

Catalytic properties of heteropoly complexes containing Fe(III) ions in benzene oxidation by hydrogen peroxide

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Abstract

Elemental analysis, magnetic measurements, IR, ³¹P NMR, and UV–VIS spectroscopy were used to study heteropoly complexes (HPC), containing Fe(III) ions and heteropoly anion [PW₁₁O₃₉]⁷⁻, isolated from aqueous solutions as tetrabutylammonium (TBA) salts and dissolved in acetonitrile. The complexes identified are: Fe(III)-substituted complexes [PW₁₁O₃₉Fe(H₂O)]⁴⁻ (**1**) and [PW₁₁O₃₉Fe(SO₄)]⁶⁻ (**1'**); Fe(III)-substituted hydroxo complex [PW₁₁O₃₉Fe(OH)]⁵⁻ (**2'**) formed during the precipitation of binuclear μ-oxo complex [(PW₁₁O₃₉Fe)₂O]¹⁰⁻ (**2**) from aqueous solutions (pH = 3 ÷ 5) by TBA cations; polynuclear Fe(III)-hydroxo complexes [PW₁₁O₃₉Fe_nO_xH_y]^{m-} (**3**) (n ~ 8). The catalytic activity of complexes both in the hydrogen peroxide decomposition and benzene oxidation in a one-phase system HPC + CH₃CN + H₂O₂(aq) + C₆H₆, with [HPC] = 6 · 10⁻³, [H₂O₂] = 0.175 ÷ 1.6, and [C₆H₆] = 1.4 ÷ 5.6 M at 70°C have been studied. In the presence of **1** or **1'**, the molar ratio between phenol formed and H₂O₂ decomposed equals 10–20%. HPC containing SO₄²⁻ ions shows a far lower activity in both reactions. The kinetics of PhOH accumulation conforms to the chain mechanism of H₂O₂ decomposition. Benzene is oxidized by OH radicals coordinated to HPC. In the presence of complex **2'** the rate of H₂O₂ decomposition is considerably lower. Thus the molar ratio of phenol formed and H₂O₂ decomposed is almost 60%. The mechanism of H₂O₂ activation by **2'** includes most likely the initial formation of a peroxo complex which was observed in absorption spectra. The state of HPC affected by the reaction mixture components was studied by UV–VIS spectra. The products of one-electron phenol (or pyrocatechol) oxidation inhibit the catalytic activity due to the complex formation with Fe(III) ions in HPC.

Keywords: Fe(III)-containing heteropoly complexes; Benzene oxidation; Hydrogen peroxide decomposition; Peroxo complexes; UV–VIS; IR; NMR spectroscopy

1. Introduction

The catalytic activity of heteropoly complexes containing transition metal ions is intensively studied (see Ref. [1] and references therein). Analyzing the factors responsible for the catalytic performance of HPC, one often

compares the activity series of complexes, where either ions of transition metals or heteropoly anions (HPA) are varied.

We have recently shown that synthesis conditions determine the mode of binding of Cr(III) ions with HPA [PW₁₁O₃₉]⁷⁻, which in turn, determines the catalytic activity of complexes obtained in cyclohexene or benzene oxidation by hydrogen peroxide [2]. Furthermore, in water

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solution, we have identified three types of complexes with regard to pH and reagents ratio during the interaction of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and Fe(III) ions: **1** Fe(III)-substituted HPC $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$ (pH 2 ÷ 3); **2** μ -oxo (or hydroxo) dimer complex $[\text{PW}_{11}\text{O}_{39}\text{Fe}-\text{O}-\text{FeO}_{39}\text{W}_{11}\text{P}]^{10-}$ (pH 3 ÷ 5) and **3** polynuclear Fe(III)-hydroxo complexes stabilized by heteropolyanion $[\text{PW}_{11}\text{O}_{39}\text{Fe}_n\text{O}_x\text{H}_y]^{m-}$ (pH ~ 4) [3]. So we had a chance to study the catalytic properties of HPC with regard to the structural features of guest metal ions bonded to the same HPA, $[\text{PW}_{11}\text{O}_{39}]^{7-}$.

Benzene oxidation by hydrogen peroxide was chosen as a model reaction since iron salts are known to catalyze this reaction [4–8]. It is also known that metal-containing HPC catalyze the oxidation of alkanes and olefins by hydrogen peroxide [2,9–11]. Thus the results of our work can also help to elucidate the regularities of organics oxidation in systems containing HPC and H_2O_2 .

2. Experimental

The aqueous solutions of HPC sodium salts were obtained by heating a 0.05 M solution of $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ (series I) at

molar ratio $n = \text{Fe}:\text{PW}_{11} = 1$, with a subsequent addition of Na_2CO_3 solution to attain the wanted pH values (Table 1) [3]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at $n = 1$ or 4 was used to obtain HPC of series II, the other steps were similar to the previously described ones.

