Relation between structure and catalytic properties of transition metal complexes with heteropolyanion $PW_{11}O_{39}^{7-}$ in oxidative reactions

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Abstract

The content and structural features of transition metals Fe(III), Cr(III), Ru(IV), Ti(IV) and V(IV) complexes with the heteropolyanion $PW_{11}O_{39}^{7-}$ depending on the starting M-compound, molar ratio of reagents, temperature and pH of the solution were studied. Heteropolycomplexes (HPC) of three types were identified using NMR ^{31}P, ^{17}O, ^{183}W, IR, UV–VIS spectroscopy, magnetic measurements and elemental analysis: I – M-substituted HPC, II – M-supported HPC, III – polynuclear hydroxocomplexes of M, stabilized by the heteropolyanion. The catalytic properties of HPC obtained have been studied in oxidation of cyclohexene, benzene, alcohols, aldehydes with hydrogen peroxide and other oxygen containing oxidants. It was demonstrated, that the nature of bonding of metal ions with the heteropolyanion, additional ligands of M ions in HPC content, as well as the composition of reaction mixture are the governing factors of HPC catalytic performance. A mechanistic study of hydrogen peroxide participated oxidations in the presence of Cr(III)- and Fe(III)-containing HPC was performed.

1. Introduction

An advance in heteropolycompound chemistry expands capabilities of designing mono- and polynuclear catalytic sites of various types for selective oxidation of organic compounds [1,2]. Our studies were aimed at the synthesis of complex ions of transition metals (M) such as Fe(III), Cr(III), Ru(IV), V(IV) and Ti(IV) with the heteropolyanion (HPA) $PW_{11}O_{39}^{7-}$, of various compositions and structures and at elucidation of factors affecting their catalytic activity for oxygen transfer reactions. The present paper comprises our recent results obtained in this direction.

2. Experimental

To prepare HPC containing Fe(III), Cr(III), Ru(IV), Ti(IV) and V(IV) ions, an appropriate M-compound was dissolved in an aqueous solution of $Na_7PW_{11}O_{39}$. The molar ratio of $M:PW_{11}$,

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pH of the solution, temperature and time of reaction were varied.

The aqueous solutions of Fe(III)-containing HPC were obtained by adding $Fe_2(SO_4)_3 \cdot 9H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ salts to the 0.05 M solution of $Na_7PW_{11}O_{39}$ in the molar ratio Fe:PW_{11} = 1 (or 4), with a subsequent addition of Na_2CO_3 solution to attain the needed pH values from 1.6 to 5.0 [3,11]. To prepare Cr(III)-containing HPC $Cr(NO_3)_2 \cdot 9H_2O$ was dissolved in 0.1 M $Na_7PW_{11}O_{39}$ taken at pH 4.4 for samples (1)–(3) and 5.7 for samples (4) and (5) in Table 2. The molar ratio of Cr:PW_{11} was 1 for (1)–(4) and 2 for (5). The resulting solutions were kept for 1 or 24 h at room temperature ((2) and (3)–(5), respectively) or 1 h at 95°C (1) [6]. The preparation of complex $P_2W_{20}Cr$ (sample (6)) is given in [7]. Ru(IV)-HPC was prepared by adding 0.39 g $K_2RuOHCl_5$ (1.05 mmol) to 100 ml of an 0.01 M $Na_7PW_{11}O_{39}$ taken at pH 4 and heating a mixture at 80°C for 30 min [8,9]. Ti(IV)-HPC was prepared from 0.01 M $Na_7PW_{11}O_{39}$ and $Ti_2(SO_4)_3$ solution in H_2SO_4 at variable Ti:PW_{11} ratio, from 1 to 12, with subsequent Ti(III) oxidation with O_2 and Na_2CO_3 solution addition up to pH 2 or 4 [12]. Oligomeric V(IV)-complexes were prepared from $H_4PW_{11}VO_{40}$ and $VOSO_4$ in 7 M CH_3COOH by adding NaOH solution until pH 4 was reached [13].

Addition of tetrabutylammonium (TBA) bromide in the molar ratio TBA:PW_{11} = 10 resulted in M-containing HPC precipitation, the salts were isolated, washed with water and dried in air.

