Reactivity of transition-metal-modified, Keggin-type heteropolycomplexes in the homogeneous oxidation of cyclohexane and adamantane

M.R. Cramarossa [a], L. Forti [a], M.A. Fedotov [b], L.G. Detusheva [b], V.A. Likholobov [b], L.I. Kuznetsova [b], G.L. Semin [b], F. Cavani [c], F. Trifirò [c,*]

[a] *Dipartimento di Chimica, Università di Modena, Via Campi 183, I-41100 Modena, Italy*
[b] *Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Science, Novosibirsk 630090, Russia*
[c] *Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, Viale Risorgimento 4, I-40100 Bologna, Italy*

Abstract

The oxidation of cyclohexane and adamantane catalyzed by Keggin-type transition-metal-containing heteropoly-complexes (TMC-HPCs) is reported. The reactions were carried out at 20°C in CCl_4 or in CH_2Cl_2 as reaction solvent in the presence of t-butylhydroperoxide (t-BuOOH) as oxidizing agent. A radical chain mechanism of oxidation by t-BuOOH in the presence of molecular oxygen is proposed for all complexes tested, involving a R–H hydrogen atom abstraction by an intermediate active form of the TMC-HPC. Under the examined conditions molecular oxygen was necessary to initiate the reaction. The preparation of Co(II), Fe(III) and Cr(III)-HPC samples and their composition under reaction conditions are also discussed, based on ^{31}P-NMR and UV–VIS absorption spectra. © 1997 Elsevier Science B.V.

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1. Introduction

A renewed interest in polyoxocompound chemistry arises from the possibility for industrial applications of early transition metal poly-oxoanions as catalysts for the selective air-oxidation of organic molecules [1–7]. An important factor concerning the choice of these materials as catalysts is that their composition can be partially modified without affecting the

Keggin-type primary structure, making it possible to tune the nature and amount of di- and tri-valent transition metals replacing molybdenum and tungsten in the anion [8–13]. In this way the reactivity of these compounds towards different organic substrates can be modified. Indeed, Keggin type heteropolycompounds (HPC) are employed as heterogeneous catalysts for the gas-phase oxidation of methacrolein to methacrylic acid and have been claimed as optimal systems for the selective transformation of isobutane to methacrylic acid [5]. Furthermore, the possibility for these compounds to be used

* Corresponding author. Fax: +39-51-6443680; e-mail: trifiro@ms.fci.unibo.it

as homogeneous catalysts for the liquid phase oxidation of several different organic substrates and their stability under strongly oxidizing conditions makes them the inorganic analogues of metal-porphyrin systems [3,14–18].

An industrially important challenge of current relevance is the oxidation of saturated hydrocarbons under mild conditions, which is accomplished in biological systems by iron in both heme and non-heme ligand environments.

In this paper, we report on the characterization in organic solvent of Co(II), Fe(III) and Cr(III)-containing heteropolycomplexes and their use as catalysts for the oxidation of alkanes such as cyclohexane and adamantane.

2. Experimental section

2.1. Preparation and characterization of TMC-HPCS

HPCs containing different transition metal ions were obtained by the well known procedures [11,19–23,46,47]. $Co(NO_3)_2 \cdot 6H_2O$ (sample 1), $Fe(NO_3)_3 \cdot 9H_2O$ (samples 2(1)–2(4)), and $Cr(NO_3)_3 \cdot 9H_2O$ (sample 3) were added to a 0.22 M $Na_7PW_{11}O_{39}$ aqueous solution (pH 5), at molar ratio $M:PW_{11} = 1:1$. For Fe(III)-containing HPCs the solution pH was varied from 1.65 (sample 2(2)) to 1.0 (sample 2(1)) by the addition of HNO_3, or to pH 2.65 (sample 2(3)) and 4.15 (sample 2(4)) by the addition of a Na_2CO_3 solution. Fe(III)-poly-nuclear hydroxocomplexes (sample 2(5)) were prepared by the slow addition of Na_2CO_3 until pH 4.0 was reached (molar ratio $Fe:PW_{11} = 4$; $[Na_7PW_{11}O_{39}] = 0.05$ mol/l) [24].

Membrane separation of NO_3^- ions from HPC solutions was carried out using the equipment and membrane described by Fedotov et al. [25]. Typical operating sequence was that reported by Semin et al. [26]. The initial solution was diluted 3–4 times, placed in the membrane cell, and the membrane treatment carried out. The concentrated non-permeate was then diluted a second time, and the cycle was repeated. Determination by ^{14}N-NMR of the residual concentration of free nitrate ions in the non-permeates showed that two or three cycles of such purification are sufficient to remove 80–90% of them from the initial HPC solutions (Table 1). Samples treated with this procedure are referred to with the letter M.