HPC obtained were precipitated from the aqueous solution as TBA salts by adding $(\text{C}_4\text{H}_9)_4\text{NBr}$ solution ($[\text{TBA}]:[\text{PW}_{11}] = 10:1$). TBANO_3 , obtained via the interaction of stoichiometric amounts of TBABr and AgNO_3 with a subsequent isolation of AgBr precipitate, was used in the preparation of sample 8 (Table 1). TBA salts of HPC were centrifuged, twice washed by water and dried at 120°C .

Benzene oxidation by H_2O_2 proceeded at 70°C on air in a thermostated reactor equipped with a magnetic stirrer and a burette to measure the rate of H_2O_2 decomposition with regard to O_2 evolved. Samples for the absorption spectra registering and GLC analysis (1 m column, 15% of TVIN-80 on a Polysorb-1) were syringed through a rubber insulation. The composition of reaction solutions was varied within $[\text{C}_6\text{H}_6] = 1.4 \div 5.6$, $[\text{H}_2\text{O}_2] = 0.175 \div 1.6$ and $[\text{HPC}] = 6 \cdot 10^{-3}$ M, while the volume ratio between acetonitrile and water was 6:1. The system remained one-phase in all runs.

Absorption spectra of solutions were recorded

Table 1

Fe(III)-HPC composition at various pHs according to ^{31}P NMR in aqueous solution, elemental analysis and magnetic measurements data of TBA salts precipitated

Series	Sample number ^a	pH	Na salts in H_2O ^{31}P , δ (ppm) ($W_{1/2}$ (Hz))	TBA salts solid		
				Fe (mass %)	P (mass %)	μ_{eff} , μ_{B}
I	1	2.1	272(2000); 103(2300) (0.06:1) ^b	1.35	0.67	5.86
	2	3.45	176; 37.6 (1000) (0.07:1)	1.20	0.68	5.76
	3	4.5	90.8(650); 13.8(740) (0.07:1)	1.03	0.72	
	4	5.0	84.7(840); 14.2(1000) – 11.9 (0.05:1:0.16)	1.35	0.67	5.77
II	5	1.65	168; 64.2 (2000); – 18.4 (0.3:1:0.3)	1.70	0.76	5.62
	6	2.7	45.6 (1200); – 13.2 (1:0.08)	1.25	0.76	6.12
	7	4.15	15.6(800); – 11.5 (1:0.07)	1.36	0.73	5.69
	8 ^c	2.7	not determined	1.11	0.74	6.18
	9 ^d	4.0	181 (1800); 38.6 (800) (0.8:1)	5.18	0.82	4.14

^a Samples 1–4 were prepared using $\text{Fe}_2(\text{SO}_4)_3$ (series I); samples 5–9 were prepared using $\text{Fe}(\text{NO}_3)_3$ (series II).

^b The ratio in these parentheses is the ^{31}P NMR intensity signal ratio; the intensity of the italic signal serves as a unit.

^c HPC is precipitated by TBANO_3 .

^d In HPC synthesis, $\text{Fe}:\text{PW}_{11} = 4:1$; in other cases the ratio is 1:1.

on a Specord M-40 in the range of 30000–11000 cm^{-1} . IR spectra of solid HPC samples in KBr were recorded on a Specord IR-75.

^{31}P and ^{17}O NMR spectra were taken on a Bruker MSL-400 spectrometer at 161.98 and 54.24 MHz with 0.05 and 50 Hz scan frequency, respectively. Chemical shifts (δ) were counted with respect to external references, namely aqueous solutions of 85% H_3PO_4 or H_2O . The magnetic susceptibility of solid TBA salts of HPC was measured by the Faraday method.

3. Results and discussion

3.1. Identification of Fe(III)-containing HPC

The catalytic activity as well as the final product yield of benzene oxidation by H_2O_2 in the presence of iron salts depend on the anion and decrease in a series: $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ [8]. With regard to the effect of SO_4^{2-} and NO_3^- ions on the composition of Fe(III)-HPC, two series of complexes were obtained. Series I originated from $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ solution and $\text{Fe}_2(\text{SO}_4)_3$ salt, series II came from the $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ and $\text{Fe}(\text{NO}_3)_3$ ones. HPC composition of series I was studied in detail using UV-VIS, IR, NMR ^{31}P , ^{183}W , ^{17}O spectroscopy and magnetic measurements [3]. Mononuclear complex **1** usually exists at $\text{pH} < 3$. It is not observed in the ^{31}P NMR spectra due to a great broadening of NMR signals. The exchange of SO_4^{2-} ions was observed in HPC solutions by NMR ^{17}O spectra, assuming the presence of sulfate complex **1'**. At $\text{pH} = 3-5$, the ^{31}P NMR spectra show the presence of binuclear complexes **2** and Fe(III)-polynuclear hydroxo complexes **3**. The ^{31}P chemical shift of complexes **2** and **3** depends on pH due to quick protonation equilibria of HPC. The spectra characterizing HPC of series I are denoted in Table 1.

