

# Catalytic properties of Cr-containing heteropolytungstates in $H_2O_2$ participated reactions: $H_2O_2$ decomposition and oxidation of unsaturated hydrocarbons with $H_2O_2$

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## Abstract

Cr-containing derivatives of  $PW_{11}O_{39}^{7-}$  heteropolyanion ( $PW_{11}Cr$ ) were synthesized under variation of precursors and procedure (increasing temperature, prolonged keeping of solution, varying molar ratio of starting reagents and acidity) and characterized by elemental analysis, UV-Vis and IR spectroscopy. Tetrabutylammonium salts of  $PW_{11}Cr$  were examined in catalysis of  $H_2O_2$  decomposition and oxygen transfer from  $H_2O_2$  to the hydrocarbon substrates, cyclohexene and benzene. With all the other conditions of synthesis identical, increasing the pH gave samples more active in  $H_2O_2$  decomposition. In the  $H_2O_2/PW_{11}Cr$  system, benzene formed phenol and cyclohexene formed a mixture of cyclohexenone, cyclohexenol and cyclohexene oxide. The activity of  $PW_{11}Cr$  in hydrocarbon oxidation was sensitive to the procedure used for sample synthesis. Variable spectral characteristics and catalytic properties of  $PW_{11}Cr$  samples were suggested to depend on the nature of bond between Cr(III) ion and  $PW_{11}O_{39}^{7-}$  anion. As distinguished from typical M-substituted polyoxometalates, the samples obtained contain Cr(III) ions which are probably connected with surface oxygen atoms of  $PW_{11}O_{39}^{7-}$  heteropolyanion near the vacancy of the Keggin structure. Surface location of Cr(III) ions is supposed to favor oxygen transfer from  $H_2O_2$  to hydrocarbon. In the presence of  $H_2O_2$ ,  $PW_{11}Cr$  solutions showed the increase of visible absorption and a shift of its maximum from 15200–16300 to 15500–18000  $cm^{-1}$ , that arose from the reaction of  $PW_{11}Cr$  with intermediate products of the  $H_2O_2$  decomposition. The resulting oxidized species  $PW_{11}Cr[O]$  are active oxidants in the reaction with unsaturated hydrocarbons.

*Keywords:* Chromium; Heteropolytungstates; Hydrogen peroxide; Oxidation; Cyclohexene; Benzene

## 1. Introduction

A new tendency has been developing recently that represents the use of polyoxometalates as polydentate ligands for guest transition metal ions stabilized in proper oxidation state

owing to rigid environment. In this respect, transition metal-containing polyoxometalates are analogous to metalloporphyrins. In contrast to porphyrin complexes, whose catalytic properties have been thoroughly investigated in different oxidations, the chemistry of metal-containing polyoxometalates is under study now. We are dealing with transition metal-containing polyoxometalates, metal ions of which can serve as

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oxygen transfer agents, normally, Fe(II), Mn(II), Co(II), Ni(II), Cu(II). Several quite successful systems for oxidation of unsaturated hydrocarbons have been published which include organic soluble forms of Keggin-type transition metal-containing polyoxometalates and active oxygen containing oxidants, most often, iodosylbenzene [1–5]. Other oxidants have been used too, for example, alkyl hydroperoxides [6], NaClO [7]. Diluted hydrogen peroxide is the second most attractive oxidant after dioxygen [8,9] because it is inexpensive, environmentally clean and easily handled. Unfortunately, the useful properties cannot facilitate the investigation of  $H_2O_2$  participated oxidations. The difficulty is that reactions with hydrocarbon substrates are accompanied by  $H_2O_2$  decomposition that is sometimes accelerated in the presence of metal complexes. Nevertheless, several systems were constructed basing on  $H_2O_2$  and metal substituted polyoxometalates. Van Bekkum used Ni(II), Co(II), Cu(II), Fe(III)-substituted derivatives of  $PW_{12}O_{40}^{3-}$  heteropolyanion in two-phase solvent conditions aqueous  $H_2O_2$ /dichloroethane [10]. Finke used  $SiW_9(NbO_2)_3O_{37}^{7-}$  for oxidation in  $CH_3CN/H_2O_2$  solution [11]. Hill reported on the considerable activity of [(n-

$C_6H_{13})_4N]_{10}[(Ni^{II})_4(B-PW_9O_{34})_2]$ , [(n- $C_4H_9)_4N]_{10}[(Fe^{II})_4(B-PW_9O_{34})_2]$ , [(n- $C_4H_9)N]_4[(Fe^{II})PW_{11}O_{39}]$  in cyclohexene oxidation with  $H_2O_2/CH_3CN$  [7].

