Hydrogen peroxide and oxygen–hydrogen oxidation of aromatic compounds in catalytic systems containing heteropoly compounds

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Abstract

Hydrogen peroxide and Pt activated mixture of gaseous O_2 and H_2 have been applied to oxidation of aromatic compounds in the presence of redox active heteropoly compounds in the form of acid $H_4PMo_{11}VO_{40}$ and tetrabuthylammonium (TBA) salts $TBA_4PMo_{11}VO_{40}$ and $TBA_4HPW_{11}Fe(OH)O_{39}$. Benzene, toluene and phenol were subjected to hydroxylation of the ring, which was accompanied by secondary oxidation in the reaction with hydrogen peroxide. Oxygenation of toluene was equally directed to the ring and to methyl group. The total reactivity of substrates was increased in the order of benzene < toluene < phenol in oxidation by both O_2/H_2 and H_2O_2. Analysis of products yield and composition indicated the identical nature of active intermediates for both oxidants. It was suggested that HPC bonded radical species are responsible for the oxidation of hydrocarbons.
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1. Introduction

Diluted solution of hydrogen peroxide is a universal, ecologically clean and convenient way to handle reagents for different oxidations in the liquid phase [1–2].

In comparison to molecular oxygen, hydrogen peroxide is a more active oxidant working for most difficult oxidations, such as oxygenation and hydroxylation of aromatic rings. In synthesis of phenols and quinines, hydrogen peroxide should be considered indispensable to refuse application of organic peroxides, sulfuric acid and stoichiometric reagents.

Reactions of hydrogen peroxide with aromatic compounds proceed in the presence of transition metal ions of variable oxidation state [3,4]. The redox active ions, such as Mo^{6+}/Mo^{5+}, V^{5+}/V^{4+}, Fe^{3+}/Fe^{2+}, and Co^{3+}/Co^{2+}, constitute a general base of molecular structure of heteropoly anions, or can be incorporated into the heteropoly anions. This composition of the HPCs makes them oriented to catalysis of peroxide reactions. Oxidation of aromatic hydrocarbons under the action of HPC-H_2O_2 has been widely covered in a number of revues, take, for

example, the fresh one [5]. Benzene is reported to be selectively converted to phenol under the action of 30% H_2O_2 in CH_3CN solution at room temperature in the presence of $H_5PW_{10}V_2O_{40}$ and $H_6PW_9V_3O_{40}$ [6] or P-Mo-V HPC [7], and at $70\,^\circ C$ in the presence of $PW_{11}Fe(OH \text{ or } H_2O)O_{39}{}^{5- \text{ or } 4-}$ [8]. In CH_3COOH solution of P-Mo-V HPC, hydrogen peroxide readily oxidized 2,3,5- and 2,3,6-trimethylphenol to 2,3,5-trimethyl-1,4-benzoquinone [9,10]. The catalytic activity was ascribed to peroxide complexes of heteropoly anions or $VO(O_2)^+$ peroxo species resulted from decomposition of the P-Mo-V heteropoly anions. For alkylaromatic compounds, oxidation of the alkyl group to form corresponding alcohols, aldehydes, ketones and acetates was observed [11]. Apart from oxidation of the hydrocarbon substrates, hydrogen peroxide is subjected to decomposition to evolve oxygen.

By analogy with Fenton reagent ($Fe^{3+}/Fe^{2+} + H_2O_2$) [3], the mechanism of the HPC catalyzed oxidation is suggested to include radical intermediates [6,8,11]. The radical intermediates are generated from peroxide by reversible oxidation and reduction of metal ions. A definite character of the active intermediates must be obviously controlled by composition of a catalytic system. As a result, catalyst and reaction conditions along with functional groups in aromatic ring determine the composition of the oxidation products, in particular, a ratio between the ring

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and alkyl group oxygenates in the oxidation of alkyl aromatics [12–16].

The reductive activation of molecular oxygen is expected to develop new pathways of hydrocarbon oxidation [17]. In particular, a mixture of molecular oxygen and hydrogen was used for benzene oxidation to phenol under mild conditions [18]. Catalysts of the O_2/H_2 oxidation include two components [19–22]. Platinum metals catalyze incomplete reduction of oxygen with hydrogen to peroxide species. Interaction of peroxide with hydrocarbon is assisted with the HPC [19,22]. The oxidation process with *in situ* generation of peroxide from a mixture of molecular oxygen and hydrogen may be more complex than reaction with hydrogen peroxide.

In the present study, the redox active HPCs were investigated as catalysts in oxidation with hydrogen peroxide, and as components of catalytic systems in the O_2/H_2 oxidation. The study was aimed at comparing the behaviour of the HPCs in oxidation with hydrogen peroxide and with an O_2/H_2 mixture under identical conditions.

