

Sandwich-type tungstophosphates in the catalytic oxidation of cycloalkanes with hydrogen peroxide

Isabel C.M.S. Santos^{a,b}, José A.F. Gamelas^{a,b}, M. Saete S. Balula^{a,b}, Mário M.Q. Simões^a, M. Graça P.M.S. Neves^a, José A.S. Cavaleiro^a, Ana M.V. Cavaleiro^{a,b,*}

^a Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

^b CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Available online 24 August 2006

Abstract

The tetrabutylammonium salts of sandwich-type tungstophosphates of general formula $B-\alpha-[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, $M = Co^{II}$, Mn^{II} and Fe^{III} , proved to be catalysts or catalyst precursors for the oxidation of cyclohexane and cyclooctane with hydrogen peroxide, affording the corresponding alcohol, ketone and alkyl hydroperoxide in variable proportions. Depending on the tungstophosphate used, the oxidation of cyclooctane could also give 1,2-epoxycyclooctane or a cyclooctanedione. With the Fe sandwich anion, cycloalkyl hydroperoxide was generally the most abundant product. The conversion of cycloalkanes was always higher than 68% after 12 h of reaction. Oxidation of cyclooctane into cyclooctanone could be obtained with high selectivity (83%) and conversion (92%) using $B-\alpha-[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$. The Fe sandwich complex showed to be the most effective catalyst, with turnover numbers of 1333 for cyclohexane and of 1930 for cyclooctane, after 12 h.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Polyoxometalates; Sandwich-type; Cyclohexane; Cyclooctane; Oxidation; Hydrogen peroxide

1. Introduction

Many sandwich-type tungstophosphates having the general formula $B-\alpha-[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, $M =$ transition metal, are easily obtained in aqueous solution by reaction of appropriate amounts of the tri-lacunary Keggin anion $B-\alpha-[PW_9O_{34}]^{9-}$ and transition metal ions [1,2]. The molecular structure of this type of anions was presented for the first time by Weakley et al. for the Co analogue [3] and is based on the linkage of two tri-lacunary Keggin sub-units $B-\alpha-[PW_9O_{34}]^{9-}$ by a belt of four metal ions (Fig. 1). Only recently was described the first tetranuclear sandwich compound containing a belt of trivalent metal ions in the centre [4].

This type of compounds have attracted special interest for their structural and magnetic properties [5,6]. A small number of reports appeared on their potential application as catalysts for the oxidation of alkenes [4,7–9]. In particular, the iron sandwich complexes, $[Fe^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Fe^{III}_4(H_2O)_2(PW_9O_{34})_2]^{6-}$, showed to be effec-

tive catalysts for the oxidation of several alkenes with hydrogen peroxide as oxidant [4,8]. The Mn^{II} analogue, $[Mn^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, was used in the oxidation of cyclohexene and *cis*-stilbene with iodosylbenzene [9].

An important area of interest in oxidative catalysis, for both academic and industrial applications, concerns the transformation of saturated hydrocarbons into oxygenated derivatives. Molecular oxygen is possibly the best oxidant choice. However, non-selective radical-chain reactions usually occur. In particular, the catalytic systems currently used in the industry for the cyclohexane oxidation employing molecular oxygen and cobalt or manganese salts limit the conversion to 5–13% (depending on the conditions) in order to achieve the required selectivity for the ketone/alcohol mixture [10,11]. Hydrogen peroxide is an interesting alternative to O_2 , due to its high availability and relatively low price, and to the fact of giving environmentally benign water as by-product [12–14].

The use of several types of polyoxometalates in cyclohexane and cyclooctane homogeneous oxidative catalysis has been reviewed [7,15–18]. In particular, Keggin-type polyoxotungstates were used in homogeneous oxidation with iodosylbenzene [19], *m*-chloroperbenzoic acid [20], *t*-butyl hydroperoxide [21–25], hydrogen peroxide [26–33] and molecular oxygen [26,30,34,35]. Zinc sandwich-type anions, like

* Corresponding author at: Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal. Tel.: +351 234 370 734; fax: +351 234 370 084.

E-mail address: ana@dq.ua.pt (A.M.V. Cavaleiro).

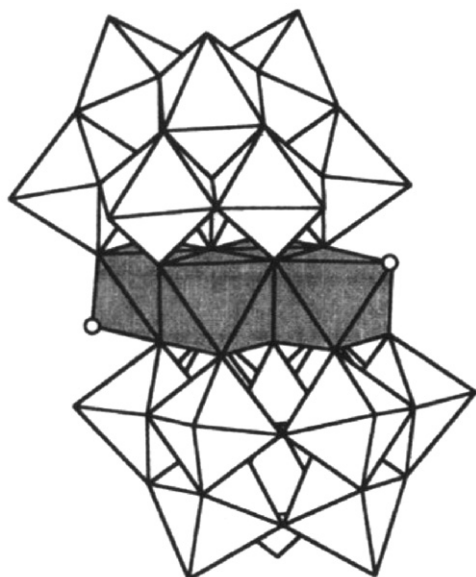


Fig. 1. Structure of the complex $B-\alpha-[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$. Each dashed octahedron represents a MO_6 group and the open circles correspond to oxygen atoms of co-ordinating water molecules.