In our previous study [12], a number of metal containing heteropolytungstates derived from  $PW_{11}O_{39}^{7-}$  anion were examined in cyclohexene reaction with  $H_2O_2$ . A subject of our especial interest was Cr(III)-containing heteropolytungstates because of the well-known activity of Cr(III) complexes in direct oxygen transfer from oxidant to hydrocarbon substrate. Moreover, for Cr(III) complexes with porphyrin and other chelating ligands, the intermediates were isolated in reaction with iodosylbenzene, and characterized as oxo-Cr(V) species [13–15]. Similar compounds were obtained by Pope under the action of iodosylbenzene on tetra-n-heptylammonium salts of  $[SiMo_{11}O_{39}Cr^{III}(OH_2)]^{5-}$  and  $[SiW_{11}O_{39}Cr^{III}(OH)]^{6-}$  [16]. Later, Hill succeeded in analogous preparation of two oxo-Cr(V) complexes  $[(C_7H_{15})_4N]_5[SiW_{11}O_{39}Cr^{VO}]$  and  $[(C_6H_{13})_4N]_4[PW_{11}O_{39}Cr^{VO}]$  using iodosylbenzene again, and investigated interaction with cyclohexene in organic solvent [4]. It has been noted that the same result can be obtained using  $H_2O_2$ . No detailed information is available about

Table 1  
Characteristics of the TBA salts of  $PW_{11}Cr$

No	pH <sup>a</sup>	Content <sup>b</sup> , % (atomic ratio)			$\nu$ , $cm^{-1}$ (A) <sup>c</sup>	$\nu$ , $cm^{-1}$ (A) <sup>d</sup>	$H_2O_2$ conversion, % <sup>e</sup>
		Cr	W	P			
1	2.1	1.38 (1.0)	56.4 (11.2)	0.88 (1.0)	15200 (0.022)	15500 (0.030)	10
2	3.2	1.71 (1.0)	57.9 (9.8)	1.0 (1.0)	16000 (0.033)	17500 (0.190)	66
3	3.1	1.42 (0.8)	67.1 (10.7)	1.06 (1.0)	15700 (0.035)	17500 (0.190)	77
4	3.7	1.67 (1.0)	65.7 (11.4)	1.04 (1.0)	15600 (0.030)	18000 (0.130)	100
5	2.2	2.0 (1.1)	70.4 (11.1)	1.07 (1.0)	16000 (0.060)	17000 (0.220)	57
6	0.6	1.38 (0.8)	62.1 (9.9)	1.06 (1.0)	16300 (0.055)	16600 (0.075)	10
7	2.0	1.44 (0.9)	58.9 (10.5)	1.0 (1.0)	16200 (0.068)	16600 (0.140)	55
8	2.5	1.91 (1.0)	72.5 (11.0)	1.1 (1.0)	16000 (0.055)	17000 (0.140)	
9	2.8	2.76 (1.5)	66.0 (10.3)	1.1 (1.0)	16000 (0.10)	17000 (0.190)	

<sup>a</sup> pH of aqueous solutions used for TBA salts precipitation.

<sup>b</sup> Content and atomic ratio according to elemental analysis.

<sup>c</sup> Position of maximum of visible absorption ( $\nu$ ) and optical density (A) for 0.016 M  $PW_{11}Cr$  in  $CH_3CN$ ;  $l = 1$  mm.

<sup>d</sup> Position of maximum ( $\nu$ ) and optical density (A) for 0.016 M  $PW_{11}Cr$ , 0.125 M  $H_2O_2$  in  $CH_3CN$ , measured at the moment of highest absorption,  $T = 35^\circ C$ ;  $l = 1$  mm.

<sup>e</sup>  $H_2O_2$  decomposition per 1 h for samples 1–5, 8, 9 and 0.5 h for samples 6 and 7; starting solution of 0.012 M  $PW_{11}Cr$ , 0.23 M  $H_2O_2$ ,  $T = 35^\circ C$ .

the  $\text{H}_2\text{O}_2/\text{Cr(III)}$ -containing heteropolytungstate system. We set out to study a behavior of  $\text{Cr(III)}$ -containing derivatives of  $\text{PW}_{11}\text{O}_{39}^{7-}$  anion in a homogeneous medium of  $\text{CH}_3\text{CN}/\text{aqueous H}_2\text{O}_2$ , particularly, oxidation of unsaturated hydrocarbons.

