state favorable for catalysis. However, the observed dependence of the behavior of the catalytic system on HPC composition suggests that, aside from coordination, some other (e.g., redox) properties of HPCs are significant in this reaction. For example, the performance of the unsaturated polyanion PW_{11} was affected by introducing a redox-active ion of a first-row transition metal such as Fe(III), Cr(III), Mn(II), or Co(II) (Fig. 8). These ions show some catalytic activity in peroxide decomposition, while the PW_{11} anions are inactive in this reaction. Of the above ions, only Fe(III) slightly increased the amount of oxidation products. The other ions, which are more active peroxide decomposers, reduce the amount of oxidation products. Similar effects of metal-containing phosphotungstates were observed in alkene oxidation. The causes of these effects are discussed below.

Copper-containing HPCs act in a special way. Cu(II) ions can oxidize a platinum surface and make it incapable of reducing dioxygen. In the presence of the $PW_{11}Cu$ HPC, we did not detect any cyclohexane oxidation products and did not observe any sorption of O_2 or H_2.

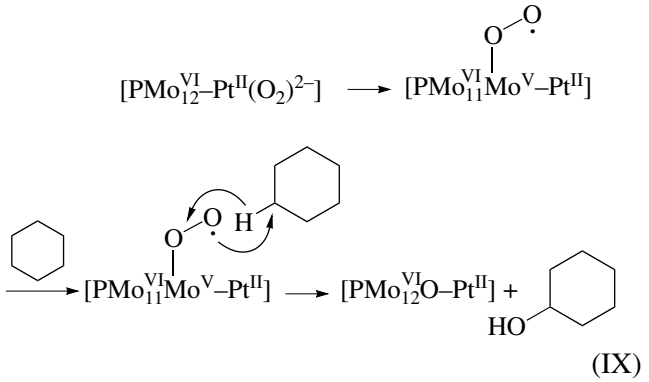
The phosphomolybdic acid H_3PMo_{12} turned out to be a more effective modifier than the phosphotungstic acid H_3PW_{12} (Fig. 7). The activity of both P–Mo and P–W HPCs can be increased by replacing one or several Mo(VI) or W(VI) ions with V(V) (Fig. 7). The highest activity in cyclohexane oxidation is shown by a catalytic system containing a P–Mo or a P–Mo–V polyacid. These HPCs can react with peroxides to form hydroperoxo compounds. At the same time, they allow V(V) ⟶ V(IV) and Mo(VI) ⟶ Mo(V) transitions

Table 3. Results of testing the heterogeneous catalysts 5% Pt/C and 5% PtPt–HPC/C in cyclohexane oxidation with an O_2–H_2 mixture

Catalyst	Composition of the liquid	Products, μmol	
		cyclohexanol	cyclohexanone
100 mg 5% Pt/C	1 ml C_6H_{12} + Hex_4NCl	0.15	–
50 mg 5% Pt-$NaPW_{11}$/C	1 ml C_6H_{12}	1	1.4
50 mg 5% Pt-Bu_4N-PMo_{12}/C	1 ml C_6H_{12}	0.7	2
50 mg 5% Pt-Bu_4N-PW_{11}/C	1 ml C_6H_{12}	2	2
50 mg 5% Pt/C	0.5 ml C_6H_{12} + 0.5 ml CH_3CN + Bu_4N-PW_{11}	64	22

Note: Conditions: 1 ml of liquid; T = 35°C; H_2 : O_2 = 2 : 1; reaction time, 1 h.

and can, therefore, act as reversible one-electron oxidizers. Initially, peroxide species located on platinum react with the oxidized form of HPC. Donating an electron to Mo(VI), they turn into radicals and become extraordinarily reactive in hydrocarbon oxidation. In particular, they are very reactive toward cyclohexane:



(IX)