$[WZnM_2(ZnW_9O_{34})_2]^{n-}$, $M = Mn^{II}$, Ru^{III} , Pd^{II} and Pt^{II} , having a structure similar to that of sandwich-type tungstophosphates considered here, were also studied as catalysts in the cycloalkane oxidation with *t*-butyl hydroperoxide [36] or ozone in the case of $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$ [37]. When using hydrogen peroxide, the most relevant results were obtained for the cyclohexane and cyclooctane oxidation in the presence of Keggin-type anions like $[XW_{11}Fe(H_2O)O_{39}]^{n-}$, $X = P$, Si and B [29,31–33] or, in the case of the cyclohexane oxidation, with γ - $[SiW_{10}Fe^{III}_2(H_2O)_2O_{38}]^{6-}$ [27].

It is reported in this paper for the first time the use of the sandwich-type tungstophosphate anions, namely $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, $M^{II} = Co$, Mn and $[Fe^{III}_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ (abbreviated as $M_4(PW_9)_2$), as catalysts or catalyst precursors in cyclohexane and cyclooctane oxidation using H_2O_2 as oxidant and acetonitrile as solvent. Catalytic oxidation occurred for all compounds. Particularly good results were obtained with the iron sandwich-type anion, with the oxidation of cyclohexane or cyclooctane occurring with high conversion, comparatively high turnover numbers, and very interesting selectivity values.

2. Experimental

2.1. Catalysts synthesis

$[(C_4H_9)_4N]_7H_3[Co_4^{II}(H_2O)_2(PW_9O_{34})_2]$ and $[(C_4H_9)_4N]_7H_3[Mn_4^{II}(H_2O)_2(PW_9O_{34})_2]$ were synthesised as previously described [38]. Analytical and spectroscopic data were in agreement with previously published values [38].

$[(C_4H_9)_4N]_6[Fe_4^{III}(H_2O)_2(PW_9O_{34})_2] \cdot 4H_2O$ was synthesised by a modification of the procedure described by Zhang et al. [4]. $FeCl_2 \cdot 4H_2O$ was substituted by $FeSO_4 \cdot 7H_2O$ and the re-crystallisation step in acetonitrile was not performed. Found (calculated): (%) C, 18.5 (18.5); N, 1.29 (1.35); H, 4.02 (3.68); H_2O , 1.0 (1.1); thermogravimetric organic loss, 25.3 (24.7).

Infrared spectra were in agreement with that found in the literature [4].

2.2. Oxidation reactions with hydrogen peroxide

The reactions were typically carried out by refluxing a stirred solution of the cycloalkane, catalyst (1.5 μ mol) and 30% hydrogen peroxide (Riedel-de Haën) in 1.5 mL of acetonitrile, with different H_2O_2 /substrate ratio. Unless otherwise stated, the reactions were carried out under air. When reactions were performed in an inert atmosphere, an argon or nitrogen flow was bubbled through the reaction mixture before the addition of hydrogen peroxide and a rubber balloon with argon or nitrogen was maintained at the top of the condenser during the reaction.

Aliquots were withdrawn from the reaction mixture and injected directly into the GC–MS apparatus (SPB-5 fused silica Supelco capillary column with 30 m \times 0.25 mm i.d. and 0.25 μ m film thickness) using helium as the carrier gas (35 cm/s). The conversion and percentages of each compound in the reaction mixture were determined by GC–MS. The chromatographic conditions for cyclohexane were: initial temperature: 40 $^\circ$ C (4 min); temperature rate: 10 $^\circ$ C/min; final temperature: 200 $^\circ$ C (2 min); injector temperature: 220 $^\circ$ C; detector temperature: 230 $^\circ$ C; for cyclooctane: initial temperature: 80 $^\circ$ C (2 min); temperature rate: 20 $^\circ$ C/min; final temperature: 220 $^\circ$ C (1 min); injector temperature: 250 $^\circ$ C; detector temperature: 250 $^\circ$ C.

Blank reactions without catalyst were performed in all conditions studied. No oxidation products were detected.

2.3. Instrumentation and methods

Electronic absorption and FTIR spectra, C, H, N elemental analysis and thermogravimetric analyses were obtained as previously described [39].

Unused H_2O_2 and hydroperoxide produced were quantified by titration of aliquots with 0.1 M $Ce(SO_4)_2$ using ferroin as indicator [40]. From the yields of the hydroperoxide determined by GC–MS, the amount of H_2O_2 used could be determined. The efficiency of usage of hydrogen peroxide was calculated according to the following formula: (amount of ketone \times 2 + amount of alcohol \times 1 + amount of alkyl hydroperoxide \times 2)/(amount of H_2O_2 used). All products were identified by GC–MS. Both hydroperoxides had been previously identified in our group by mass spectrometry [41].

At the end of the reactions, whenever H_2O_2 /substrate = 2 and substrate/catalyst = 667, a drop of the reaction mixture was dried on a KBr pellet and the infrared spectrum measured in order to assess the stability of the catalysts. Visible spectra of the reaction solutions were run at pre-determined intervals.