^{31}P NMR spectra of series II aqueous solutions are similar to those of series I. At $\text{Fe}:\text{PW}_{11} = 1:1$ and $\text{pH} > 2$ the italic signal in Table 1

predominates. As pH increases from 2 to 5, the signal shifts regularly to a weaker field, while its width decreases (Table 1, compare samples 2,4 and 5–7). As in HPC solutions of series I, the signal should be assigned to complex **2**. Aqueous HPC solutions contain small admixtures of $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (Table 1, samples 4, 6, 7) or $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (Table 1, sample 5) whose signal positions are somewhat different from the conventional ones due to the presence of paramagnetic Fe(III) ions ($\delta = -13.2 \div -11.5$ ppm and $\delta = -18.4$ ppm, respectively). According to the stoichiometry, broad weak signals with higher chemical shifts, sometimes observed, can be attributed to complexes, containing more than 1 Fe(III) ion. At $\text{Fe}:\text{PW}_{11} = 4:1$, we have detected a signal from complex **2** and a broad signal (at $\delta = 181$ ppm) with a commensurable intensity (Table 1, sample 9). The latter should be attributed to polynuclear hydroxo complexes similar to **3**. According to the relation between the ^{31}P NMR signals intensity and reagents concentration, complexes **3** contain, on average, 8 Fe(III) ions per HPA. In TBA salts of HPC, the content of Fe corresponds to HPC composition in aqueous solutions (Table 1).

IR spectra of TBA salts precipitated from aqueous solutions at $\text{Fe}:\text{PW}_{11} = 1:1$ and $\text{pH} = 2-5$ are typical of substituted Keggin HPC PW_{11}M [12]: $\nu_{\text{as}}(\text{PO}_4) = 1060-1065$ cm^{-1} , $\nu_{\text{as}}(\text{W}=\text{O}) = 955-960$ cm^{-1} , $\nu_{\text{as}}(\text{W}-\text{O}-\text{W}) = 875-883$, $805-807$ cm^{-1} , $\nu_{\text{as}}(\text{W}-\text{O}-\text{Fe}) = 690$ and 655 cm^{-1} (for example, Fig. 1, spectrum 2). IR spectra of TMA salts precipitated from the solution, pH 5 (Fig. 1, spectrum 1) exhibit an additional band at 745 cm^{-1} , belonging most probably to $\nu_{\text{as}}(\text{Fe}-\text{O}-\text{Fe})$ of binuclear complex $\{[(\text{CH}_3)_4\text{N}]_5\text{PW}_{11}\text{O}_{39}\text{Fe}_2\text{O}\}$ [3,13]. In the IR spectrum of TBA salt (sample 9), obtained at $\text{Fe}:\text{PW}_{11} = 4:1$, weak bands at 690 and 655 cm^{-1} are almost unseen. There appears a band at ~ 750 cm^{-1} (Fig. 1, spectrum 3), which presumably belongs to Fe–O–Fe stretch vibrations in polynuclear fragment $[\text{Fe}_n\text{O}_x\text{H}_y]$. The latter is located, most probably, near the coordination vacancy in the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anion.

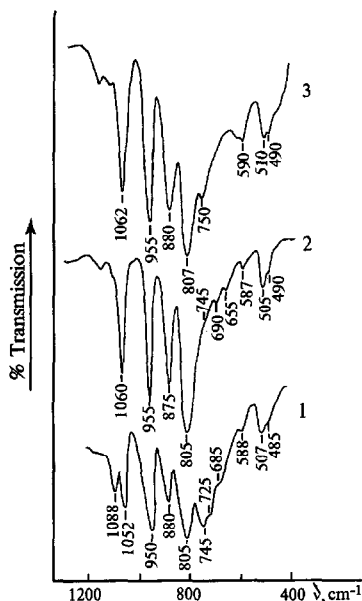


Fig. 1. IR spectra of $\{[(\text{CH}_3)_4\text{N}]_5\text{PW}_{11}\text{O}_{39}\text{Fe}\}_2\text{O}$ (1) and TBA salts of HPC (2, 3); 2 – sample 4; 3 – sample 9 (the same sample numbering as in Tables 1 and 2).

In aqueous solutions of HPC at $\text{Fe}:\text{PW}_{11} = 1:1$, the magnetic susceptibility decreases regularly as pH increases, indicating the formation of binuclear complex 2 [3]. The Fe^{3+} magnetic moment in solid TBA salts, precipitated at $\text{Fe}:\text{PW}_{11} = 1:1$ and $\text{pH} = 2 \div 5$ (Table 1, samples 1–4 and 5–8), approximates the spin-only value $5.92 \mu_{\text{B}}$, thus indicating the magnetic-isolated state of Fe^{3+} . The same value of magnetic moment was measured for these compounds in 0.1 M acetonitrile solutions. The magnetic moment of TMA binuclear complex $\{[(\text{CH}_3)_4\text{N}]_5\text{PW}_{11}\text{O}_{39}\text{Fe}\}_2\text{O}$ is significantly lower, $3.05 \mu_{\text{B}}$. For TBA salts obtained at $\text{Fe}:\text{PW}_{11} = 4:1$ (Table 1, sample 9), the magnetic moment is also markedly lower ($4.14 \mu_{\text{B}}$), since Fe^{3+} is bonded in polynuclear fragments. Thus, in acetonitrile solutions of TBA salts, at $\text{Fe}:\text{PW}_{11} = 1:1$, HPC exists as monomer ions $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{L})]^{p-}$ (L may be H_2O , OH^- , SO_4^{2-} , Br^- , CH_3CN etc.), which are not observed in the ^{31}P NMR spectra.