2. Methods

2.1. Preparation of catalysts

Pt/SiO$_2$ was prepared by impregnation of a silica powder (purchased reagent of KSK type, $S_0 = 280 \, m^2/g$) with H_2PtCl_6 solution. The sample was dried at 100 °C, then calcined at 450 °C, and reduced in H_2 flow at 300 °C for 1 h. The sample contained 5 wt. % Pt.

Heteropoly acids $H_4PMo_{11}VO_{40}\cdot13H_2O$ (H-PMo$_{11}$V) and $H_5PMo_{10}V_2O_{40}\cdot9H_2O$ (H-PMo$_{10}$V$_2$) were prepared by ether-extraction procedure [22]. Preparation of the tetrabutylammonium (TBA) salts $TBA_4PMo_{11}VO_{40}$ (TBA-PMo$_{11}$V), $TBA_5PMo_{10}V_2O_{40}$ (TBA-PMo$_{10}$V$_2$), $TBA_4HPW_{11}Co(H_2O)O_{39}$ (TBA-CoPW$_{11}$), and $TBA_4HPW_{11}Fe(OH)O_{39}$ (TBA-FePW$_{11}$) was described elsewhere [23].

2.2. UV–vis spectra

UV–vis absorption spectra of solutions were recorded with a Specord M-40 spectrometer in the range of 30000–11000 cm^{-1} at room temperature in a 0.5 cm cuvette.

2.3. Catalytic experiments

Catalytic reactions were conducted in a 30-ml glass round-bottom batch reactor under vigorous agitation of liquid at a controlled temperature, which prevents a runaway during hydrogen peroxide decomposition [24]. To measure the volume of a gas evolved or consumed during the reaction, the reactor was connected with a graduated burette.

In experiments with H_2O_2, the solution of 0.2 ml benzene (2.2 mmol) or equimolar amount of toluene or phenol, 0.2 ml 30% aqueous H_2O_2 (∼2 mmol), and 20 mg HPC (0.01–0.005 mmol) in 2 ml CH_3CN was prepared in the reactor. The reactor was blown through with N_2 and sealed, and agitation was started. Decomposition of H_2O_2 with

time was monitored by measuring the volume of oxygen evolved.

In experiments with the O_2/H_2 mixture, the reactor was loaded with the same reagents taken in half amounts, and 50 mg Pt/SiO$_2$ was added. The reactor was blown through with the O_2/H_2 mixture ($O_2:H_2 = 1:2$) and sealed, and agitation of liquid was started. Volume of the gas consumed was fixed.

GC analysis of organic products was made using a Kristall-2000M device supplied with capillary columns HP-5 (30 m × 0.25 mm) for pyrocatechol and hydroquinone, and DB-1701, JW Scientific Inc. (30 m × 0.53 mm) for the other oxidation products. The products were identified according to their retention times and by means of GC–MS analysis (a CV-2091 spectrometer).

2.4. Reagents

Benzene, toluene, phenol (Aldrich), acetonitrile (chemically pure, Kriokhrom) were used as given. Concentration of hydrogen peroxide (chemically pure, Akros) was checked with KMnO$_4$ immediately before use.

3. Results

3.1. Decomposition of H_2O_2 and oxidation of benzene, toluene and phenol with H_2O_2

Prior to oxidation of aromatic hydrocarbons with hydrogen peroxide, we studied decomposition of hydrogen peroxide dissolved together with HPC in acetonitrile. The reaction was carried out at 65 °C. The amount of oxygen evolved according to the equation

$$2H_2O_2 \rightarrow O_2 + 2H_2O$$
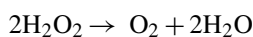
was determined experimentally, and conversion of H_2O_2 (mol%) was calculated from these data.

It is well known that the phosphomolybdic and phosphomolybdovanadic HPCs catalyze this reaction owing to Mo^{6+}/Mo^{5+} and V^{5+}/V^{4+} reversible electron transfer. Phosphotungstic HPCs are active in H_2O_2 decomposition if they contain additional redox active metal ions. In our experiments, activity of phosphomolybdovanadic heteropoly acid and two TBA salts in decomposition of hydrogen peroxide decreased in the order of H-PMo$_{11}$V > TBA-PMo$_{11}$V ≈ TBA-Fe PW$_{11}$. The heteropoly acid catalyzed a very rapid H_2O_2 decomposition that was completed in 1 h. In the presence of the TBA salts, reaction started very slowly and proceeded with progressive acceleration (Fig. 1). Complete decomposition of hydrogen peroxide took about 2 h.