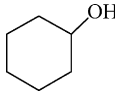
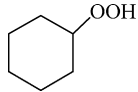
3. Results

3.1. Oxidation of cyclohexane

The results obtained for the cyclohexane catalytic oxidation with different H_2O_2 /substrate molar ratio are summarized in Table 1.

Table 1

Oxidation of cyclohexane with hydrogen peroxide catalysed by sandwich-type tungstophosphates^a

	Polyoxometalate	Conversion (%)	TON ^b	H ₂ O ₂ (%) ^c	Selectivity (%)		
							
1 ^d	Co ₄ (PW ₉) ₂	83	549	93	62	38	0
2 ^e	Co ₄ (PW ₉) ₂	91	609	81	60	40	0
3 ^d	Mn ₄ (PW ₉) ₂	68	453	76	59	41	0
4 ^e	Mn ₄ (PW ₉) ₂	98	654	76	55	45	0
5 ^d	Fe ₄ (PW ₉) ₂	94 ^f	628	96	41	6	53
6 ^e	Fe ₄ (PW ₉) ₂	98 ^f	657	99	34	14	52
7 ^g	Fe ₄ (PW ₉) ₂	100	1333	96	20	10	70

^a Cyclohexane, 1.5 μmol of catalyst in 1.5 mL of CH₃CN, H₂O₂ (30%), reflux temperature, 12 h of reaction.^b Mole of products/mol of catalyst.^c H₂O₂ used during the reaction.^d 1 mmol of substrate and 2 mmol H₂O₂.^e 1 mmol of substrate and 4 mmol H₂O₂.^f After 6 h of reaction.^g 2 mmol of substrate and 4 mmol H₂O₂.

With Co₄(PW₉)₂ and Mn₄(PW₉)₂, the products obtained after 12 h of reaction were cyclohexanone and cyclohexanol, the former being the main product. Cyclohexyl hydroperoxide could be identified during the course of the reaction in the case of Co₄(PW₉)₂, usually in low yield up to 15 %, disappearing completely after 9 h. Higher conversion values (more than 90%) were obtained when excess of hydrogen peroxide was used (H₂O₂/substrate = 4).

The oxidation of cyclohexane proceeded faster with Fe₄(PW₉)₂ than with Co and Mn analogues (Fig. 2). After 6 h of reaction, conversion values higher than 90% were obtained with the Fe complex (Table 1). In contrast to the Co and Mn sandwich complexes, cyclohexyl hydroperoxide was always the main product up to 9 h of reaction. Nevertheless, selectivity for this compound decreased with reaction time (Fig. 3).

For H₂O₂/substrate = 2 and substrate/catalyst = 667, the calculated efficiency of usage of hydrogen peroxide at the end of the reaction was 95, 72 and 72% with Fe₄(PW₉)₂, Mn₄(PW₉)₂ and Co₄(PW₉)₂, respectively. The experiments performed with excess of hydrogen peroxide gave lower efficiencies.

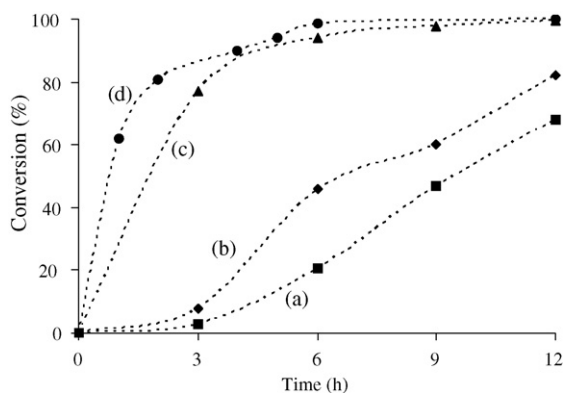


Fig. 2. Time dependence on the cyclohexane oxidation in the presence of Mn₄(PW₉)₂ (a), Co₄(PW₉)₂ (b) and Fe₄(PW₉)₂ (c) and (d). H₂O₂/substrate = 2 for (a)–(c); H₂O₂/substrate = 4 for (d). Substrate: 1 mmol; catalyst: 1.5 μmol; acetonitrile: 1.5 mL; reflux temperature.

The experiments performed with the iron sandwich-type complex with the ratio substrate/catalyst = 1333, corresponding to higher concentrations of substrate and H₂O₂ (entry 7, Table 1), illustrated the possibility of extending the reaction of oxidation of cyclohexane to higher turnover numbers. In fact, 100% of conversion was obtained after 12 h of reaction, achieving 1333 turnovers for this reaction. The cyclohexyl hydroperoxide was the main product (70% yield after 9 or 12 h, 55% after 6 h and 47% after 3 h of reaction, Fig. 4).

When the experiments with the several sandwich-type anions were performed in the presence of I₂ (radical scavenger) no reaction products were detected, suggesting the involvement of a radical-chain mechanism in the oxidation of cyclohexane [42]. A similar result was found for the oxidation of cyclooctane described below.