Electronic spectra of TBA salts in acetonitrile evidence the intensive absorption in the visible region. At $\text{Fe}:\text{PW}_{11} = 4$, the absorption maxi-

imum of polynuclear $\text{Fe}(\text{III})$ -hydroxo complexes is located at $\sim 21600 \text{ cm}^{-1}$ (Fig. 2, spectrum 1). If $\text{Fe}:\text{PW}_{11} = 1$, there are no maxima in this region for all samples. As some water ($\text{CH}_3\text{CN}:\text{H}_2\text{O} = 5:1$) is added, the absorption intensity at $\text{Fe}:\text{PW}_{11} = 1:1$ decreases (Fig. 2, spectra 2, 3), and that of polynuclear $\text{Fe}(\text{III})$ -hydroxo complexes (sample 9) does not essentially change. Such behavior is presumably caused by peculiar features of HPC interaction with solvent molecules. There are differences in absorption spectra of various TBA salts of $\text{Fe}:\text{PW}_{11} = 1$ ratio at $\text{CH}_3\text{CN}:\text{H}_2\text{O} = 5:1$. The absorption intensity of sample 5 of series II, precipitated from acidic solutions of $\text{pH} = 1.65$, exceeds that of samples 6 and 7, $\text{pH} = 2.7$ and 4.15 , respectively (see Fig. 2, spectra 3 and 5). Br^- ions in the precipitant solution do not affect the complexes composition, since the substitution of TBABr by TBANO_3 (samples 7 and 8, $\text{pH} = 2.7$) does not change the absorption spectrum of the salt obtained (Fig. 2, spectrum 5). However, the absorption intensity of TBA salts of series I is higher than that of series II, precipitated in the same pH region (Fig. 2, spectra 4 and 5).

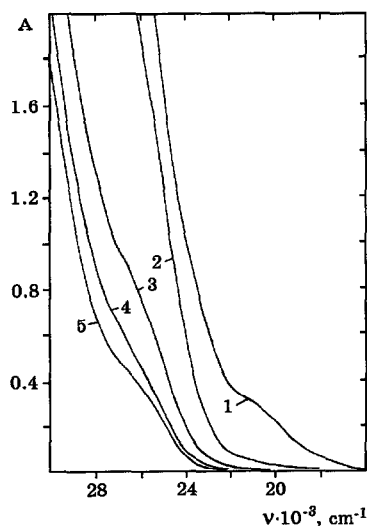


Fig. 2. Absorption spectra of TBA salts of $\text{Fe}(\text{III})$ -HPC in acetonitrile solutions (0.05 g of HPC in 1.5 ml of $\text{CH}_3\text{CN} + 0.3$ ml of H_2O): 1 – sample 9, 2 – sample 5 without H_2O , 3 – sample 5, 4 – sample 4, 5 – samples 6, 7, 8 (samples numbering as in Tables 1 and 2). $l = 0.1$ cm.

3.2. Benzene oxidation by hydrogen peroxide in the presence of HPC

We have concurrently followed the phenol accumulation and H_2O_2 decomposition during C_6H_6 oxidation in acetonitrile solutions containing HPC and aqueous H_2O_2 ($\text{CH}_3\text{CN}:\text{H}_2\text{O} = 6:1$). For all samples of series I, the kinetic curves of phenol accumulation are S-shaped (Fig. 3). The reaction rate increases until $\sim 5\%$ of the benzene is spent, then it starts to decrease. According to experimental results obtained in the absence of C_6H_6 , only insignificant amounts of phenol are spent for the oxidation under reaction conditions. C_6H_6 oxidation and H_2O_2 decomposition proceed simultaneously in the system. By the time when phenol stops to form in the presence of complexes **1** and **1'**, only one-third of H_2O_2 is spent. The yield of phenol with respect to H_2O_2 decomposed is about 10% (Table 2, samples 1–4). Under these reaction conditions, poorly soluble $\text{Fe}_2(\text{SO}_4)_3$ catalyzes H_2O_2 decomposition while phenol does not form.

For sample 2, the reaction rate, estimated from the fast-rate portions of kinetic curves (Fig. 4), grows with increasing the initial concentration of C_6H_6 . As the initial concentration of H_2O_2 increases, the phenol yield rises (Fig. 5).