In order to study the products of HPC extraction with CCl_4, 0.05 M tetraheptylammonium bromide (THABr) or 0.04 M tetraoctylammonium bromide (TOABr) in CCl_4 (9 ml) was shaken at $\simeq 25°C$ together with an aqueous solution (0.205 ml) of 0.22 M HPC. A 0.05 M aqueous HPC solution of sample 2(5) (0.9 ml) was used for extraction with 0.05 M THABr or TOABr solution in CCl_4. Under these conditions, all but sample 2(5) were almost completely extracted in the CCl_4 phase, resulting in 0.005 M HPC solutions. In some cases, a $THANO_3$ solution was used for HPC extraction, the former having been prepared in CCl_4 by the addition of an equimolar amount of $AgNO_3$ dissolved in water to the THABr solution.

Electronic absorption spectra of the HPC solutions were recorded using a Specord M-40. ^{31}P and ^{14}N NMR spectra were recorded with a MSL-400 Bruker spectrometer at room temperature, at frequencies of 161.98 and 28.9 MHz.

Table 1
HPC solution composition following the membrane treatment

No.	HPC composition, averaged	pH	[HPC] (mol/l)	[NO_3^-] (mol/l)	N [a]
1M	$Na_{3.6}H_{1.4}PW_{11}O_{39}Co(H_2O)$	5.0	0.224	0.05	3
2(2)M	$Na_{3.1}H_{0.9}PW_{11}O_{39}Fe(H_2O)$	2.25	0.223	0.06	2
2(5)M	$Na_{5.1}H_{0.9}PW_{11}O_{39}Fe_4O_xH_y$	4.0	0.0925	0	3
3M	$Na_3HPW_{11}O_{39}Cr(H_2O)$	2.3	0.282	0.03	2

[a] N = number of cycles.

The accumulation frequencies were 0.05 and 50 Hz, respectively. Chemical shifts in the δ scale were measured relative to 85% aqueous H_3PO_4 and 1 M $NaNO_3$ as external standards.

2.2. Procedure for the catalytic oxidations

A dichloromethane or carbon tetrachloride solution (1 ml) containing 1 mmol of the substrate, the metal catalysts (0.01 mmol), the oxidant (0.2 mmol) and a gas-chromatographic standard (decane, 0.005 mmol) were stirred magnetically in a 2 ml vial. The reactions were carried out at 20°C in the presence of air. Reaction rates were determined for early stages of the reaction (up to 50 turnovers) and were reproducible to within 10%. Organic analyses were carried out on aliquots withdrawn with a microsyringe using a HP 5890 Series II gas chromatograph equipped with FID, using a 30 m SE-30 capillary columns (0.25 mm i.d.) with the injection port thermostated at 250°C (carrier gas, helium). The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectra obtained with a combined HP5890-HP5989A MS Engine operating in the electron ionization mode at 70 eV.

3. Results and discussion

3.1. HPC content in solutions according to optical and NMR spectra

Heteropolytungstates containing in their Keggin lattice various transition metal ions, $PW_{11}M(H_2O)O_{39}^{n-}$, are well known, having been prepared and characterized since the 60's [8–13,19–23,46,47]. NMR, IR and UV–VIS spectral features of HPCs obtained in aqueous solution through interaction of unsaturated heteropolyanion (HPA) with Fe(III) and Cr(III) ions under a variety of pH values and reagents ratios demonstrated the existence of complex structures [22–24,27–29,47]. In particular, the water molecule in the co-ordination sphere of the metal ion in HPC can be replaced by an-

other ligand. The process of ligand substitution can also occur as a result of HPC transfer in organic solvent [27,30]. Besides the nature of the M ions, their co-ordination environment in the HPC structure, which depends on synthetic conditions and on the occurrence of other ions, is an important factor which affects the catalytic activity of these complexes [27,28]. We characterize here in detail by NMR and UV–VIS spectroscopy the composition of M-containing HPCs prepared for catalytic study, according to our previously reported results [24,27–29].

Visible absorption spectra of initial HPC aqueous solutions derived from $Na_7PW_{11}O_{39}$ and from the corresponding metal nitrate (samples 1, 2(2) and 3, Table 2) are in line with those of the same complexes after membrane separation of nitrate ions (Table 1), indicating that the composition of the HPA does not change. Therefore, the NO_3^- ions appear not to be bonded with metal ions in the HPCs in aqueous solutions.

^{14}N NMR spectra of HPC solutions in CCl_4 show a narrow peak at -65.5 ppm related to dissolved N_2 and a signal at 305 ppm of TOA^+ cations, which is broadened as a result of the interaction with the HPA containing paramagnetic ion ($[TOA^+] = 0.04$ M, $[HPC] = 0.01$ M).

Other signals were not observed suggesting that at least free nitrate is absent in CCl_4 solutions of HPC.

^{31}P NMR and electronic absorption spectroscopy was used to characterise the HPC samples prepared in water solution. Only one peak was observed in the ^{31}P NMR spectrum of sample 1 ($\delta = 485$ ppm), which certainly belongs to $PW_{11}O_{39}Co(H_2O)^{5-}$.