Catalytic reactions of HPC were carried out in a thermostatically controlled glass reactor supplied with a magnetic stirrer and connected with a gas burette, to follow the volume of gas evolved in H_2O_2 decomposition. The products were analyzed by the GC technique [6,8,11,14].

UV–VIS spectra were recorded on a Specord M-40. The IR spectra of solid TBA salts, in KBr, were recorded on a Specord M-80. ^{31}P and ^{17}O NMR spectra were taken on a MSL-400 Bruker spectrometer [3,11–14].

3. Results and discussion

3.1. Synthesis and characterization of M-containing HPC

Three types of complexes were synthesized in the presence of the same HPA $PW_{11}O_{39}^{7-}$ depending on the composition of the starting M compound, pH of the solution, temperature, and reactants ratio. UV–VIS, IR, ^{31}P and ^{17}O NMR spectroscopic as well as magnetic susceptibility and elemental analytic techniques were used to characterize the obtained compounds.

The first type is the well known M-substituted HPC, which forms mostly upon the interaction of metal aqua-ions with unsaturated

Table 1
Spectral and magnetic characterization of Fe(III)-containing HPC

N heteropolyanion [a]	pH formation	^{31}P NMR [b], δ (ppm)	VIS abs., ν_{max} (cm^{-1}) (ϵ (cm^{-1} M^{-1}))	IR, $\nu_{Fe-O-Fe}$, (cm^{-1})	μ_{eff}, μ_B
1 $[PW_{11}O_{39}Fe(H_2O)]^{4-}$	~2	no signal	no max	no band	5.6 [c]
1' $[PW_{11}O_{39}Fe(SO_4)]^{6-}$	~2	no signal	no max	no band	5.8 [c]
2 $[(PW_{11}O_{39}Fe)_2O]^{10-}$	2.7–5	45–14	24500sh (~ 300), 21700 (~ 100) [b]	750 [d]	3.0 [d]
2' $[PW_{11}O_{39}Fe(OH)]^{5-}$	2.7–5	—	no max	no band	5.6 [e], 6.1 [c]
3 $[PW_{11}O_{39}Fe_8O_xH_y]^{m-}$	~4	181	21700 (~ 800) [b,e]	745 [c]	4.1 [c]

[a] Complex 1' is prepared from $Na_7PW_{11}O_{39}$ and $Fe_2(SO_4)_3 \cdot 9H_2O$, the other complexes from $Na_7PW_{11}O_{39}$ and $Fe(NO_3)_3 \cdot 9H_2O$.
[b] Aqueous solution.
[c] Solid TBA-salt.
[d] Solid TMA-salt
[e] Acetonitrile solution of TBA-salt.

HPA [3–5]. Its characteristic feature is incorporation of a M^{n+} ion into an octahedral vacancy of Keggin's HPA lattice. HPA is a pentadentate ligand, and only one of coordination positions of M^{n+} can be occupied by another ligand. We have detected monomer complexes of iron(III), $[PW_{11}O_{39}Fe(H_2O)]^{4-}$, **1**, and μ-oxocomplexes, $[(PW_{11}O_{39}Fe)_2O]^{10-}$, **2**, in the aqueous solutions. According to their structure, in ^{17}O NMR data, there is exchange of H_2O and SO_4^{2-} ligands in complex **1** and no interaction of complex **2** with SO_4^{2-} ions [3]. When the salts with bulky TBA cations are synthesized, HPC **2** is decomposed to form the monomer complex $[PW_{11}O_{39}Fe(OH)]^{5-}$, **2'**. The spectral characteristics of the prepared Fe(III)-HPC are given in Table 1.