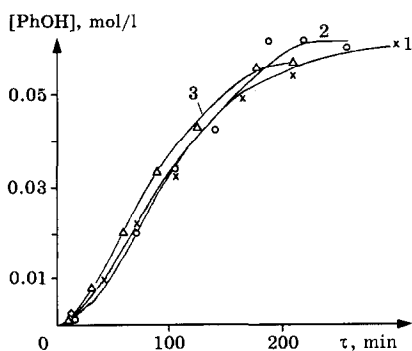


Fig. 3. Concentration of phenol formed upon benzene oxidation in the presence of HPC in CH_3CN solution as a function of time: $[\text{HPC}] = 6 \cdot 10^{-3}$, $[\text{H}_2\text{O}_2]_0 = [\text{C}_6\text{H}_6]_0 = 1.4$ mol/l; 70°C ; 1 – sample 1, 2 – sample 2, 3 – sample 3 (samples numbering as in Tables 1 and 2).

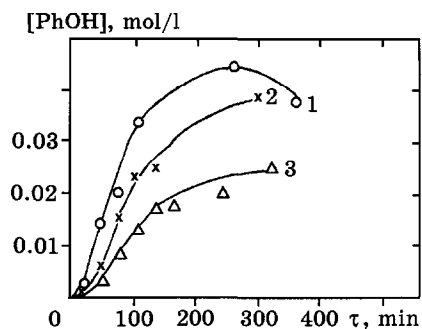


Fig. 4. Kinetic curves of phenol accumulation in benzene oxidation with H_2O_2 in the presence of HPC (sample 2) in CH_3CN solution at varied concentrations of C_6H_6 : 1 – $[\text{C}_6\text{H}_6]_0 = 5.6$, 2 – 2.8, 3 – 1.4 mol/l; 70°C ; $[\text{HPC}] = 6 \cdot 10^{-3}$, $[\text{H}_2\text{O}_2]_0 = 0.35$ mol/l.

For the samples of series II containing either $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$ or $[\text{PW}_{11}\text{O}_{39}\text{Fe}_n\text{O}_x\text{H}_y]^{m-}$ complexes, the kinetic curves of phenol accumulation obtained in the presence of both HPC are much similar (Fig. 6, curves 1, 3). The reaction rate slightly increases until the same amount of phenol is formed, then it drops. The rate of H_2O_2 decomposition in the presence of complexes **1** and **3** is almost equal (Fig. 6, curves 1' and 3'). The phenol yield towards H_2O_2 decomposed attains $\sim 10\%$ (Table 2, samples 5, 9). $\text{Fe}(\text{NO}_3)_3$ dissolves in the reaction medium, rapidly decomposes H_2O_2 and

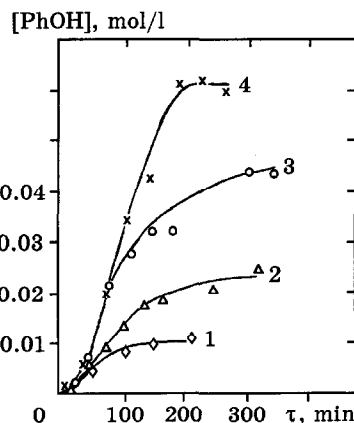


Fig. 5. Kinetics curves of phenol accumulation in benzene oxidation in the presence of HPC (sample 2) in CH_3CN solution at various H_2O_2 concentrations: 1 – $[\text{H}_2\text{O}_2]_0 = 0.175$, 2 – 0.35, 3 – 0.7, 4 – 1.4 mol/l; $[\text{HPC}] = 6 \cdot 10^{-3}$; $[\text{C}_6\text{H}_6]_0 = 1.4$ mol/l, 70°C .

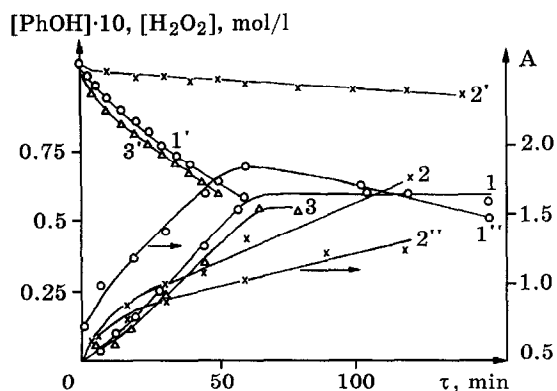


Fig. 6. H_2O_2 concentration ($1'-3'$), phenol concentration ($1-3$) and optical density (A) ($1''-2''$) in benzene oxidation in the presence of HPC in CH_3CN solution as functions of time. $[\text{HPC}] = 6 \cdot 10^{-3}$, $[\text{H}_2\text{O}_2]_0 = 1.07$, $[\text{C}_6\text{H}_6]_0 = 1.4$ mol/l; 70°C : 1, $1'$, $1''$ – sample 5; 2, $2'$, $2''$ – sample 6; 3, $3'$ – sample 9 (samples numbering as in Tables 1 and 2).

yields the same maximum phenol quantity (Table 2, sample 10) in 10 min. Complex 1 of series II allows to decrease the time of maximum phenol accumulation and H_2O_2 decomposition 3-fold (Table 2) as compared to similar complexes of series I. This means that SO_4^{2-}

ions present in HPC of series I decrease their catalytic activity in both reactions.