3.2. Oxidation of cyclooctane

The results obtained for the cyclooctane catalytic oxidation are summarized in Table 2. Reactions performed in an inert

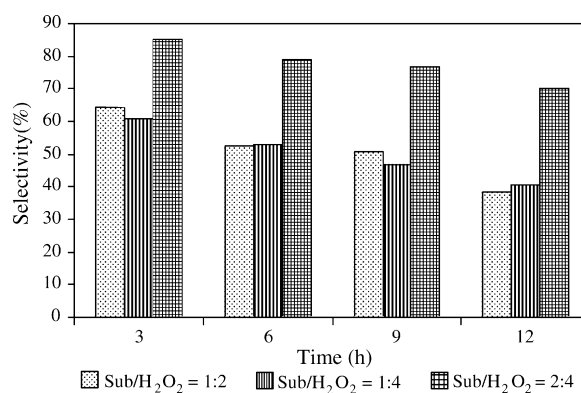





Fig. 3. Selectivity for the cyclohexyl hydroperoxide formation during the cyclohexane oxidation with hydrogen peroxide catalysed by Fe₄(PW₉)₂ (substrate/H₂O₂ = mmol substrate: mmol H₂O₂).

Table 2
Oxidation of cyclooctane with hydrogen peroxide catalysed by sandwich-type tungstophosphates^a

	Polyoxometalate	Time (h)	Conversion (%)	TON ^b	H ₂ O ₂ (%) ^c	Selectivity (%)		
								
1 ^d	Co ₄ (PW ₉) ₂	12	92	616	64	83	13	4
2 ^e	Co ₄ (PW ₉) ₂	12	85	567	88	63	32	5
3 ^{d,f}	Mn ₄ (PW ₉) ₂	12	91	605	66	64	12	13
4 ^{e,f}	Mn ₄ (PW ₉) ₂	12	68	452	81	49	16	5
5 ^{d,g}	Fe ₄ (PW ₉) ₂	7	98	651	81	45	14	6
6 ^h	Fe ₄ (PW ₉) ₂	9	97	647	72	41	6	53
7 ^e	Fe ₄ (PW ₉) ₂	12	96	645	92	41	2	57
8 ^{i,g}	Fe ₄ (PW ₉) ₂	12	96	1284	99	58	1	16
9 ^{g,j}	Fe ₄ (PW ₉) ₂	12	96	1930	99	64	1	16

^a Cyclooctane, 1.5 μmol of catalyst in 1.5 mL of CH₃CN, H₂O₂ (30%), reflux temperature.

^b Mole of products/mol of catalyst.

^c H₂O₂ used during the reaction.

^d 1 mmol of substrate and 9.8 mmol H₂O₂.

^e 1 mmol of substrate and 2 mmol H₂O₂.

^f 1,2-Epoxyoctane was also found in the products.




^g A cyclooctanedione was also found in the products.

^h 1 mmol of substrate and 4 mmol H₂O₂.

ⁱ 2 mmol of substrate and 4 mmol H₂O₂.

^j 3 mmol of substrate and 6 mmol of H₂O₂.

Table 3
Oxidation of cyclooctane with H₂O₂ catalysed by sandwich-type tungstophosphates in the absence of dioxygen^a

	Polyoxometalate	Time (h)	Conversion (%)	TON ^b	Selectivity (%)		
							
1 ^c	Co ₄ (PW ₉) ₂	12	82	547	60	34	6
2 ^c	Mn ₄ (PW ₉) ₂	12	70	467	46	20	7
3 ^c	Fe ₄ (PW ₉) ₂	12	94	627	42	6	52
4 ^d	Fe ₄ (PW ₉) ₂	12	95	633	37	3	60

^a 1 mmol of cyclooctane, 1.5 μmol of catalyst in 1.5 mL of CH₃CN, 2 mmol of H₂O₂ (30%), reflux temperature.

^b Mole of products/mol of catalyst.

^c Under nitrogen atmosphere.

^d Under argon.

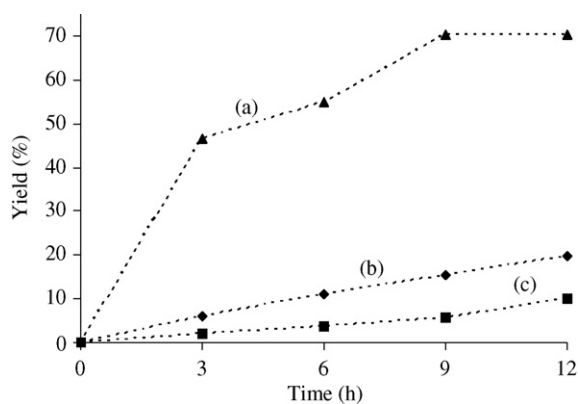


Fig. 4. Yield of all the products obtained during cyclohexane oxidation in the presence of Fe₄(PW₉)₂ with sub/H₂O₂ = 2 mmol:4 mmol. (a) cyclohexyl hydroperoxide, (b) cyclohexanone and (c) cyclohexanol. Catalyst: 1.5 μmol; acetonitrile: 1.5 mL; reflux temperature.

atmosphere yielded after 12 h results similar to those obtained in air (Table 3).

