1544 Russian Chemical Bulletin, International Edition, Vol. 52, No. 7, pp. 1544—1551, July, 2003

Oxidation of cyclohexene and α-pinene with O_2—H_2 mixture in the presence of supported platinum or palladium catalysts

N. I. Kuznetsova,[a]* *L. I. Kuznetsova,*[a] *N. V. Kirillova,*[a] *L. M. Pokrovskii,*[b]
L. G. Detusheva,[a] *J.-E. Ancel,*[c] *and V. A. Likholobov*[a]

[a]*G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,*
5 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 3056. E-mail: kuznina@catalysis.nsk.su
[b]*N. N. Vorozhtsov Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
9 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4752. E-mail: pokrovsk@nioch.nsc.ru
[c]*ARCHEMIS, 24 Jean Jaurès av., 69153 Decines Charpieu, Cédex, France.**
E-mail: Jean-Erick Ancel@archemis-eu.com

Oxidation of cyclohexene and α-pinene with an O_2—H_2 mixture in the catalytic systems containing Pt or Pd and heteropoly compounds (HPC) was studied. The main oxidation products are epoxides, allyl alcohols, and ketones. The highest yield of the oxidation products was obtained in the presence of the platinum catalyst in combination with HPC PW_{11} or $PW_{11}Fe$. The reaction mechanism was proposed. A relationship between the HPC composition and the nature of intermediates involved in oxidation was examined.

Key words: cyclohexene, α-pinene, platinum, palladium, heteropoly compounds, oxygen, hydrogen, oxidation, catalysis.

Oxidation of hydrocarbons with an O_2—H_2 mixture attracts interest due to ecological safety of the process, mild reaction conditions, and selective effect of the oxidant.[1] This oxidant is used for the selective conversion of benzene to phenol[2—4] and oxidation of alkanes[5] and alkenes.[6,7] Catalysts for this process contain platinum metals and such additives as copper chloride, halides or oxides of other transition metals, and Ti silicates.

We have previously found[8—11] that combinations of Pt or Pd with heteropoly compounds with Keggin´s structure exhibit catalytic activity in the selective oxidation of benzene to phenol, cyclohexane to cyclohexanol and cyclohexanone, and saturated hydrocarbons to the corresponding alcohols and ketones with an O_2—H_2 mixture. These systems operate due to the interaction of heteropoly compounds (HPC) with metal ions (under homogeneous conditions) or with metallic particles (in the case of solid catalysts).

The key stage of the liquid-phase reactions is believed[2] to be the formation of H_2O_2 due to the incomplete O_2 reduction with hydrogen in the presence of a Platinum Group metal.[2] The more specific details of the mechanism, including effect of the second component, are not usually considered. In this work, we studied the behavior of the Pt (or Pd)—HPC liquid-phase catalytic systems. The data on the nature of active forms of oxygen are based on changes in the activity of the systems and the composition of the oxidation products with variation of the HPC composition.

Cyclic olefins, which are autooxidized at sufficiently high temperatures, were chosen as substrates. In the presence of platinum metal complexes, cyclohexene is oxidized with oxygen at 65 °C to form cyclohexenol and cyclohexenone, and the fraction of epoxide is at most 3% of the total amount of the products determined by GLC.[12] The autooxidation of α-pinene in the presence of transition metal compounds affords α-pinene oxide, which is the product of the attack of the hydroperoxide radicals at the α-pinene double bond,[13—16] along with the products of allylic oxidation, among which verbenol and verbenone predominate. In biomimetic systems containing the Mn^{III} porphyrin complexes and an additional reducing agent, cyclohexene is oxidized at 20 °C, yielding the products with different composition.[13] When H_2 [17] or ascorbate ions[18] are used in combination with colloidal platinum, epoxide is mainly formed, which is the product of the electrophilic attack of oxygen at the olefin double bond.[19] In this work, it seemed of interest to compare the transformations of cyclohexene and α-pinene to draw conclusions on the mechanism of oxidation of hydrocarbons in the catalytic systems under study.

---

* ARCHEMIS, 24 Avenue Jean Jaurès, 69153 Decines Charpieu Cédex, France.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1462—1468, July, 2003.

Experimental

Preparation of catalysts. Commercial reagents $H_3PW_{12}O_{40} \cdot 11H_2O$ (PW_{12}) and $H_3PMo_{12}O_{40} \cdot 14H_2O$ (PMo_{12}) (reagent grade) were used, the latter being used after purification by extraction with diethyl ether. Hereinafter in parentheses the conventional designations of HPC are presented. Heteropoly compounds $H_4PMo_{11}VO_{40} \cdot 13H_2O$ ($PMo_{11}V$), $H_5PMo_{10}V_2O_{40} \cdot 9H_2O$ ($PMo_{10}V_2$), and $H_6PMo_9V_3O_{40} \cdot 12H_2O$ (PMo_9V_3) were synthesized using a known procedure.[20] The syntheses of $H_4PW_{11}VO_{40} \cdot 10H_2O$ ($PW_{11}V$) and $H_6PW_9V_3O_{40} \cdot 10H_2O$ (PW_9V_3) have been described.[21] The compound $H_3PMo_6W_6O_{40} \cdot 13H_2O$ (PMo_6W_6) was synthesized by refluxing a solution of equimolar amounts of $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ for 1 h. Water was evaporated in air to obtain crystals. The compound $H_5PW_{11}TiO_{40} \cdot 6H_2O$ ($PW_{11}Ti$) was synthesized by extraction with diethyl ether from an aqueous solution of the sodium salt in 5 *N* H_2SO_4,[22] and $H_5PW_{11}ZrO_{40} \cdot 7H_2O$ ($PW_{11}Zr$) was synthesized using a known procedure.[23]