It should be noted that in the presence of samples 1–3, obtained at varied pH values, the kinetic curves of phenol accumulation almost coincide (Fig. 3, curves 1–3). This fact can be caused by almost complete substitution of H_2O or OH^- by SO_4^{2-} in the Fe(III) coordination sphere of complexes.

For the samples containing complex $2'$ (Fig. 6, curve 2), the kinetics is different. As the reaction starts, the rate of phenol formation is high, then it decreases and becomes constant. Meanwhile, the rate of H_2O_2 decomposition is significantly lower than in the presence of other Fe(III) -complexes (Fig. 6, curve $2'$). The yield of phenol with respect to H_2O_2 decomposed attains almost 60% (Table 2, samples 6–8). For sample 8, H_2O_2 decomposition is somewhat quicker than for samples 6, 7, presumably due to Ag^+ ions admixture.

HPC exposed to the reaction mixture (aqueous H_2O_2 + benzene in CH_3CN) was studied

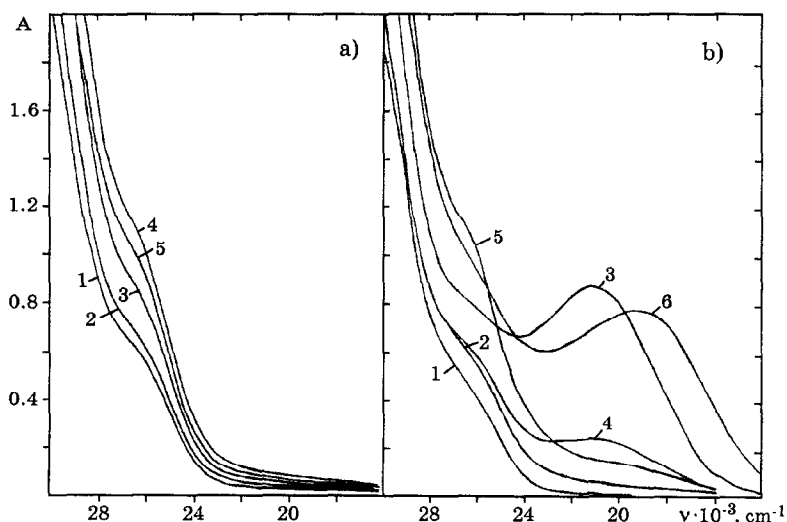
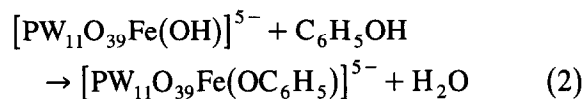


Fig. 7. (a) HPC absorption spectra during benzene oxidation: $[\text{HPC}] = 6 \cdot 10^{-3}$; $[\text{H}_2\text{O}_2]_0 = 1.07$, $[\text{C}_6\text{H}_6]_0 = 1.4$ mol/l (0.1 g of HPC (sample 6) + 3 ml of CH_3CN + 0.5 ml of 8.6 M H_2O_2); 70°C , $l = 0.1$ cm; 1 – after 5 min; 2 – 16 min; 3 – 45 min; 4 – 120 min; 5 – 3 days ($\sim 25^\circ\text{C}$). (b) Absorption spectra during the HPC interaction (sample 6) with H_2O_2 , phenol or pyrocatechol (PC): 1 – $[\text{HPC}] = 6 \cdot 10^{-3}$ mol/l (0.1 g of HPC in 3.5 ml of CH_3CN + 0.5 ml of H_2O); 2 – $[\text{HPC}] = 6 \cdot 10^{-3}$, $[\text{H}_2\text{O}_2] = 1.07$ mol/l (0.1 g of HPC in 3.5 ml of CH_3CN + 0.5 ml 8.6 M of H_2O_2), 70°C , 1 h; 3 – $[\text{HPC}] = 6 \cdot 10^{-3}$, $[\text{PhOH}] = 0.06$ mol/l (0.1 g of HPC in 3.5 ml of CH_3CN + 0.5 ml of H_2O + 0.011 g of PhOH), 70°C , 3 h; 4 – the same as in 3, 0.5 ml of 8.6 M H_2O_2 is used instead of H_2O ($[\text{H}_2\text{O}_2] = 1.07$ mol/l), 25°C , 1 h; 5 – solution 4, 70°C , 3 h; 6 – $[\text{HPC}] = 6 \cdot 10^{-3}$, $[\text{PC}] = 5.2 \cdot 10^{-3}$ mol/l (0.1 g of HPC in 3.5 ml of CH_3CN + 0.5 ml of H_2O + 0.0023 g of PC), 70°C , 1 h; $l = 0.1$ cm.