Interaction of Cr(III) ions with $PW_{11}O_{39}^{7-}$ results in the formation of complexes in which the atomic ratio of Cr:P:W = 1:1:11 but various states of Cr(III) are achieved upon little variations in conditions for their synthesis [6,7]. This is seen from the difference in the intensities and the positions of the maximum of Cr(III) d–d transitions (Table 2). IR spectra of TBA salts of the samples obtained displayed a structure close to that of Cr(III)-substituted $PW_{11}Cr^{III}$, but include new lines at the ranges of ν_{as} PO_4 1100–1050 cm^{-1} and ν_{as} W–O–W 815–600 cm^{-1} vibrations. The samples of TBA salts precipi-

tated from pre-heated at 95°C HPC solutions give IR spectra fully corresponding to the spectrum of Cr(III)-substituted HPC: ν_{as} PO_4 1088 and 1055 cm^{-1}; ν_{as} W=O 962 cm^{-1}, ν_{as} W–O–W 885 cm^{-1}, 810 cm^{-1} [15]. The spectral differences of the prepared complex may be accounted for by the possibility of binding between partially hydrolyzed Cr(III) ions of low lability and one or several 'surface' oxygen atoms located around an HPA vacancy. We assigned these complexes to the type II, of M-supported HPC.

We obtained also Ru-supported HPC, containing diamagnetic binuclear fragments ($-Ru^{IV}L_x)_2O$, via interaction of $PW_{11}O_{39}^{7-}$ with $K_2Ru(OH)Cl_5$ [8,9]. Unlike the Ru-substituted HPC, $PW_{11}RuO_{40}^{5-}$ [4], they contain additional ligands L which may be OH^-, SO_4^{2-} or Cl^- ions; the ligand substitution process can be easily detected through a change in the Ru(IV) absorption maximum position at the visible range [9]. The presence of the extra ligands is one of the reasons for the formation of several HPC in the solution that is observed in the ^{31}P NMR spectra. According to the spectral characteristics, the complexes obtained are of a structure close to those studied by Finke et al. [10] for $KLi_{15}[O\{Ru^{IV}Cl(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]\cdot2KCl\cdot60H_2O$. XRD analysis of this complex showed two Ru atoms of a Ru^{IV}–O–Ru^{IV} linkage to be

Table 2

HPC of molar ratio P:W:Cr = 1:11:1 (1–5) and P:W:Cr = 2:20:1 (6) prepared under varied conditions: VIS absorption characteristics, catalytic properties in H_2O_2 decomposition, yield of products formed from benzene (phenol) and cyclohexene (epoxycyclohexane, cyclohexenol, cyclohexenone) oxidation

N	pH precipitation	ν_{max} (cm^{-1}) (ϵ (cm^{-1} M^{-1}))	H_2O_2 conversion, (%)	Product of C_6H_6 oxidation (10^3 M) phenol	Products of C_6H_{10} oxidation (10^3 M)		
					epox-	-enol	-enone
(1)	2.1	15200 (14)	10	0	0	0	0
(2)	3.2	16000 (20)	66	0.9	0.68	0.50	2.17
(3)	3.1	15700 (22)	77	0.6	1.15	0.72	2.05
(4)	3.7	15600 (19)	100	0.8	0.56	0.34	1.14
(5)	2.2	16000 (38)	57	1.7	1.43	0.82	2.88
(6)	~ 3	15900 (30)	~ 0	—	0	0	0

H_2O_2 decomposition: 0.012 M TBA-$PW_{11}Cr$, 0.23 M H_2O_2 in CH_3CN, 35°C, reaction time 1 h;
Substrate oxidations: 0.015 M TBA-$PW_{11}Cr$, 0.16 M H_2O_2, 0.01 M C_6H_{10} or 0.1 M C_6H_6 in CH_3CN; 35°C, reaction time 40 min for C_6H_{10}; 40°C, reaction time 30 min for C_6H_6.

symmetrically placed over the lacunary site in each $\alpha\text{-}P_2W_{17}O_{61}^{10-}$ unit.