Tetrabutylammonium salts
$(Bu_4N)_3PW_{12}O_{40}$ (Bu_4N-PW_{12}),
$(Bu_4N)_5H_2PW_{11}O_{39}$ (Bu_4N-PW_{11}),
$(Bu_4N)_4HPW_{11}Fe(OH)O_{39}$ (Bu_4N-$PW_{11}Fe$),
$(Bu_4N)_4HPW_{11}Mn(H_2O)O_{39}$ (Bu_4N-$PW_{11}Mn$),
$(Bu_4N)_4PW_{11}Cr(H_2O)O_{39}$ (Bu_4N-$PW_{11}Cr$),
$(Bu_4N)_4HPW_{11}Co(H_2O)O_{39}$ (Bu_4N-$PW_{11}Co$),
and $(Bu_4N)_4HPW_{11}Cu(H_2O)O_{39}$ (Bu_4N-$PW_{11}Cu$)
were synthesized according to a described procedure.[24] The salts $(Bu_4N)_3PMo_{12}O_{40}$ (Bu_4N-PMo_{12}), $(Bu_4N)_4PMo_{11}VO_{40}$ (Bu_4N-$PMo_{11}V$), and $(Bu_4N)_5PMo_{10}V_2O_{40}$ (Bu_4N-$PMo_{10}V_2$) were synthesized similarly.

The Pt(5%)/C catalyst was prepared by the alkaline hydrolysis of H_2PtCl_6 over the Sibunit pyrocarbon powder (S_{sp} = 300 $m^2 g^{-1}$) followed by reduction with sodium formate.

The Pt(1%)/SiO_2 catalyst was prepared by the adsorption of $Pt(NH_3)_4Cl_2$ from an aqueous solution on SiO_2 (S_{sp} = 200 $m^2 g^{-1}$, granule size 0.2—0.5 mm). The sample was dried in air first at ~20 °C and then at 100 °C for 2 h, calcined at 300 °C for 2 h, and reduced in an H_2 flow at 300 °C.

The Pd(1%)/SiO_2 catalyst was prepared by the impregnation of SiO_2 with a solution of H_2PdCl_4. The sample was dried, calcined, and reduced as the previous sample.

The Na-$(PW_9O_{34})_2Pd_2Fe/SiO_2$ catalyst containing 1 wt.% Pd was prepared by the impregnation of SiO_2 with an aqueous solution of the sodium salt of the Pd^{II}- and Fe^{III}-containing HPC.[9] The sample was dried in air at ~20 °C and then at 100 °C for 2 h and reduced in an H_2 flow at 300 °C.

Catalytic experiments. Alkenes were oxidized at an atmospheric pressure. The solid catalyst was loaded in a reactor in which a constant temperature was maintained, MeCN (1.0 mL) and then soluble HPC (or tetrahexylammonium chloride (Hex_4NCl) or LiCl) were added, and the mixture was thoroughly stirred. An O_2—H_2 (1 : 2) mixture was passed through the reactor, which then was connected to a gas burette filled with the same gas mixture, α-pinene or cyclohexene was injected with a syringe, and the mixture was stirred for 1 h, maintaining an atmospheric pressure in the reactor. Then the liquid was separated from the solid catalyst by centrifuging and analyzed by GLC (Kristall 2000 chromatograph, flame-ionization detector, DB-1701 capillary column 30 m × 0.53 mm). The content of the main oxidation products (*cis*- and *trans*-verbenols, verbenone, α-pinene oxide, and *cis*-pinan-2-ol) was determined from the surface area of the chromatographic peaks using calibration plots. The other products were determined from the ratio of surface areas of the chromatographic peaks using no calibration coefficients.

Reaction products were identified by chromato-mass spectrometry (GLC-MS) (Hewlett-Packard 5890/II chromatograph and a Hewlett-Packard MSD 5971 quadrupole mass spectrometer). An HP-5 quartz column 30 m × 0.25 mm with the film thickness of the stationary phase 0.25 μm was used. Qualitative analysis was carried out by comparison of retention times of compounds in the mixture and their total mass spectra with the corresponding data for pure components or with the spectra from the Wiley275 Library of Mass Spectrometric Data (275000 mass spectra).

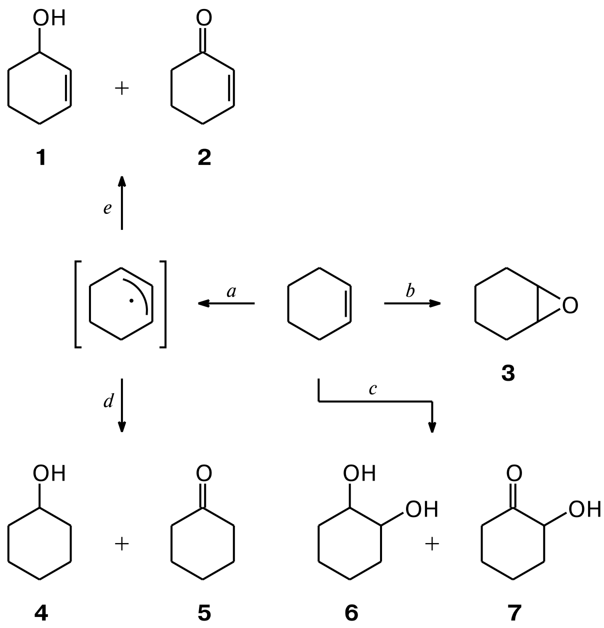
Results and Discussion

Cyclohexene and α-pinene are slowly oxidized with molecular oxygen at room temperature. The application of the platinum catalysts both without and in combination with HPC produced no noticeable amount of the reaction products. Under the same conditions, the catalytic oxidation of cyclic olefins with an O_2—H_2 mixture occurs much more rapidly. A Platinum Group metal (usually platinum or, in some experiments, palladium) supported on an inert material (carbon or silica gel) combined with HPC was used as catalyst. In some experiments, Hex_4NCl or LiCl were used instead of HPC for comparison.