## 2. Experimental

### 2.1. Synthesis of Cr-containing heteropolytungstates ( $\text{PW}_{11}\text{Cr}$ )

To prepare the samples 1–5, listed in Table 1,  $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  was dissolved in 0.1 M aqueous solution of  $\text{Na}_7\text{PW}_{11}\text{O}_{39}$  taken at pH 4.4 for samples 1–3 and pH 5.7 for samples 4 and 5. A molar ratio of  $\text{Cr(III)}/\text{PW}_{11}$  was 1 for samples 1–4 and 2 for sample 5. The pH was adjusted with  $\text{NaOH}$  and the resulting solutions were kept for 1 or 24 h at room temperature (samples 2 and 3–5, respectively) or 1 h at  $95^\circ\text{C}$  sample 1. Addition of a 10-fold excess of tetrabutyl ammonium (TBA) bromide resulted in the precipitation of  $\text{PW}_{11}\text{Cr}$  TBA salts, which were isolated by filtration, washed with water and dried in air.

Samples 6 and 7 were prepared from  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as described in [17]. Finally, they were isolated as the TBA salts.

For samples 8 and 9, aqueous solutions were prepared by mixing 0.025 M  $\text{Na}_7\text{PW}_{11}\text{O}_{39}$  taken at pH 4.4, with 0.1 M  $\text{Cr}(\text{NO}_3)_3$  solution that had been kept at pH 2 for 6 months. As long time as 6 months was reported to be necessary for  $\text{Cr}(\text{NO}_3)_3$  solution to reach equilibrium composition, that includes mainly binuclear hydroxocomplexes  $\text{Cr}_2(\text{OH})_2^{4+}$  [18]. After mixing starting reagents in molar ratio  $\text{Cr(III)}/\text{PW}_{11} = 4$ , the solutions were allowed to stay for 24 h at room temperature. Meanwhile, stable pH value was maintained by  $\text{Na}_2\text{CO}_3$  additives, to be 2.5 for sample 8 and 2.8 for sample 9. The procedure was completed by precipitation of TBA salts.

### 2.2. Methods

Elemental analysis of  $\text{PW}_{11}\text{Cr}$  TBA salts, dissolved in a mixture of sulfuric acid with hydrogen peroxide, was performed by atomic absorption spectroscopy.

For analysis of the products of hydrocarbon oxidations, GC (LXM-8MD machine with FID and a column 0.8% OV225 on graphitized carbon black for products of cyclohexene oxidation and Tenax G for benzene derivatives) and GC-MS (LKB model 2091 system operating with DS model 2130 data system) were used.

UV-Vis spectra were recorded on Specord M-40 in the  $30000\text{--}11000\text{ cm}^{-1}$  region. IR spectra were obtained on Specord M-80 instrument in the  $1200\text{--}200\text{ cm}^{-1}$  region.

### 2.3. Catalytic experiments

Catalytic reactions of  $\text{PW}_{11}\text{Cr}$  TBA salts were carried out in a temperature-controlled glass reactor. To follow the volume of gas evolved in  $\text{H}_2\text{O}_2$  decomposition, the reactor was connected to gas burette. The reactor was loaded with 0.1 g of  $\text{PW}_{11}\text{Cr}$  TBA salt dissolved in 2 ml of  $\text{CH}_3\text{CN}$ , and blown through with  $\text{O}_2$  under atm. pressure. Fixed amount of 30% aqueous  $\text{H}_2\text{O}_2$  was introduced, immediately after which stirring was started. Volume of  $\text{O}_2$  evolved was measured at the same time with solution sampling to record UV-Vis spectra.

The same type of reactor was used to oxidize the hydrocarbon substrates. The oxidation was carried out in aerobic conditions after reaction was verified to be independent of the presence of oxygen. The hydrocarbon was introduced together with or shortly after introduction of the hydrogen peroxide. From time to time, the solution was subjected to UV-Vis spectroscopy and/or to analysis of organic products.

## 3. Results

In Table 1 are collected some data on the  $\text{PW}_{11}\text{Cr}$  samples synthesized under different

conditions. Three groups of complexes were derived from different precursors: samples 1–5 from a  $PW_{11}$  solution and solid  $Cr(NO_3)_3 \cdot 9H_2O$ , samples 6 and 7 from a  $PW_{12}$  solution and solid  $Cr(NO_3)_3 \cdot 9H_2O$ , samples 8 and 9 from a solution of Cr(III) hydroxo dimers  $Cr_2(OH)_2^{4+}$  and  $PW_{11}$ . Within the group, there is a relationship between Cr content of the  $PW_{11}Cr$  TBA salts and the pH of the aqueous solution before precipitation (compare samples 3 and 4, 6 and 7, 8 and 9). Two samples, 5 and 9, included a superstoichiometric amount of Cr, which correspond to  $PW_{11}Cr_{1.1}$  and  $PW_{10.3}Cr_{1.5}$ , respectively. The samples were obtained when the starting ratio of the precursors  $Cr(III)/PW_{11}$  was greater than 1.