Aromatic substrates added in amounts of 2 mmol were completely soluble in the reaction solution. Benzene, toluene and phenol slowed down hydrogen peroxide decomposition catalyzed by the TBA-PMo$_{11}$V and TBA-Fe PW$_{11}$ salts, whereupon phenol produced the strongest effect (Fig. 1). When the HPC was taken in acidic form, the hydrogen peroxide decomposition was so rapid that no retardation by the aromatic compounds was detected (Fig. 2).
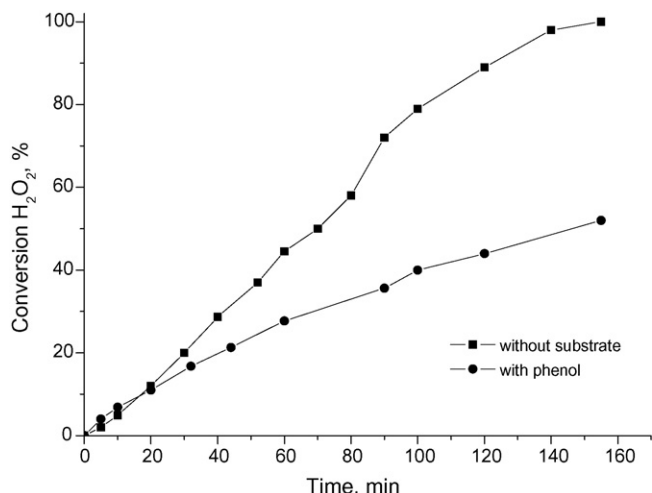
Fig. 1. Time dependency of the oxygen evolved in decomposition of H_2O_2 in the presence of TBA-FePW$_{11}$ and TBA-FePW$_{11}$ together with phenol. Conditions: 2 ml acetonitrile, 0.2 ml ~30% (1.65 mmol) H_2O_2, 0.2 g (1.9 mmol) phenol, 20 mg (0.0054 mmol) TBA-FePW$_{11}$, $T = 65\,°C$.
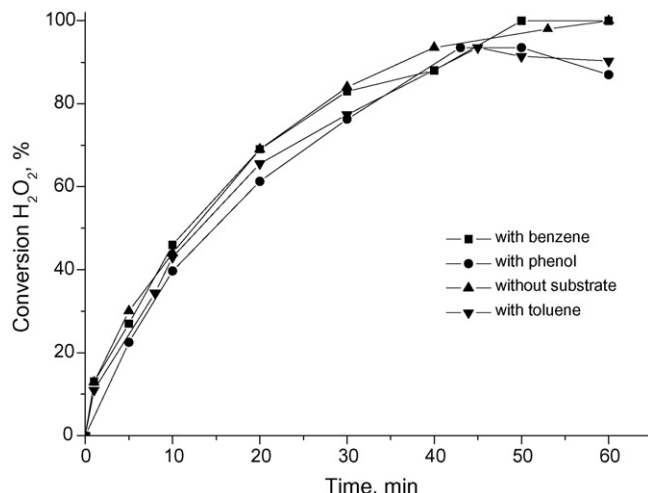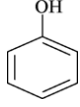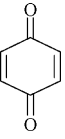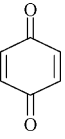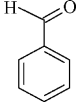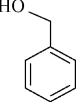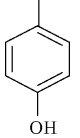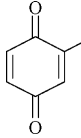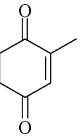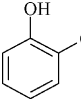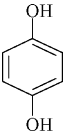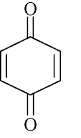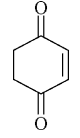

Fig. 2. Time dependency of the oxygen evolved in decomposition of H_2O_2 in the presence of H-PMo$_{11}$V and H-PMo$_{11}$V together with benzene (2.2 mmol), phenol (2,1 mmol) or toluene (1,9 mmol). Conditions: 2 ml acetonitrile, 0.2 ml ~30% H_2O_2 (1,8 mmol), 20 mg (0,01 mmol) H-PMo$_{11}$V, $T = 65\,°C$.

Table 1
Oxidation products obtained in reaction of benzene, toluene and phenol with H_2O_2 in the presence of HPCs

Substrate	Catalyst	Oxidation products (μmol)		
		Total amount	OH (phenol)	(benzoquinone)
Benzene	H-PMo$_{11}$V	38.9	30.8	8.1
	H-PMo$_{11}$V$^{(*)}$	2.1	2.1	0
	TBA-PMo$_{11}$V	1.7	1.7	0
	TBA-FePW$_{11}$	5.8	5.8	0
	TBA-CoPW$_{11}$	0	0	0
	Pt/SiO$_2$$^{(**)}$ + H-PMo$_{11}$V$^{(*)}$	2.6	2.6	0

Substrate	Catalyst	Oxidation products (μmol) Total amount						
Toluene			(benzaldehyde)	(benzyl alcohol)	(o-cresol)	(m-cresol)	(p-cresol)	(methyl quinone)	(methyl quinone)
	H-PMo$_{11}$V	46	20.3	2.7	3.9	0.6	1.7	14.4	2.4
	TBA-PMo$_{11}$V	3.4	0.4	0.3	1.9	0.3	0.5	0	0
	TBA-FePW$_{11}$	9.4	2.2	1.7	2.7	0.9	0.9	0	1

Substrate	Catalyst	Oxidation products, (μmol) Total amount				
Phenol			(catechol)	(hydroquinone)	(benzoquinone)	(quinone)
	H-PMo$_{11}$V	69.3	0	36.3	31.0	2.0
	TBA-PMo$_{11}$V	9.2	0	0	7.9	1.3
	TBA-FePW$_{11}$	42.0	0	0	31.0	11.0

Conditions: 0.2 ml benzene (2,2 mmol) or toluene (1,9 mmol) or 0,2 g phenol (2,1 mmol), 2 ml acetonitrile, 0.2 ml ~30% H_2O_2 (1,8 mmol), 20 mg HPC (0,01–0,005 mmol), $T = 65\,°C$, with the exception of T 30 °C for exps.(*), reaction time 1 h, 10 mg of Pt/SiO$_2$ in exp. (**).