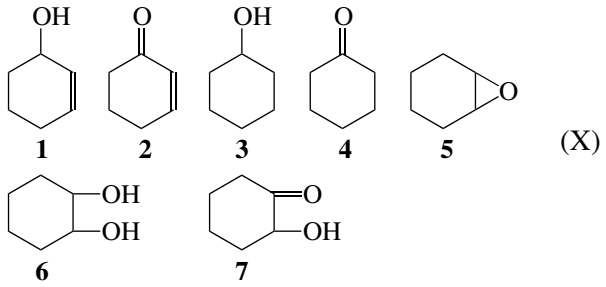
In the series of V-containing phosphomolybdates, we observed an interesting correlation between catalytic activity and the redox potential of the anions. The redox potential increases in the order PMo_{12} < $PMo_{11}V$ < $PMo_{10}V_2$. Catalytic activity increases in the same order (Fig. 7) because of the facilitation of electron transfer to the HPC, which is the process responsible for the formation of a reactive intermediate radical (scheme (IX)).

Thus, depending on modifier composition, several reactive free radicals may be involved as intermediates in cyclohexane oxidation (see schemes (VIII) and (IX)).

As is demonstrated in the previous section for α-pinene oxidation, hydrogen in the presence of the platinum catalyst suppresses the free-radical reaction at low temperatures. Earlier studies on liquid-phase systems of similar composition [27, 28] provided evidence that the free radicals react with the substrate on the catalyst surface without passing into the liquid bulk. However, when the reaction is conducted in acetonitrile, the appearance of intermediates in the liquid bulk cannot be ruled out, because the intermediates may be bound to the dissolved HPC. Nevertheless, the catalytic system is active without an HPC present in solution. This was demonstrated by testing two-component solid catalysts containing platinum and an HPC (Table 3). An Na^+ or Bu_4N^+ salt of a heteropoly acid was adsorbed onto the surface of a standard platinum catalyst. Oxidation was conducted without a solvent. The salts were not detected in the solution during the reaction because of their low solubility in cyclohexane and strong adsorption on the carbon support. For comparison, we made two runs involving the Pt/C catalyst with soluble modifiers, namely, tetrahexylammonium chloride in cyclohexane and Bu_4N–PW_{11} in a cyclohexane–acetonitrile mixture. In the Pt/C + Hex_4NCl system, we detected only traces of cyclohexanol. In pure cyclohexane with an insoluble Pt–HPC/C catalyst, we observed the formation of cyclohexanol and cyclohexanone, although their amounts were smaller than in the case of the Pt/C + Bu_4N–PW_{11} system in the solvent medium. Runs under conditions ruling out HPC dissolution demonstrated that cyclohexane can be oxidized with an O_2–H_2 mixture in the presence of a Pt–HPC heterogeneous catalyst.

Oxidation of Cyclohexene and α-Pinene with an Oxygen–Hydrogen Mixture

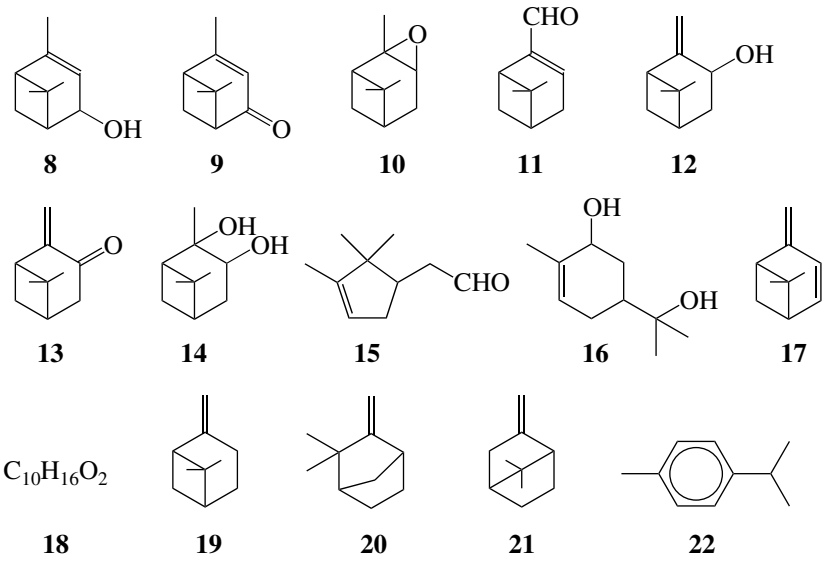
Catalytic systems based on platinum and an HPC were tested in the oxidation of the cyclic olefins cyclohexene and α-pinene with an O_2–H_2 mixture. Cyclohexene was converted into a mixture of oxygen-containing compounds, including cyclohexenol (**1**), cyclohexenone (**2**), cyclohexanol (**3**), cyclohexanone (**4**), and an epoxide (**5**) (scheme (X)). Compounds with two oxygen-containing functional groups (e.g., compounds **6** and **7**) made up approximately 25% of the total amount of products, and ~1% of the cyclohexene was converted into cyclohexane.