Oxidation of cyclohexene. The oxidation of cyclohexene with an O_2—H_2 gas mixture in the presence of the Pt/C catalyst and HPC or Hex_4NCl dissolved in acetonitrile affords oxygen-containing compounds. The oxidation products consist of cyclohexenol (**1**), cyclohexenone (**2**), epoxide (**3**), cyclohexanol (**4**), cyclohexanone (**5**), and products with two oxygen-containing functional groups (**6**) and (**7**) (according to the GLC-MS data) (Scheme 1). In addition, ~1% cyclohexene are transformed into cyclohexane. Cyclohexene is hydrogenated with almost the same rate in the presence of Hex_4NCl and various HPC.

Cyclohexanol and cyclohexanone can be formed *via* several routes: hydrogenation of the corresponding unsaturated products or epoxide, oxidation of cyclohexane formed in the reaction, and hydration of cyclohexene. We studied the transformations of cyclohexenol, cyclohexenone, and cyclohexene oxide, which were specially introduced into the reaction medium. These compounds turned out to be rather stable under the reactions conditions: they were not remarkably hydrogenated and oxidized within the standard reaction time. Cyclohexane (which is present in the mixture) cannot yield the amount of oxidation products comparable with that of cyclo-

Scheme 1



a. Homolytic mechanism; *b*. electrophilic oxidation; *c*. secondary reactions; *d*. oxidation, hydrogenation; *e*. oxidation.

hexene, because the cyclohexane concentration even to the end of the reaction is 100-fold lower and the reactivity is not higher than that of cyclohexene.[11] Finally, if a saturated alcohol was formed by the hydration of cyclohexene, it would be reasonable to expect its higher yield in the systems with HPC. In our experiments, cyclohexanol was formed in comparable amounts in the presence of acids and tetrabutylammonium salts. It is most likely that cyclohexanol and cyclohexanone are formed due to oxidation at the allyl position followed by fast hydrogenation of the double bond. Hydrogenation can be facilitated when the allyl group is bound to the surface of the platinum catalyst.

The mechanism of formation of compounds **6** and **7** with two oxygen-containing functional groups remains yet unclear.

The ratio between the yields of the oxygen-containing products depends on the composition of the second component of the catalytic system (Table 1). In the catalytic system involving Hex_4NCl, the yield of epoxide **3** is only 1.5% of the overall amount of the primary oxidation products with one oxygen-containing group (**1—5**) or ~1% of the sum of all the products found (see Table 1, entry *1*). When Hex_4NCl is replaced by $Bu_4N\text{-}PW_{11}$, the activity of the system increases considerably, and the fraction of epoxide **3** is ~5% (see Table 1, entry *2*). In the presence of the coordinatively saturated HPC $Bu_4N\text{-}PW_{12}$, the system is inactive (see Table 1, entry *3*).

The introduction of transition metal ions into the HPC composition changes substantially their behavior in the catalytic systems under study. Heteropoly acids $PW_{11}Zr$ and $PW_{11}Ti$ do not surpass $Bu_4N\text{-}PW_{11}$ in activity. However, the fraction of epoxide in the sum of the primary and all observed oxidation products in the presence of HPC containing Ti^{IV} and Zr^{IV} increases to ~20—30% (see Table 1, entries *4* and *5*). The catalytic activity of the system increases when the Fe^{III} ions are introduced into

Table 1. Yields of the main products of cyclohexene oxidation* and their fraction in the total amount of the products (in parentheses)