With M₄(PW₉)₂, M^{II} = Co or Mn, more than 90% of cyclooctane conversion was obtained for H₂O₂/substrate = 9.8, after 12 h. With H₂O₂/substrate = 2 the conversion was lower, in particular with Mn sandwich anion, even after 12 h of reaction (Table 2 and Fig. 5). After 12 h the main product was always the cyclooctanone (selectivity values between 49 and 83%), while the cyclooctyl hydroperoxide was always formed in low amount. In the presence of Mn₄(PW₉)₂, 1,2-epoxyoctane was formed with 10–30% selectivity after 12 h. This epoxide may be formed *via* dehydrogenation of the cyclooctane or through dehydration of the alcohol. Turnover numbers were higher than 600 (for a substrate/catalyst ratio = 667) when a great excess of hydrogen peroxide was used.

Using the Fe₄(PW₉)₂ sandwich-type anion near 100% of conversion was obtained, in all cases, after 12 h of reaction (Fig. 5).

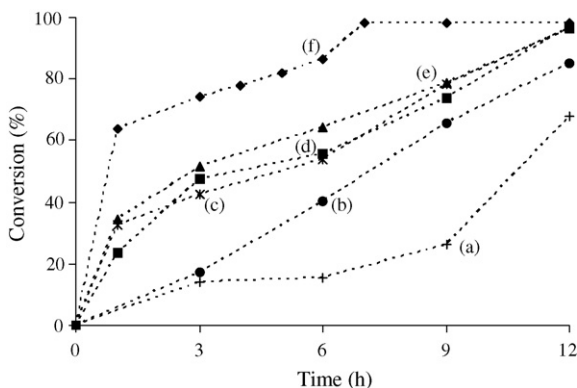


Fig. 5. Time course of the cyclooctane oxidation with H_2O_2 in the presence of $\text{Mn}_4(\text{PW}_9)_2$ (a), $\text{Co}_4(\text{PW}_9)_2$ (b) and $\text{Fe}_4(\text{PW}_9)_2$ (c)–(f). Substrate/ H_2O_2 = 1:2 for (a), (b) and (d); substrate/ H_2O_2 = 2:4 for (e); substrate/ H_2O_2 = 3:6 for (c); substrate/ H_2O_2 = 1:9.8 for (f). Catalyst: 1.5 μmol ; acetonitrile: 1.5 mL; reflux temperature (substrate/ H_2O_2 = mmol substrate: mmol H_2O_2).

With excess of hydrogen peroxide (H_2O_2 /substrate = 9.8), the conversion reached 64% after only 1 h of reaction and nearly 100% after 7 h. It should be noted that the increase of the substrate/catalyst ratio, for the fixed proportion H_2O_2 /substrate = 2, did not affect the conversion at 12 h of reaction (Fig. 5), and this originated an increase on turnover numbers (645, 1284 and 1930, respectively, for the conditions of entries 7–9 of Table 2). To our knowledge, these results represent the highest turnover numbers ever reported for the cyclooctane oxidation employing polyoxometalates.

Cyclooctyl hydroperoxide was always the most abundant product until near 2 h of reaction for all the H_2O_2 /substrate proportions used (Fig. 6). With H_2O_2 /substrate = 2 or 4 and substrate/catalyst = 667 cyclooctyl hydroperoxide was the main product up to 12 h. The higher yield was observed after 3 h of reaction for H_2O_2 /substrate = 4 (58% selectivity, 85% conversion). In all other cases, cyclooctanone was predominant after 3–4 h of reaction and a fourth product, identified as a dione, was detected.

Using H_2O_2 /substrate = 2 (and substrate/catalyst = 667) the efficiency of usage of hydrogen peroxide was higher than 60% for all the three complexes. After 12 h of reaction, 99, 64 and

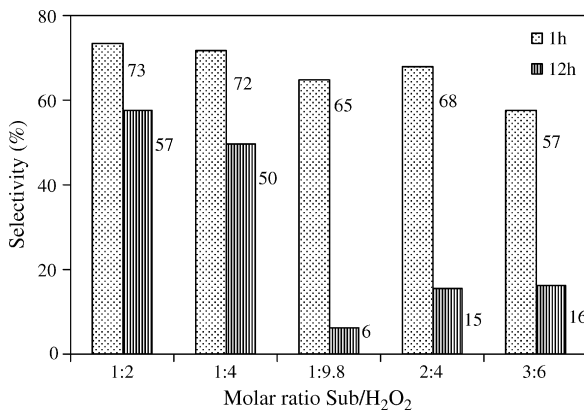


Fig. 6. Selectivity for the cyclooctyl hydroperoxide during the cyclooctane oxidation reaction with hydrogen peroxide catalysed by $\text{Fe}_4(\text{PW}_9)_2$ (catalyst: 1.5 μmol ; acetonitrile: 1.5 mL; reflux; substrate/ H_2O_2 = mmol substrate: mmol H_2O_2).

81% of efficiency were obtained with $\text{Fe}_4(\text{PW}_9)_2$, $\text{Mn}_4(\text{PW}_9)_2$ and $\text{Co}_4(\text{PW}_9)_2$, respectively.