The absorption spectrum of $PW_{11}Co^{II}$ in CCl_4 in the presence of THABr or TOABr, in the region of d–d transitions of Co(II) ions significantly differs from that of $PW_{11}O_{39}Co(H_2O)^{5-}$ in water solution; in fact, an additional maximum at 16 400 cm^{-1} appears (Table 2, Fig. 1, curves 1 and 1'). This maximum belongs to pentacoordinated Co(II) in HPA [30,31]. With $THANO_3$ in place of THABr, the maximum at

Table 2
Electronic absorption spectra of HPA in aqueous and CCl_4 solutions; Na- and THA (or TOA) salts

No.	HPA, aqueous sol.	ν_{max} (ε, l cm^{-1} mol^{-1})	HPA, CCl_4 sol.	ν_{max} (ε, l cm^{-1} mol^{-1})
1	$PW_{11}O_{39}Co(H_2O)^{5-}$ pH = 4.5	19 600 (77), 18 600 (90)	$PW_{11}O_{39}Co(L)^{m-}$ [a]	20 100 (56), 19 300 (72), 18 400 (68), 16 400 (62)
2(1)	$PW_{11}O_{39}Fe(H_2O)^{4-}$ pH = 1.0	no maxima	$PW_{11}O_{39}Fe(H_2O)^{4-}$	no maxima
2(2)	$PW_{11}O_{39}Fe(H_2O)^{4-}$ pH = 1.65	21 700sh (13.7)	$PW_{11}O_{39}Fe(H_2O)^{4-}$	21 700sh (80)
2(3)	$(PW_{11}O_{39}Fe)_2O^{10-}$ pH = 2.65	24 500sh (265), 21 700 (60), 19 300 (6.6), 15 700 (4.3)	$PW_{11}O_{39}Fe(OH)^{5-}$	$\simeq$ 20 000sh (7.3), 16 500 (4.0)
2(4)	$(PW_{11}O_{39}Fe)_2O^{10-}$ pH = 4.15	24 500sh (380), 21 700 (106), 19 300 (10.5), 15 700 (6.8)	$PW_{11}O_{39}Fe(OH)^{5-}$	$\simeq$ 20 000 (2.3), 16 500 (2.0)
2(5)	$(PW_{11}O_{39}Fe)_2O^{10-}$ (55%) $[PW_{11}O_{39} \cdot Fe_8O_xH_y]^{m-}$ (45%), pH = 4.0	21 700 (485)	$PW_{11}O_{39}Fe(OH)^{5-}$ [b]	no maxima
3	$PW_{11}O_{39}Cr(L)_x^{m-}$ [c]	$\simeq$ 27 500sh (260), 23 000 (110), 15 400 (14)	$PW_{11}O_{39}Cr(L)_x^{m-}$ [c]	$\simeq$ 27 500sh (280), $\simeq$ 23 000sh (120), 15 400 (12)

[a] L may be H_2O, NO_3^-, or be absent.
[b] The complex $[PW_{11}O_{39} \cdot Fe_8O_xH_y]^{m-}$ remained in the water layer.
[c] L may be H_2O or OH^-.

16 400 cm^{-1} disappears, and the maximum at 20 100 cm^{-1} (present as a shoulder in previous cases) becomes more intense (Fig. 1, curve 1''). According to absorption spectra in CCl_4 solu-
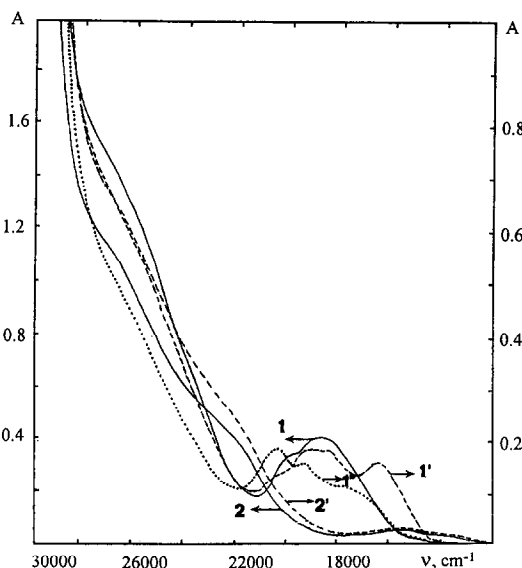

Fig. 1. Absorption spectra of $PW_{11}O_{39}Co(H_2O)^{5-}$ (1) and $PW_{11}O_{39}Cr(H_2O)^{4-}$ (2) in aqueous solutions and their extracts in CCl_4 (1', 1'' and 2', respectively): 1: $[PW_{11}Co^{II}]$ 0.22 M, L = 0.207 mm; 1': 0.05 M THABr; 1'': 0.05 M THANO$_3$ in CCl_4, $[PW_{11}Co^{II}]$ 0.005 M, L = 5 mm; 2: $[PW_{11}Cr^{III}]$ 0.22 M, L = 0.207 mm; 2': 0.05 M THABr in CCl_4, $[PW_{11}Cr^{III}]$ 0.005 M, L = 5 mm. The exact content of HPC samples is given in Table 2.

tion, it seems likely the co-ordination of NO_3^- ions by Co(II) in the HPA, while no interaction exists with Br^- ions.