Entry	Additive	Yield/μmol (mol.%)					
		1	**2**	**3**	**4**	**5**	**6** + **7**
1	Hex_4NCl	16.0 (35.0)	8.7 (19.0)	0.5 (1.1)	6.5 (14.0)	2.5 (5.5)	11.0 (25.0)
2	$Bu_4N\text{-}PW_{11}$	46.0 (44.0)	22.0 (21.0)	5.6 (5.4)	10.0 (9.6)	3.5 (3.4)	17.0 (17.0)
3	$Bu_4N\text{-}PW_{12}$	1.3	0.5	—	1.0	—	2.0
4	$PW_{11}Ti$	12.0 (21.0)	5.1 (9.0)	12.0 (21.0)	13.0 (23.0)	10.0 (18.0)	4.2 (7.5)
5	$PW_{11}Zr$	30.0 (30.5)	28.0 (28.0)	28.0 (28.0)	6.0 (6.1)	3.0 (3.0)	3.4 (3.4)
6	$Bu_4N\text{-}PW_{11}Fe$	80.0 (47.0)	30.0 (18.0)	13.0 (7.7)	14.0 (8.3)	10.0 (5.9)	22.0 (13.0)
7	$Bu_4N\text{-}PW_{11}Mn$	23.0 (41.0)	9.5 (17.0)	1.9 (3.4)	7.9 (14.0)	2.0 (3.5)	12.0 (21.0)
8	$Bu_4N\text{-}PW_{11}Cr$	12.0 (36.0)	7.2 (21.0)	1.5 (4.5)	8.0 (24.0)	—	5.0 (15.0)
9	$Bu_4N\text{-}PW_{11}Co$	1.4 (4.0)	20.0 (57.0)	7.5 (21.0)	3.0 (8.6)	—	3.0 (8.0)
10	PMo_{12}	9.7 (48.0)	3.6 (18.0)	0.1 (0.5)	1.0 (4.9)	—	6.0 (29.0)
11	$PMo_{11}V$	25.0 (51.0)	5.0 (10.0)	0.1 (0.2)	5.6 (11.0)	1.0 (2.1)	12.0 (25.0)
12	$PMo_{10}V_2$	10.0 (49.0)	1.7 (8.3)	—	1.6 (7.8)	—	7.2 (35.0)
13	PMo_9V_3	8.0 (62.0)	2.0 (16.0)	—	0.5 (3.8)	—	2.5 (18.0)
14	$Bu_4N\text{-}PMo_{12}$	8.6 (49.0)	2.1 (12.0)	0.4 (2.3)	2.2 (13.0)	—	4.2 (24.0)
15	$Bu_4N\text{-}PMo_{11}V$	29.0 (55.0)	8.4 (16.0)	0.4 (0.8)	2.6 (5.0)	—	12.0 (16.0)
16	$Bu_4N\text{-}PMo_{10}V_2$	7.8 (51.0)	2.0 (13.0)	0.4 (2.6)	1.7 (11.0)	—	3.3 (22.0)

* Conditions: 10 mg of Pt(5%)/C, 4 mg of HPC or Hex_4Cl, 1 mL of MeCN, 0.97 mmol of C_6H_{10}, $O_2 : H_2 = 1 : 2$; 25 °C, reaction duration 1 h.

the HPC composition (see Table 1, entry *6*). Other redox-active ions (Mn^{II}, Cr^{III}, and Co^{II}) decrease the yield of the products (see Table 1, entries *6—9*). The systems involving HPC P-Mo and P-Mo-V afford less oxidation products, regardless of using HPC as acids or Bu_4N salts. The yields of the oxygenation products increases on going from PMo_{12} to $PMo_{11}V$ (see Table 1, entries *10*, *11* and *14*, *15*). The introduction of the next V atom into HPC has no positive effect (see Table 1, entries *12* and *16*), and the third vanadium atom worsens the catalytic properties of HPC (entry *13*). The fraction of epoxide in the systems with Bu_4N-PMo_{12} and Bu_4N-$PMo_{12-n}V_n$ is lower than 3%.

Oxidation of α-pinene. Under the catalytic reaction conditions, α-pinene oxidation is accompanied by hydrogenation and isomerization. The complete analysis of the products of α-pinene conversion was performed for three catalytic systems: I — Pd(1%)/SiO_2 + solution of LiCl in MeCN, II — Na-$(PW_9O_{34})_2Pd_2Fe/SiO_2$, and III — Pt(1%)/$SiO_2$ + solution of $H_3PMo_{12}O_{40}$ in MeCN. The results obtained are presented in Table 2. In addition, the catalyzate contains 0.5—10% of nonidentified products.

The products of α-pinene (**8**) conversion are shown in Scheme 2.

At 25 °C the products of allylic oxidation are formed in systems I and III: verbenol (**9**) (with predomination of the *trans*-isomer) and verbenone (**10**). The highest yield of these products (30%) is achieved in system III. The temperature increase to 35 °C decreases the yield of these products (see Table 2). α-Pinene oxide (**11**) was not found but the products of its acid-catalyzed hydration and isomerization, *viz*., (1*S*,2*S*,3*R*,5*S*)-pinanediol (**12**), α-campholenaldehyde (**13**), and *trans*-sobrerol (**14**), are present. Myrtenal (**15**), the isomer of verbenone, is formed in a lower amount than verbenone. The other oxidation products are pinocarveol (**16**), pinocarvone (**17**), and verbenene (**18**) (*viz*., the product of oxidation and isomerization of the double bond). In addition to compounds with one oxygen-containing group, an unknown product with the $C_{10}H_{16}O_2$ composition (**19**) is present in considerable amounts. Judging from the molecular weight 168, this product contains two oxygen-containing functional groups.

In Pd-containing systems I and II, α-pinene is hydrogenated to pinane (**20**), which is probably oxidized further to *trans*-pinan-2-ol (**21**). The total yield of these two products was ~15%. In the presence of the Pt catalyst, α-pinene is not hydrogenated.

α-Pinene is isomerized more efficiently in the Pd-containing systems I and II, producing β-pinene (**22**), camphene (**23**), and α-fenchene (**24**) in a 10—20% yield of the total amount of the products formed.

The acid-catalyzed[25] cleavage of the C_4 cycle in the α-pinene molecule to form limonene (**25**) and terpinolene (**26**) occurs only in system III at 35 °C. The oxidative dehydrogenation of these products affords *p*-cymene (**27**) (see Table 2).