By absorption spectroscopy, we followed the composition of complexes formed in aqueous solution under various starting ratio  $Cr(III)/PW_{11}$ . Absorption of complexes  $PW_{11}Cr$  was estimated at  $\nu = 28000 \text{ cm}^{-1}$  where it was

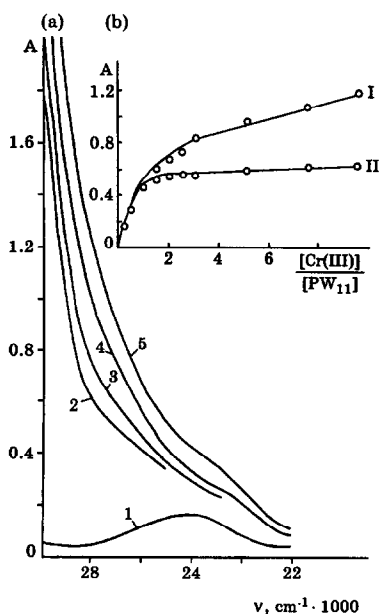


Fig. 1. (a) UV-Vis spectra of 0.1 M solution of  $Cr(NO_3)_3$ , pH 2.8 (1) and mixtures of  $Cr(NO_3)_3$  with  $Na_7PW_{11}O_{39}$ ;  $[PW_{11}] = 0.01 \text{ M}$ ,  $[Cr(III)]/[PW_{11}] = 1.5$  (2), 2.5 (3), 5.0 (4), 9.5 (5), pH 2.8. (b) A plot of visible absorption at  $\nu = 28000 \text{ cm}^{-1}$  vs.  $[Cr(III)]/[PW_{11}]$  ratio for the mixtures of  $Cr(NO_3)_3$  with  $Na_7PW_{11}O_{39}$ . The solutions were kept for 24 h at pH 2.5 (curve I) and 2.8 (curve II).  $[PW_{11}] = 0.01 \text{ M}$ .  $l = 1 \text{ mm}$ .

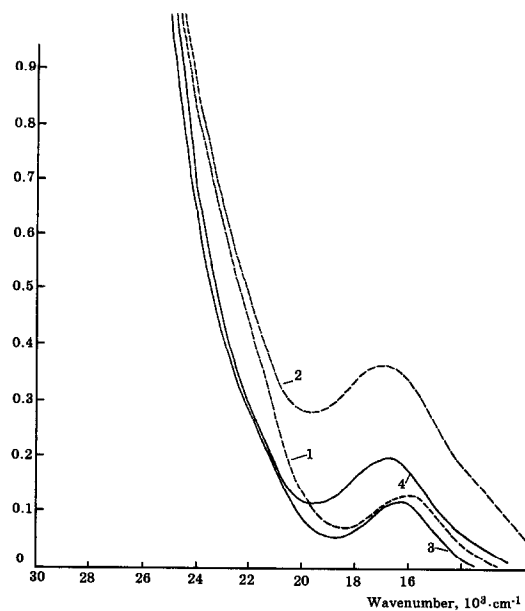


Fig. 2. UV-Vis spectra of  $PW_{11}Cr$  solutions in  $CH_3CN$ : (1) 0.013 M (sample 5); (2) 0.013 M (sample 5), 0.23 M  $H_2O_2$  after 1 h reaction at  $35^\circ C$ ; (3) 0.013 M (sample 6); (4) 0.013 M (sample 6), 0.23 M  $H_2O_2$  after 1 h reaction at  $35^\circ C$ ;  $l = 2 \text{ mm}$ .

much higher than that for precursors  $Cr_2(OH)_2^{4+}$  and  $PW_{11}O_{39}^{7-}$  (Fig. 1(a)). Aqueous solutions of fixed  $PW_{11}$  and different  $Cr(NO_3)_3$  concentrations were prepared. The pH was 2.5 or 2.8. Absorption was measured after solutions had been kept for 24 h at room temperature, and plotted vs.  $Cr(III)/PW_{11}$  ratio Fig. 1(b). An increase of absorption slowed down when  $Cr(III)/PW_{11} > 1$ . Fig. 1(b), shows that the composition of complexes is affected by pH in this region. The composition of the TBA salts, samples 8 and 9, precipitated from working solutions at  $Cr(III)/PW_{11} = 4$ , corresponded to the formulae  $PW_{11}Cr$  for pH 2.5 and  $PW_{10.3}Cr_{1.5}$  for pH 2.8.