The ^{31}P NMR spectrum of complexes prepared in aqueous solution from $Na_7PW_{11}O_{39}$ and $Co(NO_3)_2$ and extracted in CCl_4 with TOABr shows three broad peaks at 396, 259 and 56.8 ppm, which belong, apparently, to three forms of HPC in CCl_4 solution: $[PW_{11}O_{39}Co]^{5-}$ and $[PW_{11}O_{39}Co(L)]^{m-}$ (L may be H_2O and NO_3^-).

The characterization of Fe(III)-containing samples 2(1)–2(5) was made according to previously published data [24,27]. Sample 2(1) (prepared at pH = 1.0) presents no ^{31}P NMR spectrum because of significant paramagnetic broadening of the signal of mononuclear complex $PW_{11}O_{39}Fe(H_2O)^{4-}$. In addition to the former complex, sample 2(2) (pH = 1.65) contains other HPC impurities which are seen in the ^{31}P NMR spectrum: $PW_{12}O_{40}^{3-}$ (-18 ppm in the presence of paramagnetic Fe(III) ions), Fe(III)-binuclear μ-oxo-complex $(PW_{11}O_{39}Fe)_2O^{10-}$ (64.2 ppm) and apparently, a heteropoly-complex containing more than one Fe(III) ion (168 ppm). Samples 2(3) and 2(4) (pH 2.65 and 4.15) consist almost entirely of

$(PW_{11}O_{39}Fe)_2O^{10-}$, since impurities of $PW_{11}O_{39}^{7-}$ and of other heteropolyphosphates comprise about 7%. The signal position of μ-oxocomplex depends on pH value (45.5 and 15.6 ppm, respectively), indicating the equilibrium of complex protonization [24], which also influences the intensity of the absorption spectra (Table 2, samples 2(3) and 2(4)). Sample 2(5), which was prepared at molar ratio Fe:PW_{11} = 4:1 and pH 4, consists of two complexes: $(PW_{11}O_{39}Fe)_2O^{10-}$ (55% from overall intensity of ^{31}P signals) and $[PW_{11}O_{39} \cdot Fe_8O_xH_y]^{m-}$ (45% from overall ^{31}P signals) which contains an average of 8 Fe(III) ions for each $PW_{11}O_{39}^{7-}$ unit.

In aqueous solution, complex $PW_{11}O_{39}Fe(H_2O)^{4-}$ (samples 2(1) and 2(2)) does not show absorption maxima (Table 2). The μ-oxocomplex $[(PW_{11}O_{39}Fe)_2O]^{10-}$ (samples 2(3) and 2(4)) distinguishes from the first one by an increased intensity of absorption, the maxima at 24500, 21700, $\simeq$ 20000 and 16500 cm^{-1} being observed (Table 2). Polynuclear hydroxocomplexes $[PW_{11}O_{39} \cdot Fe_nO_xH_y]^{m-}$ (Table 2, sample 2(5)) are characterised by an enhanced intensity with the maximum at $\simeq$ 21700 cm^{-1}.

In CCl$_4$ the intensity of the absorption at 28000–22000 cm^{-1} decreases when passing from sample 2(1) (mononuclear complex) to samples 2(2)–2(4), but remains higher as compared with water solutions of the same samples. Absorption maxima at 24500 and 21700 cm^{-1} related to μ-oxo- and polynuclear Fe(III)-complexes (samples 2(3) and 2(4)) disappear in CCl$_4$, whereas weak maxima at low frequency ($\simeq$ 20000 and 16000 cm^{-1}) are retained for samples 2(3) and 2(4) (Table 2). When THANO$_3$ is used in place of THABr, the absorption spectra of Fe(III)-HPC in CCl$_4$ do not change. By means of ^{31}P NMR, the signal of μ-oxo-complex was not observed in CCl$_4$ solutions of samples 2(3) and 2(4) ([PW_{11}Fe] = 0.015 mol l^{-1}). Recently, based on magnetic measurements, optical and IR-spectra, it was shown that the dissociative process occurs during precipita-

tion of the binuclear Fe(III)-complex with large cations of tetrabutylammonium [27]:

$$(PW_{11}O_{39}Fe)_2O^{10-} + 10TBA^+ + H_2O$$
$$\rightarrow 2TBA_5PW_{11}O_{39}Fe(OH) \downarrow$$
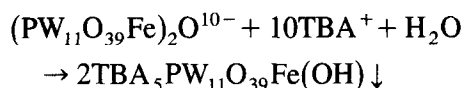
Spectral data obtained show that the same phenomenon takes place when HPC is extracted from a water solution in CCl$_4$ using THA$^+$ or TOA$^+$ cations.

When sample 2(5) (pH 4) was extracted in CCl$_4$, red Fe(III)-hydroxocomplexes $[PW_{11}O_{39} \cdot Fe_nO_xH_y]^{m-}$ remained in the water layer (as revealed by the presence of the maximum at 21700 cm^{-1}), whereas complex $(PW_{11}O_{39}Fe)_2O^{10-}$ transferred in CCl$_4$ as a THA-salt of $PW_{11}O_{39}Fe(OH)^{5-}$, the absorption spectrum of the latter being without maximum at 21700 cm^{-1}. It should be noted that CCl$_4$-extract of sample 2(2) (pH 1.65) contains some amounts of Fe(III)-polynuclear complex (ν_{max} = 21700 cm^{-1}, Table 2), which occurs as admixture in the initial water solution. It is possible that the acidity of the water solution affects the extraction of complexes containing more than one Fe(III) ion.