The study of the products of α-pinene conversion in the catalytic systems with different compositions makes it possible to determine all compounds that formed. The main transformations of α-pinene are not related to its oxidation, and the primary oxidation products undergo further transformations. We checked the stability of verbenol, verbenone, and α-pinene oxide in the presence of the catalyst in an inert atmosphere and on contact with an O_2—H_2 mixture after these compounds (6—32 μmol)

Scheme 2

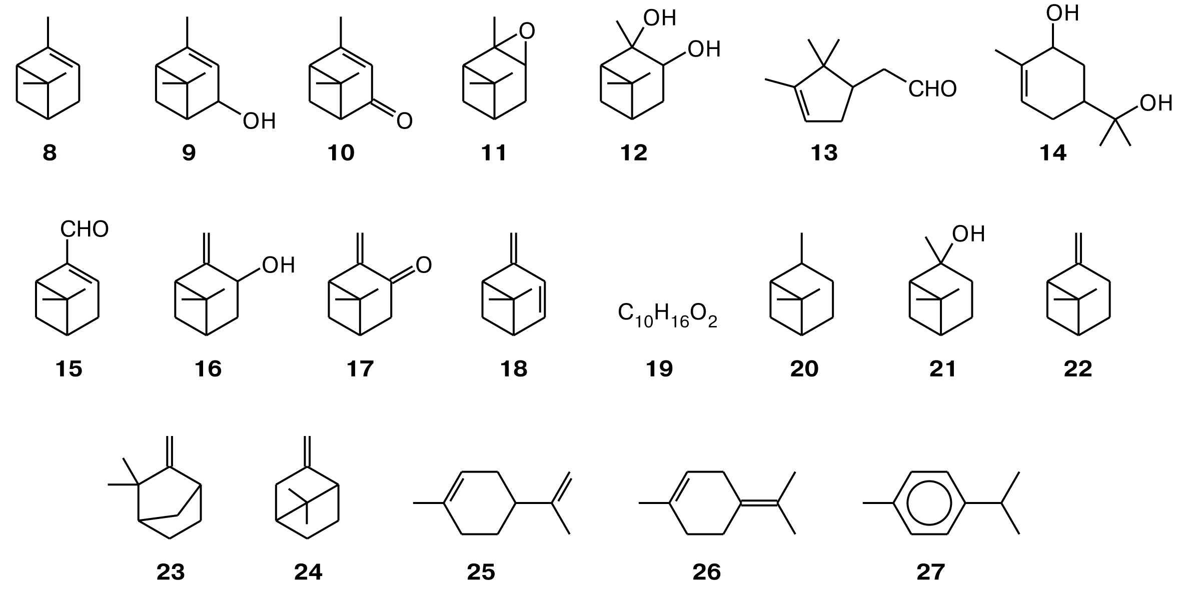


Table 2. Influence of the catalytic system (I—III),* temperature, and reaction duration on the yields of the main products of α-pinene conversion with an O_2—H_2 mixture (mol.% of the total amount of the GC detected compounds) (0.1 mmol of α-pinene, 1 mL of MeCN, $O_2 : H_2 = 1 : 2$)

Compound	Yield (mol.%)			
	I (1 h, 25 °C)	II (1 h, 35 °C)	III (3 h)	
			25 °C	35 °C
α-Pinene (**8**)	89.00	62.00	77.00	75.00
Verbenol (**9**)	1.30 (*trans*)	—	4.90 (*trans*) 0.26 (*cis*)	—
Verbenone (**10**)	0.37	—	1.70	1.30
α-Pinene oxide (**11**)	—	—	—	—
(1*S*,2*S*,3*R*,5*S*)-Pinanediol (**12**)	—	—	1.30	1.70
α-Campholenaldehyde (**13**)	0.79	2.40	0.86	0.84
trans-Sobrerol (**14**)	—	—	0.54	—
Myrtenal (**15**)	0.31	—	0.87	1.20
Pinocarveol (**16**)	0.10	1.20	1.30	1.20
Pinocarvone (**17**)	—	—	0.49	0.65
Verbenene (**18**)	0.06	0.76	0.64	1.40
Nonidentified product (**19**)	2.40	15.00	4.00	7.40
cis-Pinane (**20**)	0.39	1.30	—	—
trans-Pinan-2-ol (**21**)	1.60	3.40	—	—
β-Pinene (**22**)	1.90	1.60	0.18	0.11
Camphene (**23**)	0.75	1.20	0.90	0.82
α-Fenchene (**24**)	0.23	0.20	0.28	0.30
Limonene (**25**)	—	—	—	0.95
Terpinolene (**26**)	—	—	—	0.16
p-Cymene (**27**)	—	—	0.35	1.30

* I — Pd(1%)/SiO_2 (50 mg) + LiCl (atomic ratio Pd : Cl = 1 : 1), II — Na-$(PW_9O_{34})_2Pd_2Fe/SiO_2$, Pd content 1% (50 mg), III — Pt(1%)/SiO_2 (50 mg) + $H_3PMo_{12}O_{40}$ (7 mg).

were added to the components of the catalytic system. The amount of the introduced compounds remained unchanged for 1 h (standard duration of the catalytic reaction) in the presence of the Pt/C catalyst both under N_2 and an O_2—H_2 gas mixture. In the presence of $H_3PMo_{12}O_{40}$, verbenol is gradually consumed to be transformed into verbenone and insoluble tarry compounds, which were not identified by GLC. A similar pattern is observed for α-pinene oxide, which is partially transformed into campholenaldehyde (**13**) in the presence of $H_3PMo_{12}O_{40}$. Under the reaction conditions, verbenone is retained in the solution.