(X)

Compounds **3** and **4** probably resulted from cyclohexene oxidation followed by hydrogenation of adsorbed **1** and **2**. Compounds **1** and **5** should be viewed as a product of primary oxidation [32]. All primary products except the epoxide result from allylic oxygenation. The outcomes of cyclohexene oxidation in the presence of various HPCs were reported in an earlier paper [7].

The products of α-pinene conversion identified by chromatomass spectrometry [6] are presented in scheme (XI). The main products of the primary oxidation of α-pinene are verbenol (**8**), verbenone (**9**), and α-pinene oxide (**10**). Their amount is not larger than 20% of the total amount of α-pinene conversion products, although their secondary conversion in the presence of the platinum catalyst and polyphosphotungstates proceeds at a rather low rate. Other primary oxidation products are small amounts of myrtenal (**11**), pinocarveol (**12**), and pinocarvone (**13**). In the O_2–H_2 medium and in the presence of Pt–HPC catalysts, α-pinene oxidation is accompanied by isomerization, oxidative dehydrogenation, and acidic hydration [33]. α-Pinene conversion by-products include pinandiol (**14**), α-campholenic aldehyde (**15**), *trans*-sobrerol (**16**), verbenene (**17**), an unidentified compound (**18**), β-pinene (**19**), camphene (**20**), α-fenchene **21**, and *p*-cymene (**22**).



(XI)

It was found that the amount and composition of the primary products of cyclohexene and α-pinene oxidation depend on HPC composition. In systems involving phosphotungstates, introduction of redox-active transition-metal ions into the PW_{11} anion causes changes in catalytic properties (Figs. 9, 10) similar to the changes observed in cyclohexane oxidation.

In the presence of a Cr(III)-, Mn(II)-, or Co(II)-containing phosphotungstate, the amount of oxidation products is much smaller than in the case of pure PW_{11} or the Fe(III)-containing HPC. At the same time, these ions cause an increase in the proportion of allylic compounds and a decrease in the proportion of epoxides in the cyclohexene and α-pinene oxidation products. This effect of the ions arises from the fact that modified phosphotungstates differ in capacity to catalyze peroxide decomposition. Capacity for decomposing hydrogen peroxide increases in the order $PW_{11} < PW_{11}Fe < PW_{11}Mn < PW_{11}Cr < PW_{11}Co$ [34]. The highest yield of cyclohexene and α-pinene oxidation products is attained in the presence of phosphotungstates that show low or moderate activity in peroxide decomposition. This result can be explained using scheme (VIII). This scheme involves two intermediates, namely, the platinum peroxide compound $[HPC–Pt^{II}–O–OH]^+$ and the bound hydroxyl radical $[HPC–Pt^{II}–{}^{\bullet}OH]$. The formation of two intermediates explains why there are two primary oxidation products in alkene oxidation. Peroxides react with alkenes through electrophilic attack on the double bond, yielding an epoxide. Hydroxyl radicals are very reactive not only towards cyclohexane but also towards alkenes. In the case of alkenes, oxygenation at the allylic position takes place (reaction (XII)).