The TBA salts were characterized by spectral methods. The UV-Vis spectra of  $CH_3CN$  solutions are depicted in Fig. 2 (1, 3), including two bands: a highly intense absorption at  $\nu 23000\text{--}30000 \text{ cm}^{-1}$  and a moderate one at  $\nu 15000\text{--}18000 \text{ cm}^{-1}$ . The position of the latter peak was obviously sensitive to the preparation method of  $PW_{11}Cr$  complex. The maximum underwent a low frequency shift, when the complex was

synthesized by prolonged holding or heating of the aqueous solution prior to precipitation of the TBA salts (compare samples 1–3). Prepared from  $PW_{12}$  and Cr(III) in strong acid solution, sample 6 had an inherent maximum far from all the others. Decrease of the acidity of the aqueous solution prior to precipitation produced no changes in the maximum position but increased the absorption as the Cr(III) content increased (sample 7). The same was observed for other samples (samples 8 and 9): the position of the maximum was scarcely affected by the pH of the solution used to isolate the TBA salts.

The infrared spectra of  $PW_{11}$ Cr TBA salts are consistent with the ones for Cr-substituted heteropolytungstates reported in the literature [4,19]. Samples 1, 3, 5, 8 and 9 exhibited uniform characteristic absorption bands attributed to the vibrational frequency of the central  $PO_4$  unit  $\nu = 1088$  and  $\nu = 1055$   $cm^{-1}$ , W=O bond  $\nu = 963$ – $970$   $cm^{-1}$  and W–O–W bond  $\nu 885$ – $890$  and  $810$ – $815$   $cm^{-1}$ . Specific details were observed between  $800$  and  $600$   $cm^{-1}$ . For sample 1, precipitated after heating at  $95^\circ C$ , the weak band at  $\nu 670$   $cm^{-1}$  was well distinguished, which was supposed to refer to vibration frequency of W–O–Cr fragment [19]. Containing superstoichiometric amount of Cr, samples 5 and 9 exhibited an absorption without a clearly defined maximum at  $800$ – $600$   $cm^{-1}$ . Both spectra are shown in Fig. 3.

$PW_{11}$ Cr compounds were tested in  $H_2O_2$  decomposition.  $H_2O_2$  conversions correspond to 1 h reaction of  $0.23$  M  $H_2O_2$  solution in  $CH_3CN$  (Table 1)<sup>1</sup>.

The rate of  $H_2O_2$  decomposition showed very slight dependence on  $H_2O_2$  concentration, for example, the order with respect to  $H_2O_2$  was about  $0.3$  for sample 4. Thus the higher the starting  $H_2O_2$  concentration was, the longer was the time to complete decomposition (Fig. 4).

<sup>1</sup> It should be noted that the heteropolytungstate precursors  $PW_{11}$  and  $PW_{12}$  were absolutely inactive in the catalysis of  $H_2O_2$  decomposition.

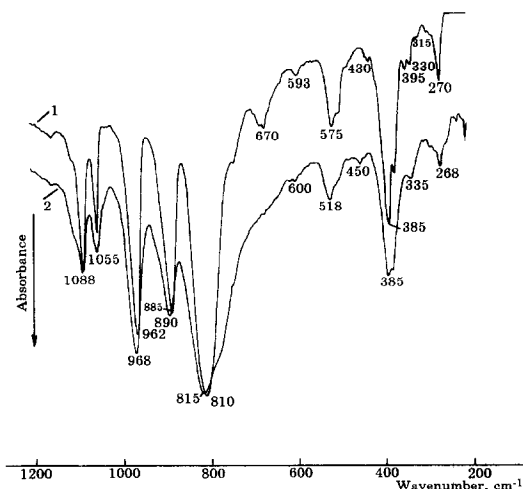


Fig. 3. IR spectra of  $PW_{11}$ Cr TBA salts: (1) sample 1; (2) sample 9 in CsI.

During the  $H_2O_2$  decomposition, a shift of a maximum from  $\nu 15200$ – $16300$   $cm^{-1}$  to  $15500$ – $18000$   $cm^{-1}$  and an increase of the visible absorption was observed (Fig. 2 and Table 1). Fig. 5 shows the intensity of absorption maximum vs. time. Comparing this picture with data of Table 1, one can see that in some cases, the intensity of absorption maximum continued growing even after 1 h of reaction, by which time substantial  $H_2O_2$  conversion was reached. For sample 4, the intensity became the greatest by the time when  $H_2O_2$  decomposition had been completed. When the experiment was started with a larger amount of  $H_2O_2$ , the decomposition process took more time, that resulted in greater absorption maximum (Fig. 4).