Fig. 3. Time dependency of H_2O_2 decomposition and phenol accumulation in oxidation of benzene. For conditions, see caption for Fig. 2.

Oxidation of the aromatic substrates proceeded along with decomposition of hydrogen peroxide in the presence of the HPC catalysts. About 2, 5 and 10% of the hydrogen peroxide totally consumed was converted into the products in reactions with benzene, toluene and phenol, respectively. Fig. 3 shows the time dependence of H_2O_2 conversion and amount of phenol accumulated in the oxidation of benzene. Identical shape of these two curves indicates a rapid accumulation of the products to occur during intensive decomposition of hydrogen peroxide. Amount of the products stopped to grow after 1 h, when decomposition of hydrogen peroxide was completed. Catalytic activity of the HPCs in oxidation of the aromatic hydrocarbons was estimated from the amount of the products obtained for 1 h (Table 1). Among the HPCs tested, H-PMo$_{11}$V heteropoly acid appeared the most active in oxidation. Fe-containing heteropoly tungstate was more active than another TBA salt in the oxidation of benzene, toluene and especially phenol.
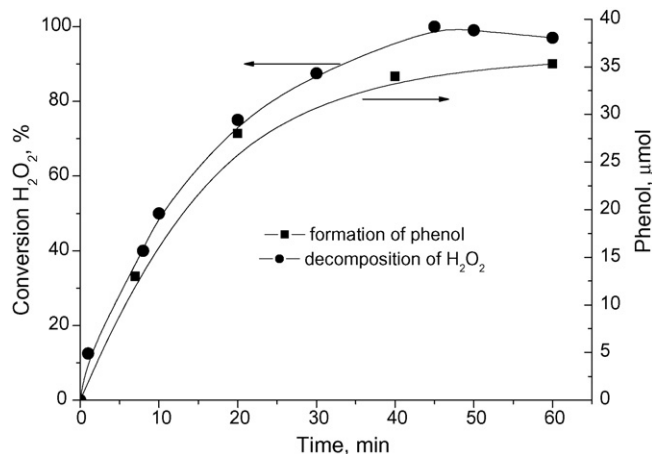
Reactivity of substrates varied in the order of benzene < toluene < phenol in all oxidations catalyzed by the HPCs tested.

Oxidation of the aromatic substrates resulted in the formation of a number of products. An exception was benzene, the low conversion of which produced mainly one product, phenol. 1,4-benzoquinone was obtained only in the presence of H-PMo$_{11}$V heteropoly acid as a minor product in addition to phenol.

Oxidation of toluene was equally directed to methyl group and to the ring, preferably to *ortho*-position. In the most active H-PMo$_{11}$V system, secondary oxidation products 2-methyl-1,4-benzoquinone and 2-methyl-1,4-dioxocyclohexene-2 were obtained in substantial amount.

In oxidation of phenol, *para*-position was subjected to hydroxylation/oxygenation, whereas no *ortho*- and *meta*-substituted products were obtained. TBA salts produced 1,4-benzoquinone and 1,4-dioxocyclohexene, whereas H-PMo$_{11}$V gave nearly equal amounts of 1,4-benzoquinone and hydroquinone.

Oxidation with hydrogen peroxide was carried out at the temperature of 65 °C. At a lower temperature, the oxidation proceeded slowly. An example of the low-temperature experiments is given in Table 1. As seen, the amount of phenol produced in the oxidation of benzene was very low even in the presence of the most active H-PMo$_{11}$V catalyst. Similarly, low amounts of oxidation products were obtained from the other substrates at 30 °C. At this temperature, the decomposition of hydrogen peroxide proceeded also slowly.

The time and temperature dependencies showed an agreement between hydrogen peroxide decomposition and oxidation of substrates, which indicates that the oxidation may result from interaction of the substrates with radical intermediates involved in hydrogen peroxide decomposition. It is often assumed that free hydroxyl radicals are responsible for oxidation [3].