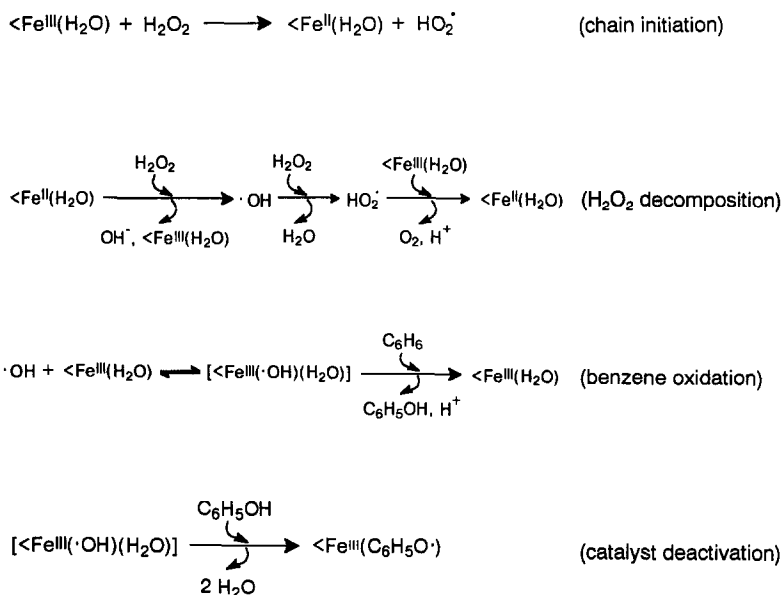
by UV–VIS spectroscopy. During the reaction, all the samples exhibit the spectrum characteristic of Fe(III)-HPC. Besides, there appears a more intensive absorption around the maximum 27000 cm^{-1} (Fig. 7a). The increase of reaction mixture absorbance versus time is symbatic to the kinetic curves of phenol accumulation in the presence of complexes **1** and **2'** (Fig. 6, curves 1 and 1''; 2 and 2''). In the presence of $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$, the absorption at 27000 cm^{-1} achieves its maximum when phenol stops to form. The adsorption decreases and the spectrum returns to its initial state during several days at room temperature. As for $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})]^{5-}$, the absorption increase is lower during the reaction. Sediments formed in the reaction did not allow us to obtain the spectra in the presence of $[\text{PW}_{11}\text{O}_{39}\text{Fe}_n\text{O}_x\text{H}_y]^{m-}$. H_2O_2 most likely causes the breakdown of Fe(III)-polynuclear fragments.

Fe(III)-HPC in CH_3CN in the presence of H_2O_2 forms peroxo complexes [10], causing absorption increase in the visible spectrum region. However, one can not attribute the absorption increase observed in the reaction process to

peroxo complexes only, since the absorption is far lower in the presence of H_2O_2 solely (Fig. 7b, spectra 1, 2). Phenol interacts with HPC **2'** to form a red complex ($\nu_{\text{max}} = 21100\text{ cm}^{-1}$, Eq. (2)), which is stable at 70°C (Fig. 7b, spectrum 3). The complex of HPC with phenol is practically not observed in the presence of H_2O_2 at room temperature (Fig. 7b, spectrum 4). The spectrum of the latter solution heated at 70°C for 3 h and the spectrum of the reaction mixture are quite similar (Fig. 7a, spectrum 4 and Fig. 7b, spectrum 5). Pyrocatechol is the product of deeper benzene oxidation in similar systems [8,15]. Like phenol, pyrocatechol and $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})]^{5-}$ form a dyed complex stable at 70°C ($\nu_{\text{max}} = 19300\text{ cm}^{-1}$, Fig. 7b, spectrum 6). The spectrum of this complex, after heating at 70°C for 0.5–1.5 h in the presence of H_2O_2 , is also similar to that obtained in benzene oxidation.



Under the same conditions, $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$ and phenol or pyrocatechol do not



Scheme 1. Catalysis of hydrogen peroxide decomposition and benzene oxidation by heteropoly complex $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$.

form a complex at $\nu_{\max} = 21100$ (or 19300) cm^{-1} , though a slight solution darkening indicates the one-electron reduction of HPC, which produces $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{5-}$. Addition of H_2O_2 causes the increase in absorption near 27000 cm^{-1} which is typical for the reaction mixtures. The spectral data allow us to attribute the changes in HPC absorption spectra during the reaction to the complex formation between HPC and organic oxidation intermediates (such as $\text{C}_6\text{H}_5\text{O}\cdot$ or semiquinone radicals) rather than to the reaction products (phenol or pyrocatechol) accumulation.

Thus, the data obtained showed different catalytic properties of the three types of Fe(III)-heteropolycomplexes.

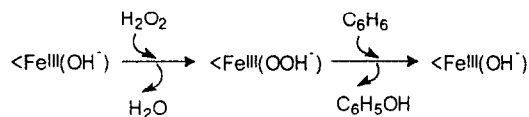
3.2.1. Catalytic properties of $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$ and related complexes

$[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$ and $\text{Fe}(\text{NO}_3)_3$ have similar catalytic properties in H_2O_2 decomposition and benzene oxidation, though nitrate is more active in both reactions. In the presence of SO_4^{2-} -containing HPA, the reaction rate is markedly lower, but kinetic features are the same. The yield of phenol with respect to H_2O_2 decomposed is only 10–20% for all these compounds.