The composition of the products of α-pinene conversion is presented in Table 3 for the systems containing the Pt(5%)/C catalyst, Hex_4NCl, and HPC. The main distinction from the reaction of cyclohexene is the higher yield of epoxide. In the oxidation of α-pinene in the presence of Bu_4N-PW_{11}, epoxide **11** constitutes ~50% of the total amount of the oxidation products **9** + **10** + **11** (see Table 3, entry *2*). The addition of Fe^{III} decreases the fraction of epoxide (entry *3*), whereas Co^{II} and Mn^{II} noticeably decrease the total amount of the oxidation products (entries *4* and *5*).

In the systems with HPC P-Mo and P-Mo-V, less oxidation products are formed. When the acidic form of HPC is used, epoxide is completely converted (see Table 3, entries *6* and *8*), unlike the runs with the corresponding Bu_4N salts (entries *7* and *9*). The overall amount of the oxidation products is somewhat higher in the case of $PMo_{10}V_2$ than that for PMo_{12}. The total amount of the products determined by GLC is smaller in the systems with HPC P-Mo and P-Mo-V, which is caused, at least partially, by secondary transformations of these substances with formation of insoluble tarry compounds.

In the case of the Pt(5%)/C catalyst and $H_3PMo_{12}O_{40}$, we also studied the temperature effect on the composition of the products of α-pinene oxidation in the interval from −5 to 25 °C (Table 4). The total yield of verbenol **9** and verbenone **10** depends slightly on the temperature, although the temperature decrease increases the fraction of the first product. α-Pinene oxide was not found in the whole temperature interval studied.

Mechanism of oxidation of cyclohexene and α-pinene. When the two-component catalytic systems are used for the synthesis of H_2O_2 from O_2—H_2 and for the oxidation of organic compounds, the key point is the formation of peroxide species coordinated with platinum[1]

$$[Pt^0] + O_2 \rightarrow [Pt^{2+}(O_2)^{2-}].$$

In our experiments, the Pt or Pd catalysts exhibited activity in combination with the second component, *viz.*, Hex_4NCl, LiCl, or HPC. The function of the second component is first of all, probably, stabilization of the oxidized platinum or palladium species.[8] This facilitates the two-electron transfer from the metal to oxygen to form a peroxo complex (Scheme 3) and a peroxide compound of Pt^{II}. The coordination of the peroxide species to the Pt^{II} atom impedes the further reduction of oxygen to water and allows the peroxide O atom to be involved in the alkene oxidation. The reactions suggested are shown in Scheme 3. Epoxide is formed due to the electrophilic attack of the peroxide oxygen atom at the double bond, while the formation of the allylic oxidation products (cyclohexenol and then cyclohexenone) occurs *via* one-electron reduction of the coordinated peroxide and generation of the $OH^{\bullet}$ radicals.

In the presence of chlorides, the yield of epoxide is low compared to the allylic oxidation products, indicating of the predomination of the radical route through the $HO^{\bullet}$ radical. However, the chemical properties of the

Table 3. Influence of the Hex_4NCl or HPC additive on the yields of verbenol (**9**), verbenone (**10**), and α-pinene oxide (**11**) in the oxidation[a] of α-pinene

Entry	Additive	Yield/μmol (mol.%)[b]			
		9	**10**	**11**	ΣP_i^c/μmol
1	Hex_4NCl	5.4 (60)	1.8 (20)	1.8 (20)	60
2	$Bu_4N\text{-}PW_{11}$	9.2 (37)	3.8 (16)	11.0 (47)	120
3	$Bu_4N\text{-}PW_{11}Fe$	8.1 (48)	3.4 (20)	5.3 (32)	130
4	$Bu_4N\text{-}PW_{11}Mn$	1.9 (100)	—	—	140
5	$Bu_4N\text{-}PW_{11}Co$	4.2 (42)	1.6 (16)	4.2 (42)	180
6	PMo_{12}	9.2 (70)	3.9 (30)	—	43
7	$Bu_4N\text{-}PMo_{12}$	5.3 (64)	1.7 (20)	1.3 (16)	19
8	$PMo_{10}V_2$	10.0 (74)	3.5 (26)	—	60
9	$Bu_4N\text{-}PMo_{10}V_2$	6.2 (58)	2.0 (19)	2.5 (23)	51

[a] Conditions: 0.6 mmol of α-pinene, 0.9 mL of MeCN, 15 °C, $O_2 : H_2 = 1 : 2$; Pt(5%)/C catalyst (50 mg) and HPC or Hex_4NCl (7 mg).

[b] Of the total amount of compounds **9** + **10** + **11**.

[c] Total amount of the conversion products.

Table 4. Temperature effect on the yields of verbenol (**9**), verbenone (**10**), and α-pinene oxide (**11**) in α-pinene oxidation in the presence of the Pt(5%)/C catalyst (50 mg) + $H_3PMo_{12}O_{40}$ (7 mg) (0.6 mmol of α-pinene, 1 mL of MeCN, $O_2 : H_2 = 1 : 2$)

Compound	Yield/μmol			
	−5 °C	5 °C	15 °C	25 °C
9	5.7	9.3	9.2	9.6
10	1.7	4.4	3.9	6.5
11	—	—	—	—