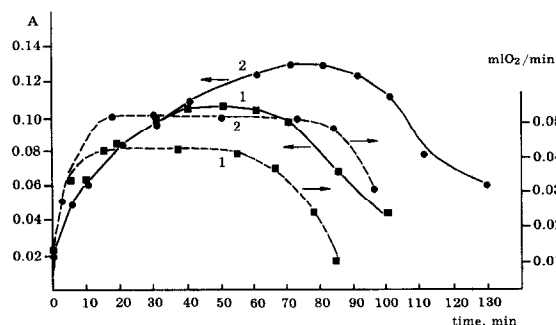


Fig. 4. The rate of  $H_2O_2$  decomposition and absorption variation at  $\nu = 18000$   $cm^{-1}$  vs. time. Conditions:  $0.015$  M (sample 5),  $0.15$  M (curve 1) and  $0.30$  M (curve 2)  $H_2O_2$ .  $T 35^\circ C$ .  $l = 1$  mm.

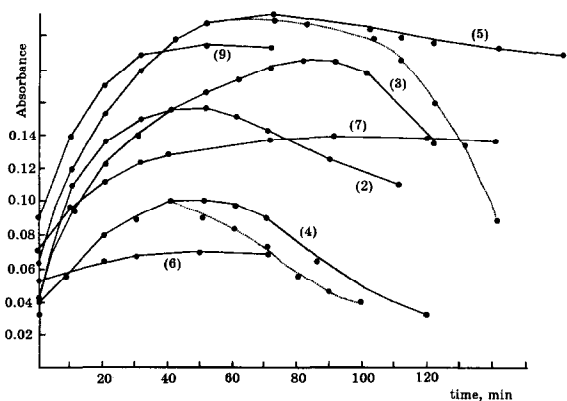


Fig. 5. Dependence of the maximum visible absorption in decomposition of  $\text{H}_2\text{O}_2$  on time. Conditions: 0.015 M  $\text{PW}_{11}\text{Cr}$ , 0.15 M  $\text{H}_2\text{O}_2$ ,  $T$  35°C. The numbers of curves correspond to samples in Table 1. Dashed lines show absorbance after adding 0.01 M  $\text{C}_6\text{H}_6$ .  $l = 1$  mm.

From Fig. 5 it can be seen that most of our samples exhibited similar spectral changes during  $\text{H}_2\text{O}_2$  decomposition: after the maximum in the visible region had reached its highest value, it began to decrease and returned to the original state, that it was before introduction of  $\text{H}_2\text{O}_2$ .  $\text{PW}_{11}\text{Cr}$  complexes avoided destruction during reaction with  $\text{H}_2\text{O}_2$ , as follows from the stable characteristic absorption at 23000–30000  $\text{cm}^{-1}$ .

When a hydrocarbon substrate was introduced into  $\text{PW}_{11}\text{Cr}/\text{H}_2\text{O}_2$  solution,  $\text{H}_2\text{O}_2$  decomposition was accompanied by oxidation of organics. The products of cyclohexene oxidation were cyclohexenone, cyclohexenol and epoxy cyclohexane; cyclohexanol, hydroxycyclohexanone and cyclohexandiol; the last three compounds comprised about 10% of the total product amount. Under very close conditions, benzene was selectively (90%) oxidized to phenol, with minor admixture of hydroquinone. The yield of main products is given in Table 2.

Time dependence of benzene to phenol transformation for sample 8 indicated initial acceleration of reaction (Fig. 6), followed by stationary rate of product accumulation. From comparison of two curves in Fig. 6: product yield and visible absorption at  $\nu = 17000 \text{ cm}^{-1}$  vs. time, it follows that oxidation is connected with spec-

Table 2

Oxidation of cyclohexene and benzene in  $\text{H}_2\text{O}_2/\text{PW}_{11}\text{Cr}$  systems

N	Products formed from $\text{C}_6\text{H}_{10}$ , $10^3 \cdot \text{M}$			Products formed from $\text{C}_6\text{H}_6$ , $10^3 \cdot \text{M}$
	Epoxycyclohexane	Cyclohexenol	Cyclohexenone	Phenol
1	0	0	0	0
2	0.68	0.50	2.17	0.9
3	1.15	0.72	2.05	0.6
4	0.56	0.34	1.14	0.8
5	1.43	0.82	2.88	1.7
6	0.92	0.25	0.30	< 0.1
7	1.25	0.56	1.17	0.6
8	0.60	0.68	1.25	1.9
9	1.40	0.90	3.50	1.7