All results obtained agree with chain radical mechanism for H_2O_2 decomposition [16] and C_6H_6 oxidation in the presence of $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$ (for brevity, $<\text{Fe}^{\text{III}}(\text{H}_2\text{O})$) and related complexes (Scheme 1).

Under similar conditions, the oxidation of benzene and cyclohexene also proceeds in the presence of Cr(III)-complexes with $[\text{PW}_{11}\text{O}_{39}]^{7-}$ due to the formation of an intermediate complex between HPC and OH radicals, formed during H_2O_2 decomposition [2]. C_6H_6 oxidation in the presence of Fe(III)-complex **1** proceeds most likely via such an intermediate too.

During the reaction proceeding in the presence of complex **1**, a colored product was accumulated. When the concentration of the latter reached its maximum, phenol stopped to form. The absorption spectra evidence that the catalyst



Scheme 2. Benzene oxidation by hydrogen peroxide in the presence of $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})]^{5-}$.

deactivation is caused by accumulation of HPC complexes with the products of one-electron oxidation of phenol (or pyrocatechol).

3.2.2. The mechanism of H_2O_2 activation in the presence of complex $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})]^{5-}$

Hydroxo complex $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})]^{5-}$, **2'**, formed from bridged μ -oxo-complex **2**, is least active in H_2O_2 decomposition and rather active in C_6H_6 oxidation. These properties allow to increase the yield of phenol with respect to H_2O_2 decomposed up to 60%.

Complex $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})]^{5-}$ ($<\text{Fe}^{\text{III}}(\text{OH}^-)$ in Scheme 2), being a more weak oxidizer than $[\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{H}_2\text{O})]^{4-}$, provides a considerable rate decrease in the outer-sphere reaction of the chain initiation during H_2O_2 decomposition, according to [16]. On the other hand, the absorption spectra show a rapid formation of the colored product during the interaction between complex **2'** and H_2O_2 . Benzene oxidation has no induction period if complex **2'** is present. These data support our previous assumption regarding the cyclohexene oxidation [10] in a similar system, i.e. the initial formation of peroxo complexes is the most probable way of H_2O_2 activation by complex **2'** (see Scheme 2).

For complex **2'**, the concentration of the radical products of phenol (pyrocatechol) oxidation is lower than that obtained in the presence of complex **1** due to a low concentration of OH radicals in the system. Hence, $[<\text{Fe}(\cdot\text{OR})]$ forms less and the catalyst works longer.

3.2.3. Behavior of $[\text{PW}_{11}\text{O}_{39}\text{Fe}_n\text{O}_x\text{H}_y]^{m-}$ complexes in the catalytic system

Catalytic activity of Fe(III)-polynuclear hydroxo complexes in benzene oxidation and H_2O_2 decomposition is similar to that of mononuclear

complex **1**. Extra Fe(III) ions in complexes **3** do not increase the catalytic activity in C₆H₆ oxidation, presumably owing to polynuclear Fe(III) fragments destruction by H₂O₂.

4. Conclusion

UV–VIS, ³¹P NMR, IR spectroscopy and magnetic measurements allowed us to find out that the composition of Fe(III)-complexes with heteropoly anion [PW₁₁O₃₉]⁷⁻ depends on (i) the formation conditions in aqueous solutions, (ii) the procedure of HPC transfer to organic solvents and, (iii) on the reaction mixture composition.

In both reactions, H₂O₂ decomposition and benzene oxidation, the catalytic performance of mononuclear iron HPC, [PW₁₁O₃₉Fe(L)]^{p-} (L = H₂O, SO₄²⁻, OH⁻), depends dramatically on ligand L in the Fe(III) coordination sphere. In the presence of [PW₁₁O₃₉Fe(H₂O)]⁴⁻ formed at pH ~ 2, benzene oxidation proceeds via the chain radical mechanism. The intermediates of H₂O₂ decomposition, OH radicals bonded to HPC, act as oxidant. When H₂O is substituted by SO₄²⁻ in the Fe(III) coordination sphere in HPC, the rates of H₂O₂ decomposition and C₆H₆ oxidation decrease. Binuclear μ-oxocomplex [(PW₁₁O₃₉Fe)₂O]¹⁰⁻, formed at pH = 3 ÷ 5, converts to [PW₁₁O₃₉Fe(OH)]⁵⁻ during HPC precipitation by TBA cations.

The mechanism of benzene oxidation in the presence of the latter complex differs from that for the above mentioned monomer HPC. Namely, at a low rate of H₂O₂ decomposition, benzene is oxidized by the initially formed peroxo complexes of HPC. We have also obtained the polynuclear hydroxo complexes [PW₁₁O₃₉Fe_nO_xH_y]^{m-}, preserving their compo-

sition in acetonitrile. Yet, we did not manage to study their activity in benzene oxidation by H₂O₂ molecules, since the latter decompose partially polynuclear Fe(III) fragments during the interaction.

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