The validity of this assumption for our catalytic systems was tested in two experiments with catalysts extremely active in the decomposition of hydrogen peroxide. In the presence of TBA-CoPW$_{11}$ HPC at 65 °C, we observed a very rapid decomposition of hydrogen peroxide, but no oxidation of benzene was detected under these conditions. In the second experiment, the reaction between hydrogen peroxide and benzene was carried out with a combination of solid Pt/SiO$_2$ and soluble H-PMo$_{11}$V HPC. The platinum sample is known as an active catalyst of hydrogen peroxide decomposition, but a poor catalyst of peroxide oxidation. The combination of Pt/SiO$_2$ and H-PMo$_{11}$V HPC provided intensive decomposition of peroxide, but produced only a small amount of phenol, equal to that obtained with Pt/SiO$_2$ in the absence of HPC. From these results, we concluded that free hydroxyl radicals could be hardly responsible for the oxidation of benzene.

3.2. Oxidation with the O_2/H_2 mixture

The stoichiometric mixture of $O_2/H_2 = 1/2$ (vol/vol) reacted in suspension of the platinum catalyst in HPC and substrate solution. Along with production of water, a part of gases was utilized in oxidation of the aromatic substrates. Estimation of the gases consumed and products obtained showed 10 to 30 mol % of gases to be spent for the oxidation of substrates.

Benzene was hydroxylated by the O_2/H_2 mixture to form phenol that was subjected to secondary hydroxylation to hydroquinone. Activity of the catalytic systems containing HPC was found to decrease in the following order: H-PMo$_{11}$V > TBA-PMo$_{11}$V > TBA-FePW$_{11}$ (Table 2).

Under the same conditions, oxidation of toluene resulted in both hydroxylation of the ring to form cresols, and oxygenation of methyl group to form benzaldehyde and benzyl alcohol. Activity of the HPCs varied in the order of H-PMo$_{11}$V > TBA-FePW$_{11}$ > TBA-PMo$_{11}$V, that meant phosphomolybdovanadic heteropoly acid together with Pt/SiO$_2$ represented the most active catalytic system.

Phenol was oxidized to pyrocatechol and hydroquinone. According to the order of HPCs activity TBA-FePW$_{11}$ > TBA-PMo$_{11}$V ≈ H-PMo$_{11}$V, Fe-containing heteropoly tungstate exhibited the highest activity in the oxidation of phenol.

Reactivity of the aromatic compounds in reaction with the O_2/H_2 mixture increased in a series of benzene < toluene < phenol, which was observed with each of the HPCs tested. Irrespective of catalyst and substrate, the

Table 2
Oxidation products obtained in reaction of benzene, toluene and phenol with O_2/H_2 in the presence of Pt/SiO_2 and HPCs

Substrate	Catalyst	Oxidation products, (µmol)		
		Total amount	OH (phenol)	OH...OH (hydroquinone)
Benzene	$Pt/SiO_2 + H\text{-}PMo_{11}V$	19.3	12.2	7.1
	$Pt/SiO_2 + TBA\text{-}PMo_{11}V$	8.9	7.3	1.6
	$Pt/SiO_2 + TBA\text{-}FePW_{11}$	4.5	2.7	1.8

Substrate	Catalyst	Oxidation products, (µmol) Total amount	benzaldehyde	benzyl alcohol	o-cresol	m-cresol	p-cresol	2-methyl-1,4-benzoquinone	2-methyl-1,4-benzoquinone
Toluene	$Pt/SiO_2 + H\text{-}PMo_{11}V$	43.8	2.6	16.4	14.5	7.7	2.6	0	0
	$Pt/SiO_2 + TBA\text{-}P\,Mo_{11}V$	10.8	1.1	2.7	4.7	1.8	0.5	0	0
	$Pt/SiO_2 + TBA\text{-}FePW_{11}$	15.1	5.5	1.8	5.2	1.7	0.9	0	0

Substrate	Catalyst	Oxidation products, (µmol) Total amount	catechol	hydroquinone	1,4-benzoquinone	1,4-benzoquinone
Phenol	$Pt/SiO_2 + H\text{-}PMo_{11}V$	71.4	49.9	21.5	0	0
	$Pt/SiO_2 + TBA\text{-}PMo_{11}V$	68.8	50.5	18.3	0	0
	$Pt/SiO_2 + TBA\text{-}FePW_{11}$	128.1	97.2	30.9	0	0

Conditions: 0.1 ml benzene (1,1 mmol) or toluene (1.0 mmol) or 0,1 g phenol (0,95 mmol), 1 ml acetonitrile, 50 mg Pt/SiO_2, 10 mg HPC (0,005–0,0025 mmol), $O_2/H_2 = 1/2$, $T = 30\,°C$, reaction time 1 h.

oxidation of aromatic ring with the O_2/H_2 led to hydroxylation, quinones were detected in trace amounts, if any. However, 1,4-benzoquinone appeared in the absence of hydrogen. When reaction of benzene with the O_2/H_2 mixture was stopped, and air was substituted for the O_2/H_2 mixture in the reactor, 1,4-benzoquinone formed after some time in substantial amounts because of secondary oxidation of hydroquinone (Fig. 4).