Conditions: 0.015 M  $\text{PW}_{11}\text{Cr}$ , 0.16 M  $\text{H}_2\text{O}_2$ , 0.01 M  $\text{C}_6\text{H}_{10}$  or 0.1 M  $\text{C}_6\text{H}_6$ , solvent  $\text{CH}_3\text{CN}$ ;  $T$  35°C, reaction time 40 min for  $\text{C}_6\text{H}_{10}$ ;  $T$  40°C, reaction time 30 min for  $\text{C}_6\text{H}_6$ . Characteristics of samples are given in Table 1

tral characteristics of solutions, that in turn, reflect the composition of  $\text{PW}_{11}\text{Cr}$  complexes. The connection was confirmed by the following experiments. The decomposition of hydrogen peroxide in the presence of samples 4 and 5 was conducted as described below. When absorptions at  $\nu = 18000$  and  $\nu = 17000 \text{ cm}^{-1}$ , achieved the highest intensity, cyclohexene was introduced into solution, which caused a more rapid decrease of absorption than it was observed without organic substrate (curves 4 and 5 in Fig. 5). After completion of cyclohexene

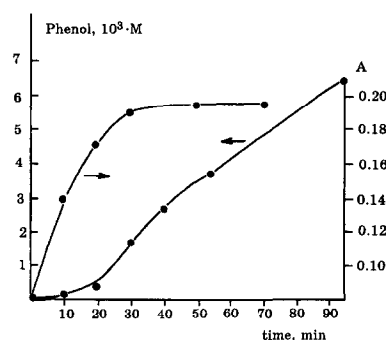


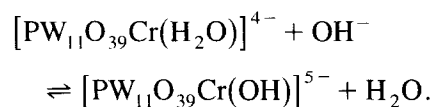
Fig. 6. Visible absorption at  $\nu = 17000 \text{ cm}^{-1}$  vs. time and concentration of phenol product vs. time in benzene oxidation. Conditions: 0.015 M sample (9), 0.16 M  $\text{H}_2\text{O}_2$ , 0.1 M  $\text{C}_6\text{H}_6$ ,  $T$  40°C.  $l = 1$  mm.

oxidation, addition of a further portion of  $\text{H}_2\text{O}_2$  gave a repeat of the first process.

#### 4. Discussion

The methods of  $\text{PW}_{11}\text{Cr}$  synthesis used in our study, were modifications of published procedures. In doing so, we observed that small variations in the conditions can cause changes in the composition, spectral and catalytic properties of the resulting compounds. A pronounced correlation was found between the pH of the aqueous solution used for the precipitation of the TBA salts, and the catalytic activity in the  $\text{H}_2\text{O}_2$  decomposition. The explanation is as follows.

Variation of the pH affects the acid–base equilibrium



The  $\text{PW}_{11}\text{Cr}$  sample precipitated from less acidic solution is more enriched with OH groups. Metal hydroxocomplexes are more active than aqua-complexes in the catalysis of  $\text{H}_2\text{O}_2$  decomposition because hydroxo ligand facilitates inner-sphere interaction of the metal ion with  $\text{H}_2\text{O}_2$  to generate radicals. On the other hand, dissolving  $\text{PW}_{11}\text{Cr}$  in  $\text{CH}_3\text{CN}$  in the presence of water, releases  $\text{OH}^-$  ions which increase  $\text{H}_2\text{O}_2$  decomposition. However, consideration only of the protolytic equilibrium cannot give a complete explanation of our results. The problem is that protolytic equilibrium is normally achieved rapidly [20], in contrast to the slow transformation of  $\text{PW}_{11}\text{Cr}$  compounds, whose characteristics change, depending on the time and temperature of synthesis. The second point is a lack of pH effect on some properties of the  $\text{PW}_{11}\text{Cr}$  separated from aqueous solution: (1) activity in  $\text{H}_2\text{O}_2$  reaction with hydrocarbon substrates, (2) transformation of visible absorption spectra during  $\text{H}_2\text{O}_2$  decomposition.

In a subsequent study, we came across an

other notable result. Increased pH is favorable for obtaining samples containing superstoichiometric Cr(III) ions, when the starting ratio of reagents is  $\text{Cr(III)}/\text{PW}_{11} > 1$ . This result was expected because of the tendency of Cr(III) hydroxocomplexes to form bi- and polynuclear Cr–O–Cr units. It was believed that whole polynuclear fragments would join with the heteropolyanion. However, the results gave no support to this expectation. In fact, the dimeric hydroxocomplexes  $\text{Cr}_2(\text{OH})_2^{4+}$  transformed in contact with  $\text{PW}_{11}$  at pH 2.5 to give the final compounds of content  $\text{Cr}/\text{PW}_{11} = 1$ . Increasing pH gave rise to an increase of an extra number of Cr(III) ions in the  $\text{PW}_{11}\text{Cr}$  TBA salt. The structure of the complexes containing the extra Cr(III) ions is not clear. The question is whether the additional Cr(III) ions form the polynuclear Cr–O–Cr fragments or are fixed separately on the surface of the heteropolyanion.