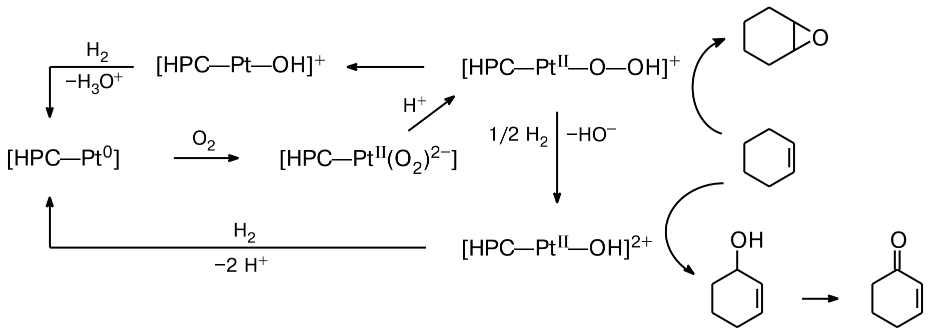
second component, for example, some HPC, can exert a substantial effect on the behavior of the catalytic system.

It is known[24] that the PW_{11}^- anions react with peroxides to produce peroxo complexes and catalyze the selective epoxidation of alkenes. The presence of $Bu_4N\text{-}PW_{11}$ in the system under study increases the fraction of epoxide in the oxidation products compared to Hex_4NCl. The yield of epoxide is low in the case of cyclohexene but becomes more substantial for α-pinene in which the double bond is easily subjected to the electrophilic attack.

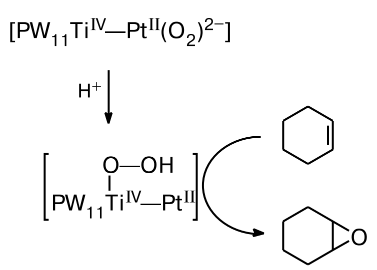
A similar effect is manifested in the case of the HPC $PW_{11}Ti$ and $PW_{11}Zr$, which are known as catalysts of epoxidation of alkenes with peroxide compounds.[26] In the presence of these HPC, cyclohexene epoxidation is much more selective compared to that in the case of Hex_4NCl or other HPC. We assume that the formation of epoxide involves the Ti^{IV} or Zr^{IV} peroxide complexes (Scheme 4).

The iron ions in the HPC composition direct the reaction predominantly toward allylic oxidation. It is most likely that the presence of Fe^{III} favors the formation of the $HO^\bullet$ radicals from peroxide. The replacement of Fe^{III} by other transition metals decreases the yield of the oxidation products, although H_2O_2 decomposition in the presence of HPC $PW_{11}Mn$, $PW_{11}Cr$, and $PW_{11}Co$, according to the previously obtained data,[24] is more efficient compared to that in the presence of $PW_{11}Fe$. It is most likely that oxidation in our systems requires the optimum activity of HPC in peroxide decomposition. The radical route of alkene oxidation also predominates in the presence of HPC P-Mo and P-Mo-V or their Bu_4N salts, as shown by the ratio between epoxide and the products of allylic oxi-

Scheme 3



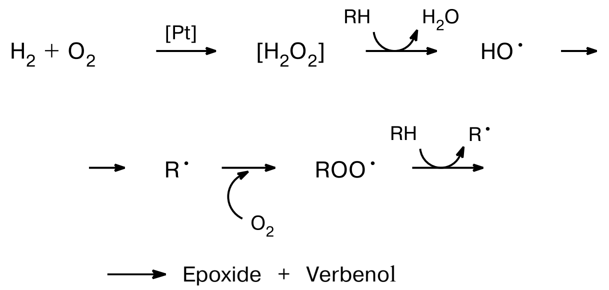
Scheme 4



dation in the reactions with cyclohexene and α-pinene. The radical character of the reaction is caused by the redox activity of these HPC, which increases in the presence of the V^V ions in HPC.[27]

A specific feature of α-pinene oxidation should be noted. In all systems where epoxide did not undergo intense secondary transformations, its yield relative to the sum of the primary oxidation products was higher than that in the case of cyclohexene. This was manifested even in the systems in which H_2O_2 was intensely decomposed, in particular, in the presence of the Fe^{III}- and Co^{II}-containing HPC. This fact can be explained by the higher reactivity of the double bond of α-pinene with respect to the electrophilic attack of the peroxide oxygen atom. Unlike cyclohexene, the radical oxidation of α-pinene with oxygen at ~90 °C in the presence of the Co, Cr, and Cu complexes[15] and noncatalyzed autooxidation[14] exhibit the same high yield of α-pinene oxide: to 50% of the total amount of verbenol, verbenone, and α-pinene oxide. These reactions also afford myrtenal, pinocarveol, and pinocarvone, *viz*., the products of radical transformations of α-pinene. Taking into account these facts, an alternative mechanism of the reaction can be proposed. Earlier[8—11] we believed that active intermediates are formed on the metallic catalyst surface modified by the second component, in particular, HPC. However, the escape of some intermediates into the liquid phase bulk cannot be excluded. In this case, oxidation proceeds *via* Scheme 5.

Scheme 5



The formation of other products of α-pinene oxidation, including myrtenal (**15**), pinocarveol (**16**), and products of its transformation (see Scheme 2), agrees with the radical mechanism of the reaction. In the presence of H_2, α-pinene is oxidized in MeCN at much lower temperatures (≤25 °C) than the temperatures of autooxidation due to the initiation of the chain radical process by the $HO^{\bullet}$ radicals formed on the platinum surface.