The secondary oxidation of the aromatic hydroxyl derivatives with air proceeded at room temperature. As seen in Fig. 4, the reaction was catalyzed by the HPCs. 1,4-benzoquinone formed more rapidly in the presence of heteropoly acids than with TBA salts, and in the presence of V_2-, better than with V_1-substituted phosphomolydovanadic heteropoly compounds. In other words, the higher the redox potential of the HPC was, the larger the amount of the secondary products accumulated in the absence of hydrogen.

When contacting with the O_2/H_2 gaseous mixture in the presence of Pt catalyst, the HPCs solutions changed their color: from yellow to blue for $H\text{-}PMo_{11}V$, and from pale yellow to black for $TBA\text{-}FePW_{11}$. To refine the oxidation state of the HPC during catalysis, we stopped catalytic reaction in the ($Pd/SiO_2 + H\text{-}PMo_{11}V + $ benzene) mixture several minutes after beginning,

filtered off the solid platinum catalyst, and recorded the UV–vis spectrum of the solution (spectrum 3 in Fig. 5). For comparison, Fig. 5 shows the other two spectra. Spectrum 1 belongs to acetonitrile solution of $H\text{-}PMo_{11}V$ containing benzene. After addition of H_2O_2 to the solution and its heating to $65\,°C$ to start

Fig. 4. Accumulation of benzoquinone at storing the mixtures after reaction with the O_2/H_2 in air at room temperature for 20 h. 1, 2, 3, 4 and 1-O_2, 2-O_2, 3-O_2, 4-O_2–mixtures containing $H\text{-}PMo_{11}V$, $H\text{-}PMo_{10}V_2$, $TBA\text{-}PMo_{11}V$, $TBA\text{-}PMo_{10}V_2$ after reaction with O_2/H_2 and after storing, respectively. Conditions: 2 ml acetonitrile, 0,2 g (1,9 mmol) phenol, 0,2 ml ~30% H_2O_2, 20 mg HPC, $T = 30\,°C$.

Fig. 5. Absorbance of the H-PMo$_{11}$V + benzene solutions in acetonitrile: 1—10 mg H-PMo$_{11}$V, 0.1 ml benzene in 2 ml acetonitrile; 2—solution 1 added with 0.1 ml H$_2$O$_2$; 3—solution 1 after reaction with 25 mg Pt/SiO$_2$ in O$_2$/H$_2$ atmosphere.

oxidation, we recorded spectrum 2. Both spectra 1 and 2 are typical of the phosphomolybdovanadic heteropoly acid, whereas spectrum 3 was close to the spectrum of reduced form of the heteropoly acid [25].

4. Discussion

Hydroxylation of aromatic compounds by the Fenton reagent goes via attack of the ring by hydroxyl radicals [3]. In the systems under study, $^\bullet$OH radicals could be generated from hydrogen peroxide and also from molecular oxygen reductively activated with hydrogen. Nevertheless, the experimental data obtained indicate the reactive species other than free hydroxyl radicals to be responsible for oxidation under the given conditions. First of all, this follows from inertness of benzene in the presence of other active HPC catalysts of H$_2$O$_2$ decomposition. Intensive decomposition of hydrogen peroxide proceeded in the presence of the TBA-CoPW$_{11}$ at 65 °C in CH$_3$CN solution, but no oxidation of benzene was detected. Furthermore, decomposition of H$_2$O$_2$ was slow in the presence of H-PMo$_{11}$V at the room temperature. Addition of the platinum catalyst accelerated low-temperature decomposition of hydrogen peroxide and, probably, the production of $^\bullet$OH radicals. However, we did not manage to perform the oxidation of benzene in the Pt - H-PMo$_{11}$V system at low temperature as rapidly as in the typical reaction at 65 °C without Pt.

Presumably, the HPC bonded radical species are more reactive intermediates in the oxidation of aromatic as compared to free hydroxyl radicals. This assumption has been made earlier for the catalytic system containing TBA-PW$_{11}$Fe HPC that worked under close conditions [8], and was confirmed by the results presented below.

The HPC bonded hydroxyl radical intermediates arose from peroxide interacted with reduced Fe^{2+}, Mo^{5+}, and V^{4+} ions of the HPC (1).

$$M^{n+} + H_2O_2 = [M^{(n+1)+}(^\bullet OH)] + OH^- \qquad (1)$$

Oxidized form of the HPC may generate coordinated hydroperoxyl via the preliminary coordination of peroxide [4] and further inner-sphere electron transfer (2). Some changes in coordination sphere of V^{5+} ion under the action of hydrogen peroxide accounted for enhanced visible absorption of the HPC observed for H$_2$O$_2$ containing solution (Fig. 5, spectra 1 and 2) [23].

$$M^{(n+1)+} + H_2O_2 \underset{-H+}{\rightleftarrows} [M^{n+}(^\bullet OOH)] \underset{-H+}{\rightleftarrows} [M^{n+}(^\bullet OO)^-] \qquad (2)$$