3.3. Catalysts stability

Catalyst recover was only attempted for reactions performed with H_2O_2 /substrate = 2 and substrate/catalyst = 667. The infrared spectra of the residue obtained at the end of the reactions indicated that decomposition of the catalyst had occurred. The visible spectra of the reaction media obtained during the course of reactions also suggested that the catalysts were not stable in the reaction conditions. $\text{Co}_4(\text{PW}_9)_2$ and $\text{Mn}_4(\text{PW}_9)_2$ seemed to decompose with formation of $[\text{PW}_{11}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$ (PW_{11}Co) and $[\text{PW}_{11}\text{Mn}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$ (PW_{11}Mn), respectively. Bands tentatively attributed to the mono substituted Keggin anions were observed in the FTIR and visible spectra [43,44]. The decomposition was more extensive for Mn than for the Co anion. Catalysis with PW_{11}Mn in similar conditions had been previously described [33], but the results differed from those reported here. Some preliminary studies with PW_{11}Co were performed in this work. Conversions did not exceed 35% after 12 h of reaction. In the case of $\text{Fe}_4(\text{PW}_9)_2$, the infrared spectra of the solid recovered at the end of the reaction also suggested the formation of $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$ (PW_{11}Fe) [44]. Due to the lack of d–d bands, analyses of visible spectra were not conclusive. Hill and collaborators reported that a serious of yellow solids could be isolated during the preparation of the $\text{Fe}_4(\text{PW}_9)_2$ anions [4]. Possibly one or more of these species may also be formed in the reaction conditions used.

Studies on the hydrolytic stability of these sandwich anions in the presence of H_2O_2 have not yet been published and are out of the scope of this paper. $\text{Fe}_4(\text{PW}_9)_2$ was found to be stable under conditions of deficiency of H_2O_2 , at room temperature [4]. The stability of $\text{Fe}_4(\text{PW}_9)_2$ was also confirmed for reactions with other substrates under conditions similar to those here used, but for the H_2O_2 /catalyst ratio up to 600 [45]. The H_2O_2 /catalyst ratios used in this work were above 1330, what may account for the occurrence of catalyst degradation. Further studies are needed to clarify the observed behaviour.

4. Discussion

In this work, the oxidation of cyclohexane and cyclooctane with H_2O_2 , in the presence of sandwich-type polyoxotungstophosphates $[\text{M}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$, $\text{M}^{\text{II}} = \text{Co}, \text{Mn}$ and $[\text{Fe}^{\text{III}}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{6-}$, was achieved with high conversions and comparatively high selectivity. When $\text{Fe}_4(\text{PW}_9)_2$ was used, cyclohexyl or cyclooctyl hydroperoxides were produced in amounts depending on the conditions and time of reaction, the other major product being cyclohexanone or cyclooctanone. In some conditions a cyclooctanedione was formed. The results described in this paper for cyclooctane oxidation with the Fe sandwich-type anion at low H_2O_2 /substrate molar ratio are comparable with those obtained in previous work with $[\text{XW}_{11}\text{Fe}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}]^{n-}$ (XW_{11}Fe), $\text{X} = \text{P}, \text{Si}$ or B , as catalysts [31–33]. However, the possibility of reaching up to almost 2000

turnovers without significant alteration of the reaction profile is presented here by the first time: with the iron-sandwich complex turnovers higher than 1900 were reached after 12 h of reaction in the appropriate conditions. The oxidation of cyclohexane with H_2O_2 , in acetonitrile, had been previously studied with PW_{11}Fe and BW_{11}Fe as catalysts [29,31]. In the study with BW_{11}Fe , in the same experimental conditions of this work, 98% conversion (TON 1307) was observed after 12 h of reaction, along with 57% selectivity to the cyclohexyl hydroperoxide [31]. With $\text{Fe}_4(\text{PW}_9)_2$, 100% of conversion (TON 1333) with 70% selectivity to the cyclohexyl hydroperoxide was obtained. The reactions with the Fe sandwich-type catalyst occurred faster (more than 60% of conversion after 6 h on comparison to about 40% with BW_{11}Fe in similar conditions). This may be due to the fact that sandwich-type anions have more iron atoms available for catalysis, even considering that, possibly, only the iron ions of the Fe–OH₂ group are catalytically active.

Another catalytic study of the oxidation of cyclohexane with H_2O_2 in acetonitrile, with the iron-substituted polyoxotungstate $\gamma\text{-}[\text{SiW}_{10}\text{Fe}^{\text{III}}_2(\text{H}_2\text{O})_2\text{O}_{38}]^{6-}$, was reported by Mizuno et al. [27]. The reactions were carried out with a H_2O_2 /substrate molar ratio equal to 1, the products being cyclohexanol and cyclohexanone. Considering the turnover numbers and time of reaction, the results presented here with $\text{Fe}_4(\text{PW}_9)_2$ seem to be considerably better than those previously reported [27]. Nevertheless, in our work, the efficiency of usage of H_2O_2 is lower and products distribution is different.