Results of $PW_{11}O_{39}^{7-}$ interaction with Cr(III) ions depend on small changes of reaction conditions in aqueous solution [28]. Sample 3 gives a complicated NMR spectrum [29] and most likely contains partially hydrolysed Cr(III) ions supported on the $PW_{11}O_{39}^{7-}$ anion [28].

Nevertheless, absorption spectra of $PW_{11}O_{39}Cr(H_2O,OH^-)^{m-}$ originally obtained in water solution and after extraction of the complex in CCl$_4$ are identical (Fig. 1, curves 2 and 2'), showing invariant HPC content in the two solvents.

Thus, the following HPCs were assumed in CCl$_4$ solutions: $[PW_{11}O_{39}Co]^{5-}$ or $[PW_{11}O_{39}Co(L)]^{m-}$ (L = H$_2$O, NO$_3^-$), $[PW_{11}O_{39}Fe(H_2O)]^{4-}$ (when extraction was made from aqueous solution at pH $\leq$ 2), $[PW_{11}O_{39}Fe(OH)]^{5-}$ (when extraction was made in the presence of THABr or TOABr from an aqueous solution at pH > 2), and $[PW_{11}O_{39}Cr(H_2O,OH^-)]^{m-}$.

Table 3
Catalytic performance of HPC in cyclohexane oxidation, after 48 h reaction time, solvent CCl_4

Sample	HPC composition	Cyclohexanol (mM)	Cyclohexanone (mM)	Chlorocyclohexane (mM)
1	$PW_{11}Co(L)O_{39}^{n-}$ [b]	1	1.8	3.5
1M [a]	$PW_{11}Co(L)O_{39}^{n-}$ [c]	4	7	3.5
2(1)	$PW_{11}Fe(H_2O)O_{39}^{4-}$	1.5	3.9	1
2(2)	$PW_{11}Fe(H_2O)O_{39}^{4-}$ (mostly)	3.5	6	2.5
2(2)M	$PW_{11}Fe(H_2O)O_{39}^{4-}$ (mostly)	2.8	3.7	2.2
2(3)	$PW_{11}Fe(OH)O_{39}^{5-}$	2.0	3.8	2.4
2(4)	$PW_{11}Fe(OH)O_{39}^{5-}$	5.2	10	3
2(5)	$PW_{11}Fe(OH)O_{39}^{5-}$ [d]	3.3	6.6	4.0
2(5)M	$PW_{11}Fe(OH)O_{39}^{5-}$ [d]	5.5	10.8	3.5
3M	$PW_{11}Cr(H_2O,OH^-)O_{39}^{m-}$ [e]	2.4	2.4	3.8

[a] The HPC samples, subjected to membrane separation from NO_3^- ions are indicated with the letter M.
[b] L may be H_2O, NO_3^-, or be absent from the HPC.
[c] L may be H_2O, or be absent from the HPC.
[d] According to absorption spectra, the HPC concentration is 0.0035 M (0.005 M in other experiments).
[e] L may be H_2O or OH^-.

3.2. Catalytic results

In order to perform the catalytic tests the compounds were solubilized in the organic phase as tetraalkylammonium salts, following the well-known procedure [32]. The compounds were studied in the oxidation of cyclohexane by t-BuOOH under aerobic conditions. All reactions with TBHP took place in the organic phase (dichloromethane or carbon tetrachloride) containing the substrate, the catalyst and the oxidant. H_2O_2 (30% aqueous solutions) was also tested as the oxidizing species, but it underwent vigorous decomposition in the presence of the catalysts with little oxygenation of the substrates. The products obtained from the aerobic oxidation of cyclohexane with the catalysts examined after 48 h of reaction time are listed in Table 3.

Cyclohexane provided two major oxidation products, cyclohexanol and cyclohexanone; the time course of the reaction, examined for all the complexes, showed that in the first 10 h of reaction the ratio cyclohexanol-to-cyclohexanone remained close to 1 (Figs. 2–4, referring to the results obtained with samples 2(4), 2(5)M and 3), suggesting that the alcohol and ketone are produced from a common intermediate oxidation product. After this reaction time, the cyclohexanone formed resulted at least partially from the oxidation of the cyclohexanol
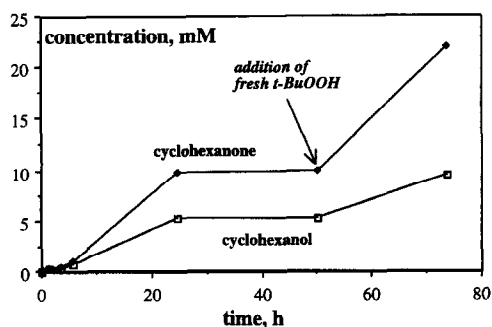