The type III complexes are HPA stabilized oligomeric hydroxocomplexes which are formed upon alkalization (to pH ~ 4) of M^{n+} salts in the presence of unsaturated HPA. The complexes contain an average of 2 to ~ 10 ions of Fe(III), Ti(IV), V(IV) per one PW_{11}: $[PW_{11}O_{39}Fe_nO_xH_y]^{m-}$, 3, $[PW_{11}TiO_{40} \cdot Ti_{n-1}O_xH_y]^{p-}$, 4, $[PW_{11}VO_{40} \cdot V_{n-1}O_xH_y]^{q-}$, 5 [3,11–13]. Complexes 3 differ in their spectral and analytic characteristics from other Fe(III)-HPC (Table 1) and behave as individual compounds, i.e., are deposited by TBA cations, the salts obtained are soluble in some organic solvents with no change in their compositions. About a half of their Fe(III) ions may be reduced to Fe(II) and reoxidized by O_2 which results not in the complex destruction [3,11]. IR spectra of complexes 3–5 coincide with those of corresponding mono-M-substituted HPC; hence, one of their metal ions is incorporated into the HPA lattice. The rest of the ions can be attached to either a M ion of the lattice through an oxo-bridge or the neighboring oxygen atoms of HPA to form polynuclear hydroxide fragments. In the latter case the Ti(IV) ion of the lattice of complex 4 remains capable of undestructive interacting with H_2O_2 to bind the peroxide group. Other Ti(IV) ions can also attach the peroxide, but the polynuclear Ti(IV)-complex is destructed in the excess of H_2O_2.

3.2. Catalytic tests of M-containing HPC

HPC of the three types were tested for oxidation of organics with hydrogen peroxide and other oxygen-containing oxidants [6,8,11,14].

Complexes of iron(III) catalyze the decomposition of H_2O_2 and oxidation of benzene to phenol. In the presence of mononuclear Fe(III) complex 1 the formation of phenol is accelerated in time but stops when only a half of H_2O_2 is decomposed. The polynuclear Fe(III) complex 3 and complex 1 showed close rates in both reactions (Fig. 1, curves 1, 1′ and 3, 3′).
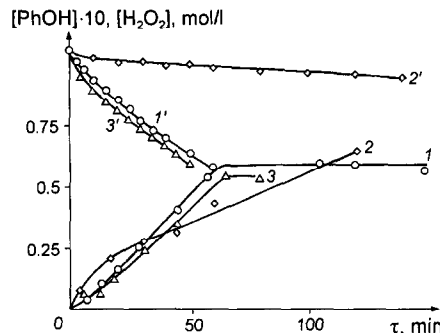

Fig. 1. H_2O_2 concentration (1′–3′) and phenol concentration (1–3) in benzene oxidation in the presence of HPC in CH_3CN solution as functions of time. [HPC] = $6 \cdot 10^{-3}$, $[H_2O_2]_0 = 1.07$, $[C_6H_6]_0 = 1.4$ mol/l; 70°C; 1,1′ – complex 1; 2,2′ – complex 2′; 3,3′ – complex 3.

On the other hand, the catalytic behavior of mononuclear Fe(III)-substituted HPC is strongly influenced by the terminal ligand of the Fe(III) coordination sphere. Thus, sulphate complex 1′ is one third as active as aqua complex 1 is for both reactions. The rate of hydrogen peroxide decomposition is low in the presence of hydroxo complex 2′, and the kinetic curve of phenol accumulation has no induction period, in contrast to complexes 1 and 1′ (Fig. 1, curves 2, 2′). The molar ratio of phenol formed to decomposed H_2O_2 approaches 60% in the presence of 2′, but 10–20% in the presence of 1 and 1′.

Cr(III)-containing complexes were tested in catalysis of H_2O_2 decomposition and oxidation of benzene and cyclohexene with H_2O_2 [6,14]. Under our conditions the Cr(III)-substituted $PW_{11}Cr_1$ complex appeared catalytically inactive for either decomposition of H_2O_2 or oxidation of benzene and cyclohexene with hydrogen peroxide (Table 2, sample (1)). Samples (2)–(5) of $PW_{11}Cr_1$ (Table 2) reveal catalytic activity for the decomposition of H_2O_2 and the substrate oxidation. Benzene is oxidized to phenol; a mixture of an epoxide and allylic alcohol and ketone is formed on oxidation of cyclohexene. After completion of H_2O_2 decomposition, a new portion of H_2O_2 initiates again the process of substrate oxidation. Cr(III)-substituted HPC, $P_2W_{20}Cr_1$, which is, probably, presented as an

impurity in the samples obtained [7], appeared absolutely inactive (Table 2, sample 6). Hence, catalytically active are Cr(III)-supported complexes of type II.