The HPC bonded radical intermediates are involved in competitive reactions (3) with aromatic substrate, for example, benzene to form phenol, and (4)–(6) without substrate to evolve molecular oxygen.

$$[M^{(n+1)+}(^\bullet OH)] + C_6H_6 = M^{n+} + C_6H_5OH + H^+ \qquad (3)$$

$$[M^{(n+1)+}(^\bullet OH)] + M^{n+} = 2M^{(n+1)+} + OH^- \qquad (4)$$

$$M^{(n+1)+} + H_2O_2 = M^{n+} + {}^\bullet O_2H + H^+ \qquad (5)$$

$$M^{(n+1)+} + {}^\bullet O_2H = M^{n+} + O_2 + H^+ \qquad (6)$$

Two-way conversion of the active intermediate explains possible retardation of hydrogen peroxide decomposition in the presence of substrate, as shown in Fig. 1. The retardation was substantial for the system with moderate activity in hydrogen peroxide decomposition, and was undetectable in the presence of H-PMo$_{11}$V heteropoly acid active in H$_2$O$_2$ decomposition.

Oxidation with the O$_2$/H$_2$ mixture proceeded via peroxide compound, which was generated on platinum catalyst from oxygen and hydrogen and may interact with the HPC to form active intermediates, probably, like [M$^{(n+1)+}$($^\bullet$OH)] and [M^{n+}($^\bullet$OOH)] radical species suggested for oxidation with H$_2$O$_2$. Activity of the O$_2$/H$_2$ oxidant toward different hydrocarbons has been studied earlier versus the HPC composition [22]. It was shown that the HPC bonded radical species are involved in the oxidation in the catalytic systems including the redox active HPC. Identity of intermediates in the HPC catalyzed oxidation with H$_2$O$_2$ and O$_2$/H$_2$ mixture was confirmed by similar behavior of the two oxidants in reactions with benzene and with the other aromatic substrates.

Relative reactivity of the aromatic compounds increased in the order of benzene < toluene ≪ phenol in both reactions with the H$_2$O$_2$ and O$_2$/H$_2$ mixture. The difference in reactivity of substrates was more pronounced in reaction with the O$_2$/H$_2$ mixture than with H$_2$O$_2$, and in the presence of TBA-FePW$_{11}$ than with the other HPCs. A substantial increase in reactivity of aromatic compound under the action of electrodonating groups in the ring indicates the radical intermediate to possess some electrophilic properties owing to its bonding with the HPC.

Oxidation products obtained from benzene, toluene and phenol were typical of the radical oxidation. Oxidation of benzene produced primarily phenol, whose further conversion depended on oxidative properties of the medium, and led to 1,4-benzoquinone under the action of H$_2$O$_2$ or hydroquinone in the presence of a strong reducer, platinum activated H$_2$. The absence of biphenyl in the case of O$_2$/H$_2$ and H$_2$O$_2$ points to the HPC bonded intermediates. Interaction of benzene with hydroxyl followed by transformation of phenyl radical occurred

Table 3
Molar ratio between products of toluene oxidation with the O_2/H_2 mixture

No.	System	Benzyl alcohol + benzaldehyde	*ortho*-Cresol	*meta*-Cresol	*para*-Cresol
1	$H_4PMo_{11}VO_{40}$ + Pt/SiO$_2$, O$_2$/H$_2$	57	36	13	4
2	$TBA_4PMo_{11}VO_{40}$ + Pt/SiO$_2$, O$_2$/H$_2$	65	22	10	3
3	$TBA_4HW_{11}Fe(OH)O_{39}$ + Pt/SiO$_2$, O$_2$/H$_2$	52	32	11	5
4	Fe^{2+}_{aq} + H$_2$O$_2$ [26]	90	7	0.5	2.5
5	$TBA_4PMo_{11}VO_{40}$ + H$_2$O$_2$ [16]	53	30	14	3
6	$TBA_4PMo_{11}VO_{40}$ + H$_2$O$_2$	21	55	9	15

Conditions: 0,1 ml toluene, 1 ml CH$_3$CN, 50 mg Pt/SiO$_2$, 10 mg HPC, O$_2$/H$_2$ = 1/2, T = 30 °C (Nos. 1–3); 0,2 ml toluene, 2 ml CH$_3$CN, 0,2 ml∼30% H$_2$O$_2$, 20 mg HPC, T = 65 °C (No. 6); reaction time 1 h (Nos. 1–3, 6); toluene suspension in aqueous FeSO$_4$ + H$_2$O$_2$ at room temperature (No. 4); two-phase system toluene + CH$_3$CN/30% aq. H$_2$O$_2$, room temperature (No. 5).

without penetration of radical species to the volume. Otherwise, biphenyl could result from recombination of the phenyl radicals.