Fig. 2. Concentrations of cyclohexanol and cyclohexanone as functions of the reaction time in cyclohexane oxidation. Catalyst: sample 2(4) (Table 3).
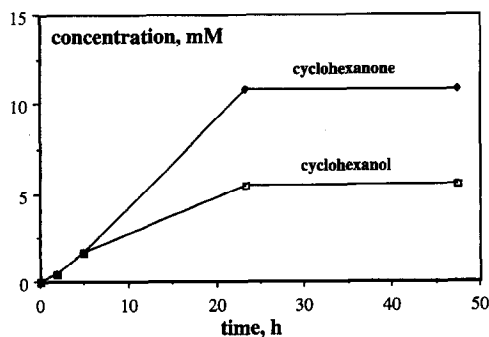

Fig. 3. Concentrations of cyclohexanol and cyclohexanone as functions of the reaction time in cyclohexane oxidation. Catalyst: sample 2(5)M (Table 3).
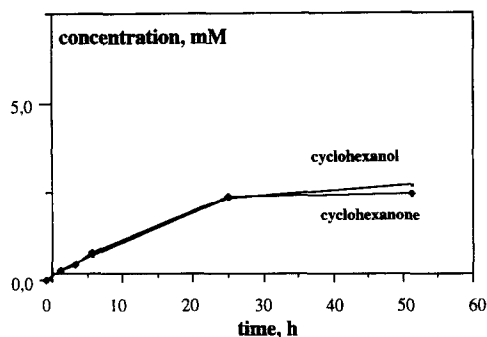
Fig. 4. Concentrations of cyclohexanol and cyclohexanone as functions of the reaction time in cyclohexane oxidation. Catalyst: sample 3 (Table 3).

produced, since the latter was readily oxidized by the catalytic systems even in the absence of cyclohexane. After about 48 h the reaction practically stopped, because of the consumption of the hydroperoxide; however, further addition of t-BuOOH led to a further cyclohexane consumption (as shown in Fig. 2, where a further t-BuOOH addition was made at reaction time 50 h). The catalyst thus proved still active, and was not decomposed in the reaction environment.

Specifications of HPC building from $PW_{11}O_{39}^{7-}$ and metal salts in water solution as well as the content of the reaction mixture, the solvent, the occurrence of additional ligands and also the phase carrier (in our case THA^+ or TOA^+ cations) markedly affect the state of the metal ions in HPCs, as has also been shown in previous papers [27,28]. The influence of membrane separation of nitrate ions from the initial aqueous HPC solutions on the catalytic properties of the HPC is more evident in experiments with $PW_{11}Co$ catalyst. For sample 1 which was not subjected to membrane treatment, the yield of cyclohexanone is about 4 times lower with respect to sample 1M which contained a very low NO_3^- concentration. When free nitrate ions were present in aqueous solution, we observed spectrophotometrically the replacement of H_2O molecules by NO_3^- ion in the coordination sphere during HPC extraction in CCl_4. From the results obtained it may concluded that the catalytic activity of untreated samples is lower than

that of membrane-treated ones, the ratio cyclohexanol-to-cyclohexanone being unchanged in the case of Co-HPC. The effect of nitrate on catalytic performance may be ascribed to a ligand replacement in the coordination sphere of Co(II).

The nature of the metal does not affect remarkably the yield of products and selectivity in the series of Co(II), Fe(III) and Cr(III) complexes, as has also been observed in the same reactions but under different conditions [33].

The alkane functionalization reactions were found to depend on the molecular oxygen gas concentration. In fact, when the solutions were thoroughly flushed with argon gas throughout the course of the reactions, the oxygenation reactions were found to be totally inhibited, and only chlorocyclohexane in trace amounts was found as the reaction product. The same behaviour was found when the reaction was made under argon at 50°C. Thus, O_2 from air and/or formed upon hydroperoxide decomposition seems to be involved in the reactions catalyzed by HPCs. However, the role of molecular oxygen coming from hydroperoxide decomposition seems less likely, due to the low reaction temperature used in the present tests. These results seem to be in contrast with the literature data [33–35]; however, it is possible that under the reaction conditions used by these authors, i.e., 65°C (a temperature higher than that used in the present work), molecular oxygen is formed in-situ by hydroperoxide thermal decomposition.