In binuclear Ru-supported complexes, ruthenium(IV) ions undergo rapid reduction to Ru(III) with organics and innersphere oxidation to Ru(V) with chlorate ions [9]. Basing on these reactions, the process of catalytic oxidation of primary alcohols and aldehydes in their aqueous solutions to the corresponding carboxylic acids was developed with almost 100% yields (pH 2; 25–70°C; $[PW_{11}Ru] = 10^{-3}$ M; $[ClO_3^-] = 0.3$– 0.6 M; $[S] = 0.1$–0.5 M) [8]:

$$3R-CH_2OH + 2KClO_3$$

$$\rightarrow 3R-COOH + 2KCl + 3H_2O.$$
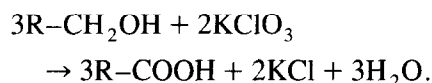
HPC of type III, containing both an M ion of the lattice and electron-conducting oligomeric M-hydroxofragments, can catalyze processes involving both activation of reacting molecules and multielectron transfer. For example, this is oxidation of vanadyl ions with molecular oxygen catalyzed by $[PW_{11}VO_{40}]^{5-}$; both of these species taken individually are not oxidized by molecular oxygen under these conditions (acetate buffer, pH 3–4). The reaction follows, preferably, the four-electron mechanism [16] involving complexes of $[PW_{11}V^{IV}O_{40} \cdot V_{n-1}^{IV}O_xH_y]^{q-}$ ($n \geq 4$) [13,17].

3.3. Mechanism of H_2O_2 activation in the presence of Cr(III)- and Fe(III)-containing HPC

There are two important features of M-containing HPC which make it attractive for mechanistic studies of catalytic reactions involving these compounds. First, the metal ions constituents often form rather stable complexes with the substrate or oxidant at their various transformation stages. Second, HPA is as a probe which provides a way to follow transformations of these complexes using appropriate spectroscopic techniques (^{31}P NMR, UV–VIS, etc.). We have studied the mechanism of hydrogen peroxide activation during oxidation of unsaturated hy-
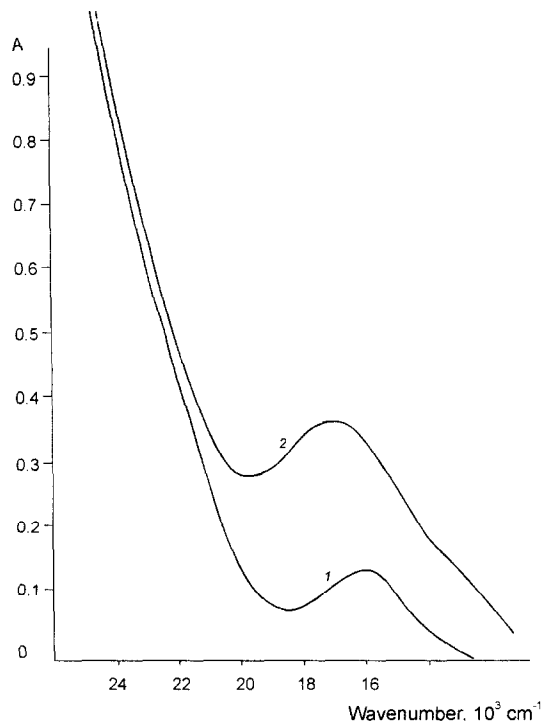

Fig. 2. UV–VIS spectra of $PW_{11}Cr$ solutions in CH_3CN; 1 – 0.013 M sample (5), 2 – 0.013 M sample (5), 0.23 M H_2O_2 after 1 h reaction at 35°C; $l = 0.2$ cm.

drocarbons catalyzed by Cr(III) and Fe(III) constituents of HPC [6,11].

Those $PW_{11}Cr^{III}$ species, which are active for oxidation, produce rather stable colored compounds (Fig. 2, spectrum 2; Fig. 3, curve 1) under the action of H_2O_2. Introduction of hydrocarbon substrate (cyclohexene or benzene) resulted in formation of corresponding O-con-
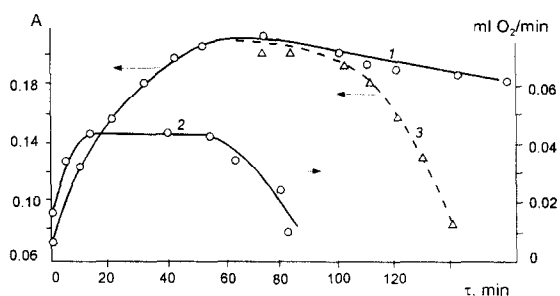