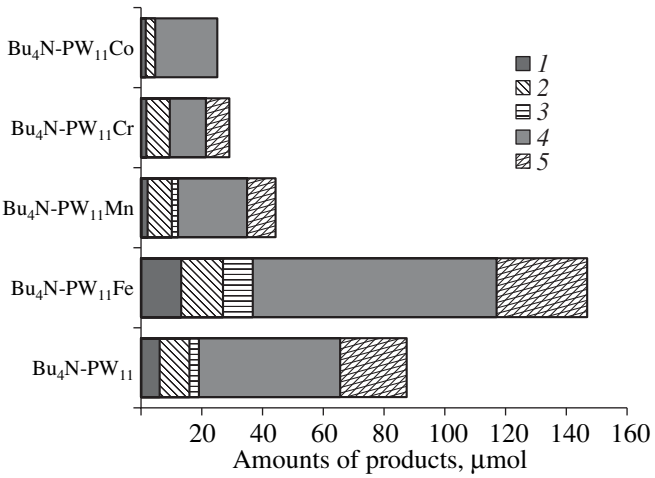


Fig. 9. Proportions of products resulting from the allylic oxidation of cyclohexene in the presence of various HPCs: (*1*) epoxide, (*2*) cyclohexanol, (*3*) cyclohexanone, (*4*) cyclohexenol, and (*5*) cyclohexenone. Reaction conditions: 10 mg of 5% Pt/C; 1 ml of CH_3CN; 970 μmol of C_6H_{10}; 4 mg of HPC; $T = 25°C$; $O_2 : H_2 = 1 : 2$; reaction time, 1 h.

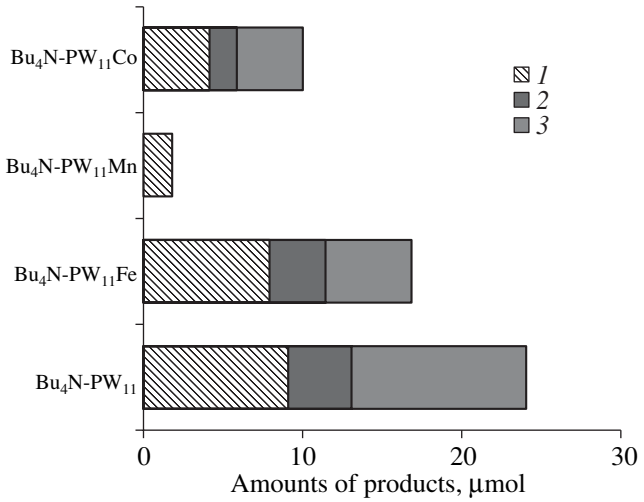
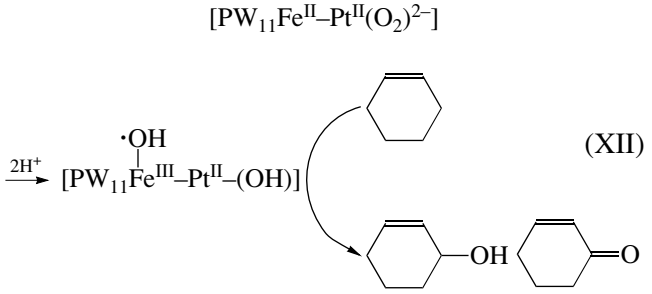


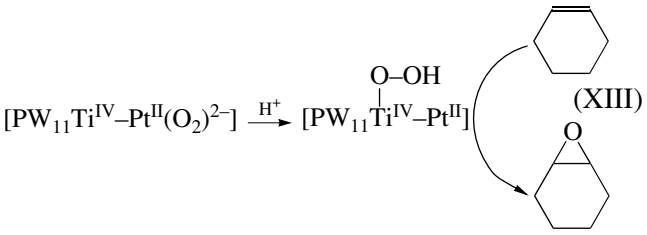
Fig. 10. Proportions of (*1*) verbenol, (*2*) verbenone, and (*3*) epoxide in the product of α-pinene oxidation in the presence of various HPCs. Reaction conditions: 50 mg of 5% Pt/C; 0.9 ml of CH_3CN; 600 μmol of α-pinene; 7 mg of HPC; $T = 15°C$; $O_2 : H_2 = 1 : 2$; reaction time, 1 h.