In our work all the studies with iron catalysts were performed with H_2O_2 /substrate molar ratio equal or larger than 2 ([29,31–33] and this study), and hydroperoxides were generally found in significant amounts. We believe that the mechanism proposed for the oxidation of cyclooctane with excess of H_2O_2 in the presence of the monosubstituted Keggin anions [33] applies to the case of the $\text{Fe}_4(\text{PW}_9)_2$ anion. In this mechanism, it was assumed that the formation of the hydroperoxide occurred by a Fe(III) initiated generation of HO• [14,46–48]. Generation of molecular oxygen *in situ* from H_2O_2 has been suggested by others, and this would favour extensive hydroperoxidation in the presence of excess of H_2O_2 [14,49,50]. The amount of hydroperoxide in the products, at a given time of reaction, is probably dependent on the existence of several possible concurrent reactions, namely the hydroperoxidation or hydroxylation of cycloalkane, the decomposition of cycloalkyl hydroperoxide and the dismutation of H_2O_2 [33]. We may note that different aqueous H_2O_2 /acetonitrile molar ratios in the reaction media correspond also to different percentage of water in the solvent, leading to different O₂ solubility (it is known that this decreases as the water content increases [51]) and, in this way, affecting conversion and product distribution.

The use of iron polyoxotungstates as catalysts in the oxidation of cycloalkanes seems to be a promising area of research. It is very interesting to note that tuning of the outcome of the oxidation of cycloalkanes may be possible through the choice of catalyst and reaction conditions.

Catalysis with $\text{Co}_4(\text{PW}_9)_2$ and $\text{Mn}_4(\text{PW}_9)_2$ yielded little or no hydroperoxides in the course of the oxidative reactions of the studied substrates. This behaviour of $\text{Mn}_4(\text{PW}_9)_2$ is notably

different from that of $\text{XW}_{11}\text{Mn}^{\text{III}}$, X = P, Si and B [29,31–33]. The usage of $\text{Mn}_4(\text{PW}_9)_2$ brought no clear improvement in conversion or selectivity in relation to PW_{11}Mn [33]. Besides the absence of hydroperoxides, the only noticeable difference was the detection, with the former, of 1,2-epoxycyclooctane among the products. The results obtained with $\text{Co}_4(\text{PW}_9)_2$ were more interesting, as PW_{11}Co was a poor catalyst in the same conditions. With the sandwich compound, cyclooctanone could be obtained with 83% selectivity and 92% conversion of cyclooctane. As the metal centres in these catalysts are in the +2 oxidation state, generation of molecular oxygen, *in situ* from H_2O_2 , may not be as extensive as proposed for anions with Fe^{III} [14,33], what would account for the absence of the hydroperoxides.

An important point to consider is the efficiency of usage of the oxidant in the reaction. Shuchardt et al. stated that for practical purposes the efficiency of usage of H_2O_2 in the case of cyclohexane oxidation should not be lower than 40% [15]. At lower efficiencies the cost of the oxidant may be too high for the industrial production of oxygenated derivatives of cyclohexane [15]. We report here some hydrogen peroxide efficiency values that seem quite good. Nevertheless, these calculations were done based on global reactions that were assumed to occur, and should be considered as an estimation, allowing the comparison with others obtained in similar conditions.

5. Conclusions

Sandwich-type tungstophosphates of general formula B- α - $[\text{M}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{n-}$ (M = Co^{II}, Mn^{II} and Fe^{III}) were used as tetra-*n*-butylammonium salts for the catalytic oxidation of cyclohexane and cyclooctane with hydrogen peroxide in acetonitrile. Oxidative reactions occurred in all studied cases. The reactions of the cycloalkanes in the presence of the iron sandwich-type anion were faster and had higher turnover numbers than those with the Mn^{II} or Co^{II} anions.

It was demonstrated that the oxidation reactions of cyclohexane and cyclooctane with Fe sandwich-type complex can lead to very high turnover numbers, up to almost 2000. In fact, the results described here correspond to the highest turnovers ever reported in the literature for the oxidation of this type of substrates employing polyoxometalates as catalysts. Oxidation of cyclooctane into cyclooctanone could be obtained with high selectivity (83%) and conversion (92%) using B- α - $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$.

Acknowledgments

Thanks are due to the University of Aveiro, Fundação para a Ciência e a Tecnologia (FCT) and FEDER (POCTI/QUI/38377/2001) for funding and to FCT and FEDER for PhD grants.

References

- [1] R.G. Finke, M.W. Droegge, P.J. Domaille, *Inorg. Chem.* 26 (1987) 3886.
- [2] R.G. Finke, M.W. Droegge, J.R. Hutchinson, O. Gansow, *J. Am. Chem. Soc.* 103 (1981) 1587.