Fig. 3. Time dependence of maximum absorption at 17000 cm^{-1} during decomposition of H_2O_2 (1) and the rate of O_2 evolution (2): 0.015 M sample (5), 0.15 M H_2O_2; absorbance after adding 0.01 M cyclohexene (3), 35°C, $l = 0.1$ cm.

taining products and decreasing visible absorption (Fig. 3, curve 3). After some time, the spectrum returned to the initial one (Fig. 2, spectrum 1). This complex behaves as an intermediate for the oxidation process but not for decomposition of H_2O_2, as its concentration continues increasing even if the constant rate of the H_2O_2 decomposition has been reached (Fig. 3, curve 2). Moreover, there is no clean correlation between the activity for H_2O_2 decomposition and that for oxidation of substrates on various Cr(III)-HPC samples (Table 2). The only satisfactory explanation of the phenomena is that the active oxidizing species are accumulated in the system under the action of starting Cr(III)-containing HPC with intermediates of H_2O_2 decomposition, which may be OH radicals:

$$PW_{11}Cr^{III} + \cdot OH \rightarrow PW_{11}Cr[O].$$
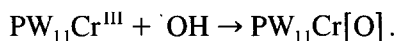
The Cr(V)-substituted oxocomplex $PW_{11}CrO_{40}^{4-}$ prepared by treatment of Cr(III)-substituted HPC with iodosylbenzene or H_2O_2 at pH 10.8 and characterized by an absorption maximum near 14900 cm^{-1}, was an active species of unsaturated hydrocarbons oxidation [15]. However, it did not form under conditions of our catalytic studies. As was shown before, the oxidation with hydrogen peroxide is catalyzed by Cr-supported HPC rather than Cr-substituted ones. The maximum of visible absorp-

tion of active oxidizing species formed during reaction with H_2O_2 is observed at 18000–16700 cm^{-1} for various samples of catalytically active Cr(III)-HPC, for example, Fig. 2, spectrum 2.

Mononuclear Fe(III)-substituted HPC are active catalysts for oxidation with H_2O_2. The state of HPC in the course of benzene oxidation with hydrogen peroxide and also under the action of various components of the reaction mixture, was studied using UV–VIS spectroscopy. As phenol is accumulated, the HPC absorption intensity increases in the visible range, a larger increase being observed for complex **1** than for complex **2'**. This is a much higher absorption than that observed upon the formation of complexes of HPC with H_2O_2 (Fig. 4, spectra 1 and 2). Phenol and pyrocatechol with complex **2'** form colored compounds producing different spectra (Fig. 4, spectra 3 and 4). When these compounds are heated in the presence of H_2O_2, their spectra become resembling those recorded for the reaction solutions (Fig. 4, spectrum 5). The data obtained argue for the formation of stable complexes of HPC with the oxidation products of phenol or pyrocatechol (likely, RO$\cdot$ radicals of semiquinone type) during oxidation of benzene. Apparently, this process bears responsibility for the catalyst deactivation.