The nature of the C–H bond cleavage step was probed for these reactions. Significant kinetic isotope effects were observed in a competitive oxidation of cyclohexane and cyclohexane-D_{12} (Table 4). The K_H/K_D values are in the range between 3–7 for the oxidation of cyclohexane over cyclohexane-D_{12} by TBHP in CH_2Cl_2. This suggests that the rate-determining step probably involves the abstraction of hydrogen radical or hydride ion. However, the hydride abstraction can be excluded on the basis of literature data [3] and of results obtained when the reactions were performed in the pres-

Table 4
Isotopic effect in cyclohexane oxidation and C^3/C^2 selectivity in adamantane oxidation, reaction time 8 h

| Catalyst	K_H/K_D	C^3/C^2
$PW_{11}Co(L)O_{39}^{n-}$ [a]	3.4	
$PW_{11}Co(L)O_{39}^{n-}$ [b]	6.7	9.6
$PW_{11}Fe(H_2O)O_{39}^{4-}$	4.0	5.4
$PW_{11}Fe(OH)O_{39}^{5-}$	5.4	6.4
$PW_{11}Cr(H_2O,OH)O_{39}^{n-}$		6.0

Solvent CCl_4.
[a] L may be H_2O, NO_3^-, or be absent.
[b] L may be H_2O, or be absent.

ence of CCl_4, an effective radical trapping agent [36]. In fact under these conditions significant amounts of chlorocyclohexane (the amount of which is also given in Table 3) and C_2Cl_6 (likely as a dimer of the $\cdot CCl_3$ radical) were formed, demonstrating the involvement of radicals in this reaction. Chlorocyclohexane is likely obtained by reaction between the cyclohexyl radical and the chlorinated solvent.

Furthermore, in all the catalytic systems examined, other reaction products, such as t-butylperoxycyclohexane, di-t-butylhydroxycyclohexane and t-butylcyclohexylether, were found. This means that all the complexes catalyzed the homolytic decomposition of t-BuOOH giving rise to radical intermediates that evolved to give the observed products [37,38].

Reduction of the HPC to black $PW_{11}Fe^{II}$, which could occur according to the following mechanism:

$$PW_{11}O_{39}Fe^{III} + t\text{-BuOOH}$$

$$\rightarrow PW_{11}O_{39}Fe^{II} + t\text{-BuOO}^\cdot + H^+$$
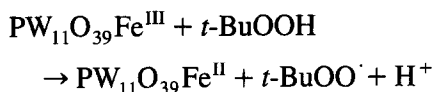
could be excluded because when the 0.01 M solution of sample 2(4) in CCl_4 was mixed with a 0.2 M solution of t-BuOOH in toluene and kept under nitrogen at 25°C for 48 h, no visible change in the solution colour occurred.

The oxidation of adamantane (0.5 M), a mechanistic probe for the homogeneous oxidation of alkanes [39,40] supplied 1-adamantanol, 2-adamantanol and 2-adamantanone. In the case of the reaction carried out in CCl_4, 1-adaman-

tylchloride was also detected. The normalized C^3/C^2 values were found to be in the range 5–10 for the catalysts examined (Table 4), and they are typical of autoxidation processes; thus, adamantane hydroperoxide should be the intermediate of the reaction [41].

All these results confirm the involvement of radicals in this reaction. The alkyl radical may be generated by the reaction of alkane with a variety of species [37,42]. In this way, the metallic centre can be either directly or indirectly involved in the oxidation reaction of cyclohexane, in the latter case generating radicals for homolysis of t-BuOOH and causing a series of radical chains (Scheme 1).
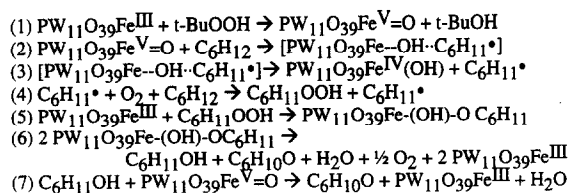
The peroxide heterolysis generates a high-valent iron-oxo-species that may be the actual catalytic species.

Based on reaction kinetics data, product yields and K_H/K_D and C^3/C^2 values, the chain radical mechanism of alkane oxidation by t-BuOOH in the presence of O_2 can be proposed for all the complexes tested. The key stages of this process are (i) the formation of alkoxy radicals as a result of t-BuOOH decomposition catalyzed by the HPC, (ii) the substrate activation via H-atom abstraction by these radicals and/or by high-valent metal-oxo species of HPCs, intermediately formed in the system, and (iii) molecular oxygen involvement in the process of chain extension.

The mechanism that can be possibly deduced from the data reported here is shown in Scheme 2; it involves the reaction of the HPA with TBHP to form an intermediate oxo-metallic

(1) $PW_{11}O_{39}Fe^{III} + t\text{-BuOOH} \rightarrow PW_{11}O_{39}Fe^{IV}(OH) + t\text{-BuO}^\cdot$
(2) $PW_{11}O_{39}Fe^{IV}(OH) + t\text{-BuOOH} \rightarrow PW_{11}O_{39}Fe^{III} + t\text{-BuOO}^\cdot + H_2O$
(3) $2\ t\text{-BuOO}^\cdot \rightarrow (t\text{-BuOO})_2 \rightarrow O_2 + (t\text{-BuO})_2$
(4) $t\text{-BuO}^\cdot + C_6H_{12} \rightarrow t\text{-BuOH} + C_6H_{11}^\cdot$
(5) $2\ t\text{-BuO}^\cdot \rightarrow (t\text{-BuO})_2$
(6) $t\text{-BuOO}^\cdot + C_6H_{11}^\cdot \rightarrow t\text{-BuOOC}_6H_{11}$
(7) $t\text{-BuO}^\cdot + C_6H_{11}^\cdot \rightarrow t\text{-BuOC}_6H_{11}$
(8) $C_6H_{11}^\cdot + O_2 \rightarrow C_6H_{11}OO^\cdot$
(9) $C_6H_{11}OO^\cdot + C_6H_{12} \rightarrow C_6H_{11}OOH + C_6H_{11}^\cdot \rightarrow$ etc.
(10) $C_6H_{11}^\cdot + C_6H_{11}OO^\cdot$ (or $t\text{-BuOO}^\cdot$) $\rightarrow C_6H_{11}OOC_6H_{11}$ (or $C_6H_{11}OOtBu$)
(11) $2\ C_6H_{11}OO^\cdot \rightarrow (C_6H_{11}OO)_2 \rightarrow O_2 + C_6H_{11}OH + C_6H_{10}O$
(12) $C_6H_{11}^\cdot + 2\ CCl_4 \rightarrow C_6H_{11}Cl + C_2Cl_6$