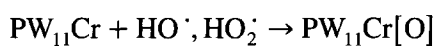
Thus, we put forward the idea of the so-called heteropolyanion supported complexes, first formulated by Finke for Ir complexes [21,22], we have now obtained further confirmation of this idea. Apart from classical Cr-substituted heteropolycompounds, we are dealing with Cr-supported compounds whose Cr(III) ions are attached to the surface oxygen atoms of the parent  $\text{PW}_{11}$  anion. Hypothetically, the bond is located near the edge of a vacancy in the Keggin structure.

In such a situation, the properties of the compounds depend on the depth of penetration of the Cr(III) ion into the cavity of the structure, which in turn is affected by the conditions of the synthesis. Probably, heating of a solution produces a real M-substituted sample containing Cr(III) ions incorporated into the Keggin structure, which makes the Cr(III) ion inactive in oxidations with  $\text{H}_2\text{O}_2$ . Active samples contain one or more Cr(III) ions on the edge of a vacancy. It can be supposed that the location of the ions is not well defined. This is reflected by the variable shape of the visible absorption for different samples and broadening of the W–O–Cr lines in the IR spectra. There are similarities

in the properties of the Cr-containing heteropolyanions and the parent heteropolyanions  $PW_{11}$  and  $PW_{12}$ . Having a vacancy, the first one is known to be more active in cyclohexene oxidation than coordinatively saturated  $PW_{12}$  [10,12].

#### 4.1. On the mechanism of $H_2O_2/PW_{11}Cr$ oxidation of unsaturated hydrocarbons

In our previous study, we have mentioned a change of visible spectra of  $PW_{11}Cr$  during reaction with  $H_2O_2$  or  $H_2O_2/C_6H_{10}$ . We believe it was caused by oxidized  $PW_{11}Cr$  complexes, for example, peroxides of type  $PW_{11}Cr-OOH$  which are considered intermediates in both  $H_2O_2$  decomposition and reaction with cyclohexene. However, the recent data show that the compounds detected cannot be intermediates in  $H_2O_2$  decomposition. In fact, we observed a constant rate of  $H_2O_2$  decomposition while the visible absorption increased permanently (as shown in Fig. 4), which reflects the increasing concentration of the oxidized complexes. In some experiments, the concentration was higher when the  $H_2O_2$  decomposed nearly completely. On the other hand, addition of NaOH to a working solution, which resulted in acceleration of  $H_2O_2$  decomposition, gave rise to the increase of absorption. The only hypothesis consistent with all these observations is that the oxidized  $PW_{11}Cr$  complexes are formed under the action of intermediate products of  $H_2O_2$  decomposition, which may be  $HO^\cdot$  or  $HO_2^\cdot$  radicals.



For most samples, at high  $H_2O_2$  conversion, the concentration of the oxidized  $PW_{11}Cr[O]$  species began to slow down. Comparison of the appropriate curves in Fig. 5, shows that the oxidized species are of different stability with respect to decomposition, which probably proceeds by redox reaction with the solvent  $CH_3CN$  to form the original compound  $PW_{11}Cr$ .

More rapid is the reaction of the oxidized

species with unsaturated hydrocarbons, as shown in Fig. 4. The interaction of oxidized species with cyclohexene becomes especially pronounced when  $H_2O_2$  decomposition approaches completion, i.e. 60 min for sample 4 and 100 min for sample 5.

As to the curves in Fig. 6 of visible absorption vs. time and phenol product concentration vs. time, we explain the initial acceleration of benzene oxidation by accumulation of active oxidized  $PW_{11}Cr[O]$  species. The subsequent process is characterized by steady rate of oxidation under constant concentration of reactive species.

The nature of oxidized  $PW_{11}Cr[O]$  species is under consideration now. We could suppose they are similar to Hill's oxo-Cr(V) complexes [4]. To support this idea, we found that the product composition in our experiments with cyclohexene/ $H_2O_2$  being very close to one for the cyclohexene/iodosylbenzene reaction. However, the absorption band of the reactive intermediates  $\nu$  18000–16700  $cm^{-1}$  does not coincide with 14900  $cm^{-1}$  of  $[(C_6H_{13})_4N]_4[PW_{11}O_{39}Cr^VO]$ . Thus, we reserve this point for further study.

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