According to scheme (VIII), the decomposition of the peroxide species and the formation of hydroxyl radicals take place under the effect of platinum. Acceleration of these processes by the Fe-containing HPC increases the concentration of hydroxyl radicals in the medium, thus raising the yield of products of allylic oxidation (XII):



At the same time, the high activity of the Mn-, Cr-, and Co-containing HPCs results in unproductive peroxide decomposition yielding dioxygen without oxidizing the substrate. A similar situation was observed in the reaction between cyclohexene and hydrogen peroxide, in which cyclohexene was not oxidized because of the rapid decomposition of H_2O_2 [34].

Introduction of Ti(IV) or Zr(IV) ions into the HPC does not increase the yield of cyclohexene oxidation products, but it increases the proportion of the epoxide to 30–40% against 7–10% for PW_{11} (Fig. 11). Apparently, the Ti- and Zr-containing phosphotungstates are involved in oxygen transfer through formation of intermediate peroxo and hydroperoxo complexes. Oxygen in these complexes, as in other Ti- and Zr-containing peroxides, is more electrophilic than oxygen in the Pt(II) peroxide shown in scheme (VIII). As a consequence, these complexes are more active in the epoxidation reaction (XIII), but they do not afford allylic oxidation products.



In the presence of the platinum catalyst and a pure or metal-containing phosphotungstate, cyclohexene is more readily oxidizable than cyclohexane: cyclohexene oxidation at 25°C yields more products than cyclohexane oxidation at 35°C (Figs. 8, 9). A different situation is observed when a P–Mo HPC is used as the modifier (Figs. 8, 12). In these systems, the yield of cyclohexene oxidation products is lower and decreases as the redox potential of the polyanion increases in the order $PMo_{11}V$ (E_0 = 0.64 V) < $PMo_{10}V_2$ (E_0 = 0.70 V) < PMo_9V_3 (E_0 = 0.75 V) [35]. We cannot suggest a unique explanation for these results. Probably, the high activity of the systems containing a P–Mo or P–Mo–V–HPC causes rapid side reactions yielding high-boiling products that are undetectable by GC. Raising the redox potential of the HPC makes the system more active, accelerating secondary reactions at the same time. In subsequent studies, we will optimize the composition of the catalytic systems so as to achieve a higher selectivity with respect to primary products of alkene oxidation.

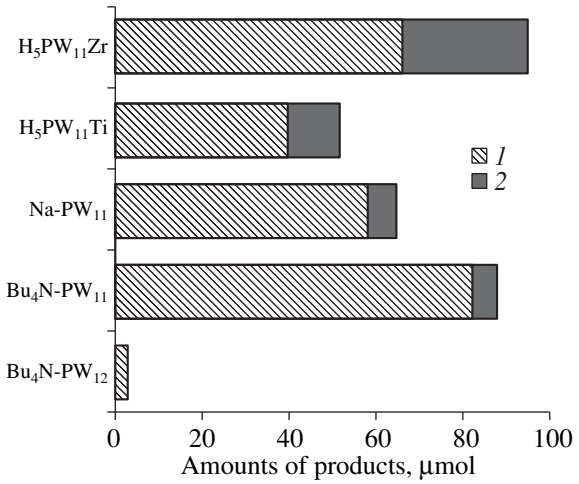


Fig. 11. Proportions of (*1*) products resulting from the allylic oxidation of cyclohexene and (*2*) epoxidation in the presence of various HPCs. Reaction conditions: 10 mg of 5% Pt/C; 1 ml of CH_3CN; 970 μmol of C_6H_{10}; 4 mg of HPC; $T = 25°C$; $O_2 : H_2 = 1 : 2$; reaction time, 1 h.