Scheme 1. t-BuO$^\cdot$ participated processes of the substrate oxidation.

(1) $PW_{11}O_{39}Fe^{III} + t\text{-BuOOH} \rightarrow PW_{11}O_{39}Fe^{V}=O + t\text{-BuOH}$

(2) $PW_{11}O_{39}Fe^{V}=O + C_6H_{12} \rightarrow [PW_{11}O_{39}Fe\text{--OH}\cdots C_6H_{11}\bullet]$

(3) $[PW_{11}O_{39}Fe\text{--OH}\cdots C_6H_{11}\bullet] \rightarrow PW_{11}O_{39}Fe^{IV}(OH) + C_6H_{11}\bullet$

(4) $C_6H_{11}\bullet + O_2 + C_6H_{12} \rightarrow C_6H_{11}OOH + C_6H_{11}\bullet$

(5) $PW_{11}O_{39}Fe^{III} + C_6H_{11}OOH \rightarrow PW_{11}O_{39}Fe\text{-(OH)-O } C_6H_{11}$

(6) $2\ PW_{11}O_{39}Fe\text{-(OH)-O}C_6H_{11} \rightarrow$
$C_6H_{11}OH + C_6H_{10}O + H_2O + \tfrac{1}{2} O_2 + 2\ PW_{11}O_{39}Fe^{III}$

(7) $C_6H_{11}OH + PW_{11}O_{39}Fe^{V}=O \rightarrow C_6H_{10}O + PW_{11}O_{39}Fe^{III} + H_2O$

Scheme 2. The proposed mechanism of aerobic alkane oxygenation participated with high-valent HPC species.

species $PW_{11}O_{39}Fe^{V}=O$ and t-BuOH. The oxo-metal complex homolitically reacts with the C–H bond to generate a carbon-radical that gives rise, by reaction with O_2, to an alkylhydroperoxide (or an alkylhydroperoxide radical) which subsequently decomposes to afford the alcohol and the ketone (the ol/one ratio depends on the nature of the peroxide) [43,44], analogously to the so-called Russel mechanism [45] (reaction (11) in Scheme 1); these products are therefore primary products of oxidation. The alcohol that is formed can be further oxidized to ketone, without implication of O_2.

The fact that the oxygenated products were not detected in the absence of dioxygen indicates that the oxidation of the substrates via oxygen atom transfer from high-valent oxo species (i.e., $[PW_{11}O_{39}Fe\text{--OH} \cdots R\bullet] \rightarrow PW_{11}O_{39}Fe^{III} + ROH$) can be neglected, at least under the conditions employed in the present study.

The alkane oxidation by t-BuOOH in the presence of HPCs has previously been studied by Faraj and Hill [33]. Under the conditions used by these authors for cyclohexane oxidation the yield to oxygenated products with regard to t-BuOOH consumed was higher, and the yield of products from radical recombination, di-t-butylperoxide, was lower than in our experiments. Nevertheless, in both studies there was not a strong influence of transition metal variation on the yields of products. Furthermore, the same values of K_H/K_D and C^3/C^2 were found upon adamantane oxidation in the presence of the same complex $PW_{11}Co(H_2O)O_{39}^{5-}$: 6.7 and 9.6, respectively, in this work, and 6.5 and 9.8 in the work of Faraj and Hill [33]. These obser-

vations indicate that the mechanism of alkane functionalization does not change markedly with different reaction conditions.

The following conclusions can be drawn from the results reported:

(1) The nature of the metal in the HPC framework and the presence of nitrate ligand do not remarkably affect the catalytic performance.

(2) The mechanism is in agreement with that proposed by other authors for analogous catalytic systems, involving radicalic intermediates. However, one fundamental difference concerns the role of molecular oxygen, which under our experimental conditions (i.e., low temperature) is necessary in order to initiate the reaction. Under more severe conditions, molecular oxygen may arise from t-butylhydroperoxide decomposition.

(3) Cyclohexanol and cyclohexanone are originated from a common intermediate, probably a hydroperoxy derivative; then, for prolonged time of reaction, the consecutive reaction of cyclohexanol transformation to cyclohexanone becomes the main source of ketone production.

Acknowledgements

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