All the results obtained agree with the chain radical mechanism for H_2O_2 decomposition [18] and C_6H_6 oxidation in the presence of
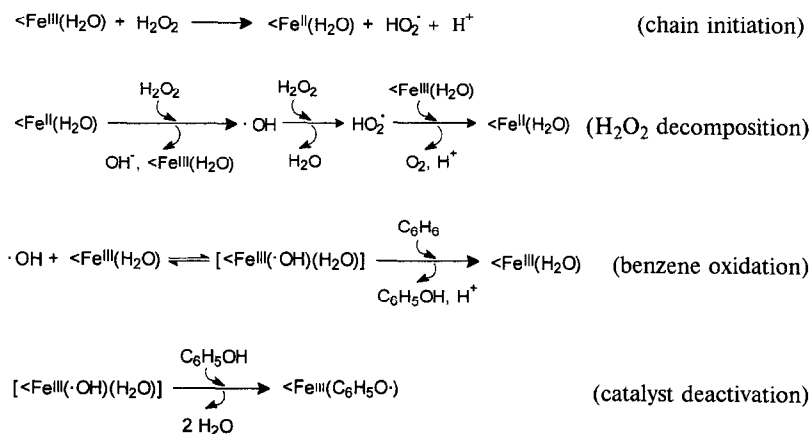
Scheme 1. Catalysis of hydrogen peroxide decomposition and benzene oxidation by heteropolycomplex $[PW_{11}O_{39}Fe(H_2O)]^{4-}$.
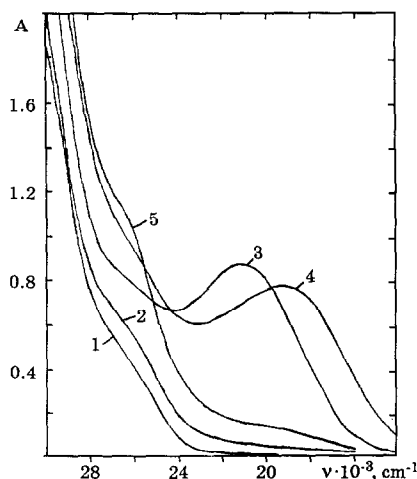
Fig. 4. Absorption spectra during the HPC 2' interaction with H_2O_2, phenol or pyrocatechol (PC): (1) [HPC] = $6 \cdot 10^{-3}$ mol/l (0.1 g of HPC in 3.5 ml of $CH_3CN + 0.5$ ml of H_2O); (2) [HPC] = $6 \cdot 10^{-3}$, [H_2O_2] = 1.07 mol/l (0.1 g of HPC in 3.5 ml of $CH_3CN + 0.5$ ml 8.6 M of H_2O_2), 70°C, 1 h; (3) [HPC] = $6 \cdot 10^{-3}$, [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) [HPC] = $6 \cdot 10^{-3}$, [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; (5) the same as in 3, 0.5 ml of H_2O_2 is used instead of H_2O ([H_2O_2] = 1.07 mol/l).

[PW$_{11}$O$_{39}$Fe(H$_2$O)]$^{4-}$, **1** (for brevity, < Fe^{III}(H$_2$O), Scheme 1), or the **1'** complex. An active oxidizing species is the HPC complex formed during H_2O_2 decomposition (Scheme 1). The complex [PW$_{11}$O$_{39}$Fe(OH)]$^{5-}$, **2'**, being a weaker oxidizer than **1**, provides a considerable rate decrease in the outersphere stage of chain initiation during H_2O_2 decomposition. On the other hand, its absorption spectrum shows a rapid formation of the colored product as a result of interaction between **2'** and H_2O_2. Benzene oxidation has no induction period in the presence of complex **2'**. Thus, the initial formation of peroxocomplexes is the most probable way of H_2O_2 activation by complex **2'** (Scheme 2).
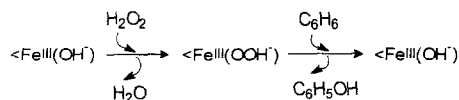
Scheme 2. Benzene oxidation by hydrogen peroxide in the presence of [PW$_{11}$O$_{39}$Fe(OH)]$^{5-}$

4. Conclusions

The catalytic performance of mononuclear iron-substituted complexes [PW$_{11}$O$_{39}$Fe(L)]$^{p-}$ (L = H_2O, SO_4^{2-}, OH^-) in oxidation with H_2O_2 depends dramatically on the kind of ligand L in the Fe(III) coordination sphere. Cr(III)-supported complexes, [PW$_{11}$O$_{39}$ · Cr(L)$_x$]$^{m-}$, seem to be catalytically active species in unsaturated hydrocarbons oxidation rather than Cr-substituted ones under the same conditions. This exemplifies the process when M^{n+} ions, bonded to the HPA surface, reveal a higher catalytic activity than the same ions, incorporated in the Keggin HPA lattice have. Another example of active oxidation catalysts are binuclear Ru-supported complexes.

The presence of a sole metal ion in the active catalyst site is sufficient for oxidation of organics with hydrogen peroxide. HPA-stabilized polynuclear hydroxocomplexes of Fe(III), V(IV), or Ti(IV) are of importance to achieve multielectron redox transformations among which is the process of reduction of O_2 molecules.

Acknowledgements

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