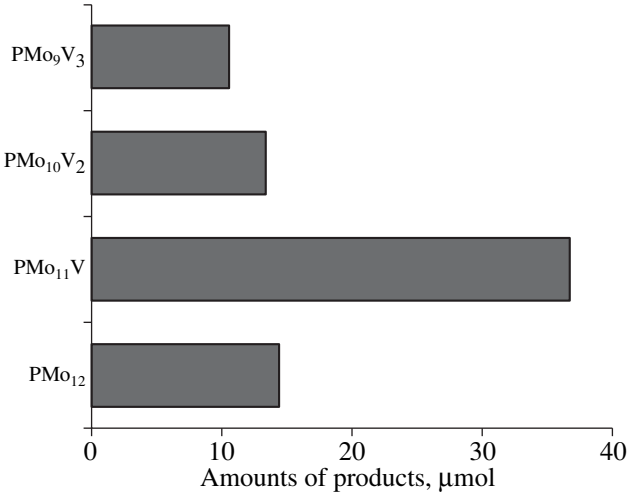


Fig. 12. Total yield of primary cyclohexene oxidation products in the presence of P–Mo–V–HPCs. Reaction conditions: 10 mg of 5% Pt/C; 1 ml of CH_3CN; 970 μmol of C_6H_{10}; 4 mg of HPC; $T = 25°C$; $O_2 : H_2 = 1 : 2$; reaction time, 1 h.

CONCLUSION

The two-component catalysts examined enabled us to achieve a high selectivity with respect to primary products in autooxidation reactions. At a cyclohexane conversion of 3.5%, cyclohexanol + cyclohexanone selectivity is above 90% and the reaction mixture contains no hydroperoxide. In the catalytic oxidation of α-pinene, primary-product selectivity is 86% at a substrate conversion of about 20%. Furthermore, the catalyst increases the proportions of verbenol and verbenone, which are the most valuable compounds among the primary oxidation products.

Conjugate oxidation reactions involving hydrogen have not been commercialized as yet. They are now at the conceptual design stage. Two results of this study are significant for practice: (1) The two-component catalysts Pt–PMo_{12} and Pt–$PMo_{11}V$ are the most active in the oxidation of unactivated hydrocarbons such as cyclohexane. (2) Pt–HPC solid catalysts are applicable when no component dissolution takes place.

Peroxide compounds participate in both types of reaction. Hydroperoxides are involved in autooxidation, and Pt(II) peroxides take part in conjugate oxidation with O_2–H_2 mixtures. Cyclohexyl hydroperoxide decomposes via the formation of free hydroxyl radicals. However, the molar yield of cyclohexanol + cyclohexanone does not exceed 100%; therefore, $^{\bullet}OH$ radicals do not react with cyclohexane. The other oxygen atom of hydroperoxide either spends itself for conversion of cyclohexanol into cyclohexanone or forms dioxygen. In the case of more reactive substrates such as alkenes, the peroxide can not only dissociate homolytically but also make an electrophilic attack on the substrate to produce an epoxide.

In conjugate oxidation with an O_2–H_2 mixture, the peroxo groups bound to Pt(II) turn into bound radical species. These species are responsible for cyclohexane oxidation. Although intermediate free radicals are present in this system, no free-radical chain reaction develops in the liquid bulk at the low temperatures typical for conjugate reactions. At higher temperatures, chain reaction is possible, but it is suppressed by hydrogen, as in the case of α-pinene oxidation.

Both peroxide and free-radical intermediates are involved in alkene oxidation reactions. The role of either of them can be judged from the ratio of the allylic oxidation products to the epoxidation products. Typical epoxidation catalysts, such as PW_{11}, $PW_{11}Ti$, and $PW_{11}Zr$, can form peroxide intermediates. This possibility is realized only in part, so the formation of allylic products is not ruled out.

The intermediates that are involved in oxidation with O_2–H_2 mixtures are very reactive, leading to low selectivity in the case of readily oxidizable substrates. Another complication comes from platinum-catalyzed side reactions. Further investigation is required to adapt the systems examined to oxidation of, e.g., α-pinene.

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