Oxidation of toluene with both H$_2$O$_2$ and O$_2$/H$_2$ mixture was nearly equally directed into the ring to form cresols, and to methyl group to form benzyl alcohol and benzaldehyde (Tables 1 and 2), whereas methyl group is usually more open for radical attack in Fenton oxidation [26]. The corresponding ratios of the products in oxidation by the O$_2$/H$_2$ mixture and by Fenton reagent are given in Table 3, Nos. 1–4. Hydroxylation of the toluene ring was preferably directed to *ortho*-position that was typical of the Fenton system. However, a part of *para*-cresol appeared surprisingly low, and a part of *meta*-cresol was respectively higher in oxidation by the O$_2$/H$_2$ mixture than in the Fenton system. This specificity can be considered as a result of bonding between the radical center and metal ion of the heteropoly compound. The ratio of products observed in the O$_2$/H$_2$ oxidation resembles the ratio reported by Nomiya et al. [16] for toluene oxidation in two-phase mixture of aqueous H$_2$O$_2$ and CH$_3$CN in the presence of TBA$_4$PMo$_{11}$VO$_{40}$ (Table 3, No. 5). Essential characteristics of the both systems were low temperature and low concentration of peroxide in acetonitrile solution containing HPC.

The percent composition of the products in oxidation of toluene with H$_2$O$_2$ appeared not quite precise because of low activity of the TBA salts and intensive secondary oxidation in case of the H$_4$PMo$_{11}$VO$_{40}$ heteropoly acid. In addition to methyl-1,4-benzoquinone, secondary oxidation of the ring led to the formation of 2-methyl-1,4-dioxocyclohexene-2. This product was detected in reaction with hydrogen peroxide, not with the OH$_2$/O$_2$ mixture. Both *ortho-* and *para*-cresols could be its precursors. More or less satisfactory estimation of the percent composition of products can be made in the case of low-active *TBA-PMo$_{11}$V* catalyst. The system was characterized by a small contribution of benzylic oxidation and hydroxylation of the ring preferably into *ortho*-position (Table 3, No. 6).

Oxidation of phenol produced no *meta*-isomers, which confirmed the radical mechanism. Radical attack to phenol started with hydrogen removal from hydroxyl group. The radical center was delocalized between *ortho-* and *para*-carbons, which attached hydroxyl radical to form pyrocatechol and hydroquinone in oxidation with the O$_2$/H$_2$ mixture. We have not found yet an explicit explanation of the fact that only hydroquinone was detected in reaction with H$_2$O$_2$. It may relate to geometry of the HPC-bonded intermediate.

As seen, most of the regularities were substantially identical for oxidation with the O$_2$/H$_2$ mixture and with hydrogen peroxide. However, some details were different. The specificity of the O$_2$/H$_2$ oxidant was produced by a strong reducer, platinum-activated hydrogen.

The O$_2$/H$_2$ mixture and hydrogen peroxide operate at different temperatures. The O$_2$/H$_2$ oxidation proceeded with a substantial rate at room temperature, whereas hydrogen peroxide oxidation required the temperature as high as 65 °C. The thing was that the HPC was involved in the oxidations that include reversible one-electron transfer, for instance, V^{4+}/V^{5+}. Reduction of the metal ions proceeded rapidly under the action of H$_2$. As a result, reduced form of the HPC predominated even at low temperature, which was indicated by intensive absorbance in a region of frequencies below 18000 cm^{-1}. Oxidized form of the HPC interacted more slowly with the poor reducer hydrogen peroxide. As a result, the total reaction appeared limited by reduction in the case of H$_2$O$_2$, which was confirmed by absorbance spectra of solutions in Fig. 5. At increasing temperature, reduction of the HPC was accelerated, which made more rapid the total reaction with hydrogen peroxide.

The other thing we should pay attention was secondary oxidation. At low temperature in reductive medium we obtained products of hydroxylation in reaction with the O$_2$/H$_2$ mixture. On the contrary, intensive secondary oxidation proceeded under the action of hydrogen peroxide to form quinones and benzaldehyde. So, strong reducing ability of hydrogen does create some specific features of the O$_2$/H$_2$ oxidation, but they do not concern the principal mechanism.

5. Conclusion

Being activators of peroxide compounds, the redox active HPCs catalyzed oxidation of benzene, toluene and phenol with hydrogen peroxide, and performed similar functions in oxidation with the O$_2$/H$_2$ mixture. Active intermediates were suggested to be HPC bonded radical species in both oxidations. They were generated from hydrogen peroxide or reductively activated oxygen, and were responsible for oxidation of the aromatic substrates. Identical nature of the active HPC bonded intermediates was confirmed in both oxidations by similarities in behavior of the catalytic systems, in particular, relative reactivity of the aromatic substrates, composition of the oxidation products, and relative activity of the HPCs. Application of the O$_2$/H$_2$ oxidant

appeared effective, providing high activity in oxidation at low temperature. Reducing medium prevented secondary oxidation, which made the O_2/H_2 oxidant preferable for selective synthesis of phenols.

Acknowledgment

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