The results obtained show that the catalytic effect of the Platinum Group metals in alkene oxidation with an O_2—H_2 gas mixture is determined, to a great extent, by the nature of the second component of the system. The reaction involves several types of active intermediates, which manifest the radical or electrophilic character in the reactions with alkenes. For example, PW_{11} and, to a greater extent, $PW_{11}Ti$ and $PW_{11}Zr$ can form intermediates of the peroxide type responsible for the transformation of alkenes into epoxides, whereas Fe-, Mn-, Cr-, and Co-containing heteropolytungstates, as well as PMo_{12} and $PMo_{12-n}V_n$, generate oxygen species of the radical character leading to oxidation at the allyl position.

The authors thank A. S. Lisitsyn (Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences) for the kindly presented Pt(5%)/C catalyst.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-15-97447).

References

1. M. G. Clerici and P. Ingallina, *Catal. Today*, 1998, **41**, 351.
2. T. Miyake, M. Hamada, Y. Sasaki, and M. Oguri, *Appl. Catal.*, 1995, **131**, 33.
3. T. Kitano, T. Nakai, M. Nitta, M. Mori, S. Ito, and K. Sasaki, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2850.
4. H. Ehrich, H. Berndt, M.-M. Pohi, K. Jähnisch, and M. Baerns, *Appl. Catal. A*, 2002, **230**, 271.
5. EP Pat. 469662 A1; *Chem. Abstr.*, 1991, **116**, 818.
6. N. I. Kuznetsova, A. S. Lisitsyn, and V. A. Likholobov, *React. Kinet. Catal. Lett.*, 1989, **55**, 205.
7. N. I. Kuznetsova, A. S. Lisitsyn, A. I. Boronin, and V. A. Likholobov, *Stud. Surf. Sci. Catal.*, 1990, **55**, 89.
8. N. I. Kuznetsova, L. G. Detusheva, L. I. Kuznetsova, M. A. Fedotov, and V. A. Likholobov, *J. Mol. Catal. A: Chem.*, 1996, **114**, 131.
9. N. I. Kuznetsova, L. I. Kuznetsova, L. G. Detusheva, V. A. Likholobov, M. A. Fedotov, S. V. Koscheev, and E. B. Burgina, *Stud. Surf. Sci. Catal.*, 1997, **110**, 1203.
10. L. I. Kuznetsova, N. I. Kuznetsova, L. G. Detusheva, M. A. Fedotov, and V. A. Likholobov, *J. Mol. Catal. A: Chem.*, 2000, **158**, 429.
11. N. V. Kirillova, N. I. Kuznetsova, L. I. Kuznetsova, and V. A. Likholobov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 894 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 975].
12. A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, *J. Organomet. Chem.*, 1971, **26**, 417.
13. V. L. Rubailo and S. A. Maslov, *Zhidkofaznoe okislenie nepredel´nykh soedinenii* [*Liquid-Phase Oxidation of Unsat-*

urated Compounds], Khimiya, Moscow, 1989, 222 pp. (in Russian).

14. R. N. Moore, C. Golumbic, and G. S. Fisher, *J. Am. Chem. Soc.*, 1956, **78**, 1173.
15. G. Rothenberg, Y. Yatziv, and Y. Sasson, *Tetrahedron*, 1998, **54**, 593.
16. E. F. Murphy, T. Mallat, and A. Baiker, *Catal. Today*, 2000, **57**, 115.
17. I. Tabushi and A. Yazaki, *J. Am. Chem. Soc.*, 1981, **103**, 7371.
18. D. Mansuy, M. Fontecave, and J.-F. Bartoli, *J. Chem. Soc., Chem. Commun.*, 1983, 253.
19. R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds*, Academic Press, New York—London—Toronto—Sydney—San Francisko, 1981, 424 pp.
20. N. A. Polotebnova, Nguen Van Cheu, and V. V. Kal´nibolotskaya, *Zh. Neorg. Khim.*, 1973, **18**, 413 [*J. Inorg. Chem. USSR*, 1973, **18** (Engl. Transl.)].
21. L. I. Kuznetsova, R. I. Maksimovskaya, and K. I. Matveev, *Inorg. Chim. Acta*, 1986, **121**, 137.
22. L. G. Detusheva, M. A. Fedotov, L. I. Kuznetsova, A. A. Vlasov, and V. A. Likholobov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 914 [*Russ. Chem. Bull.*, 1997, **46**, 874 (Engl. Transl.)].
23. G. M. Maksimov, R. I. Maksimovskaya, and I. V. Kozhevnikov, *Zh. Neorg. Khim.*, 1992, **37**, 2279 [*Russ. J. Inorg. Chem.*, 1992, **37** (Engl. Transl.)].
24. N. I. Kuznetsova, L. G. Detusheva, L. I. Kuznetsova, M. A. Fedotov, and V. A. Likholobov, *Kinet. Katal.*, 1992, **33**, 516 [*Kinet. Catal.*, 1992, **33** (Engl. Transl.)].
25. L. Grzona, N. Comelli, O. Masini, E. Ponzi, and M. Ponzi, *React. Kinet. Catal. Lett.*, 2000, **69**, 271.
26. T. Yamase, E. Ishikawa, Y. Asai, and S. Konai, *J. Mol. Catal. A: Chem.*, 1996, **114**, 237.
27. V. F. Odyakov, L. I. Kuznetsova, and K. I. Matveev, *Zh. Neorg. Khim.*, 1978, **23**, 457 [*J. Inorg. Chem. USSR*, 1978, **23** (Engl. Transl.)].

Received November 25, 2002;
in revised form March 11, 2003