- [3] T.J.R. Weakley, H.T. Evans, J.S. Showell, G.F. Tourné, C.M. Tourné, *J. Chem. Soc. Chem. Commun.* (1973) 139.
- [4] X. Zhang, Q. Chen, D.C. Duncan, R.J. Lachicotte, C.L. Hill, *Inorg. Chem.* 36 (1997) 4381.
- [5] E. Coronado, C.J. Gomez-Garcia, *Comments Inorg. Chem.* 17 (1995) 255.
- [6] E. Coronado, C.J. Gomez-Garcia, *Chem. Rev.* 98 (1998) 273.
- [7] C.L. Hill, C.M. Prosser-McCartha, *Coord. Chem. Rev.* 143 (1995) 407.
- [8] A.M. Khenkin, C.L. Hill, *Mendeleev Commun.* (1993) 140.
- [9] X. Zhang, M.T. Pope, *J. Mol. Catal. A: Chem.* 114 (1996) 201.
- [10] A.K. Suresh, M.M. Sharma, T. Sridhar, *Ind. Eng. Chem. Res.* 39 (2000) 3958.
- [11] A. Bréhéret, C. Lambeaux, S. Ménage, M. Fontecave, F. Dallemer, E. Fache, J. Pierre, P. Chautemps, M.T. Averbusch-Pouchot, *C. R. Acad. Sci. Paris Série IIc, Chim.* 4 (2001) 27.
- [12] G. Strukul (Ed.), *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer, Dordrecht, 1992.
- [13] W.R. Sanderson, *Pure Appl. Chem.* 72 (2000) 1289.
- [14] C.W. Jones, *Applications of Hydrogen Peroxide and Derivatives*, The Royal Society of Chemistry, 1999.
- [15] U. Shuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinacé, E.L. Pires, *Appl. Catal. A: Gen.* 211 (2001) 1.
- [16] R. Neumann, *Prog. Inorg. Chem.* 47 (1998) 317.
- [17] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [18] R. Neumann, in: J.E. Bäckvall (Ed.), *Modern Oxidative Methods*, Wiley-VCH, Weinheim, 2004, Chap. 8.
- [19] D. Mansuy, J.F. Bartoli, P. Battioni, D.K. Lyon, R.G. Finke, *J. Am. Chem. Soc.* 113 (1991) 7222.
- [20] W. Nam, S.J. Yang, H. Kim, *Bull. Korean Chem. Soc.* 17 (1996) 625.
- [21] M. Faraj, C.L. Hill, *J. Chem. Soc. Chem. Commun.* (1987) 1487.
- [22] R. Neumann, C.A. Abu-Gnim, *J. Chem. Soc. Chem. Commun.* (1989) 1324.
- [23] C.L. Hill, R.F. Renneke, M. Faraj, *Stud. Surf. Sci. Catal.* 66 (1991) 21.
- [24] M. Bressan, A. Morvillo, G. Romanello, *J. Mol. Catal.* 77 (1992) 283.
- [25] Y. Matsumoto, M. Asami, M. Hashimoto, M. Misono, *J. Mol. Catal. A: Chem.* 114 (1996) 161.
- [26] N. Mizuno, C. Nozaki, T. Hirose, M. Tateishi, M. Iwamoto, *J. Mol. Catal. A: Chem.* 117 (1997) 159.
- [27] N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, *J. Am. Chem. Soc.* 120 (1998) 9267.
- [28] N. Mizuno, I. Kiyoto, C. Nozaki, M. Misono, *J. Catal.* 181 (1999) 171.
- [29] M.M.Q. Simões, C.M.M. Conceição, J.A.F. Gamelas, P.M.D.N. Domingues, A.M.V. Cavaleiro, J.A.S. Cavaleiro, A.J.V. Ferrer-Correia, R.A.W. Johnstone, *J. Mol. Catal. A: Chem.* 144 (1999) 461.
- [30] N. Mizuno, *Catal. Surv. Jpn.* 4 (2000) 149.
- [31] I.C.M.S. Santos, M.S. Balula, M.M.Q. Simões, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, *Synlett* (2003) 1643.
- [32] M.M.Q. Simões, I.C.M.S. Santos, M.S.S. Balula, J.A.F. Gamelas, A.M.V. Cavaleiro, M.G.P.M.S. Neves, J.A.S. Cavaleiro, *Catal. Today* 91–92 (2004) 211.
- [33] M.S. Balula, I.C.M.S. Santos, M.M.Q. Simões, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, *J. Mol. Catal. A: Chem.* 222 (2004) 159.
- [34] C. Nozaki, M. Misono, N. Mizuno, *Chem. Lett.* (1998) 1263.
- [35] T. Hayashi, A. Kishida, N. Mizuno, *J. Chem. Soc. Chem. Commun.* (2000) 381.
- [36] R. Neumann, A.M. Khenkin, *Inorg. Chem.* 34 (1995) 5753.
- [37] R. Neumann, A.M. Khenkin, *Chem. Commun.* (1998) 1967.
- [38] M.S. Balula, J.A. Gamelas, H.M. Carapuça, A.M.V. Cavaleiro, W. Schlindwein, *Eur. J. Inorg. Chem.* (2004) 619.
- [39] J.A.F. Gamelas, A.M.V. Cavaleiro, E. de Matos Gomes, M. Belsley, E. Herdtweck, *Polyhedron* 21 (2002) 2537.
- [40] A.I. Vogel, *A Text-Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, 3rd ed., Longmans, London, 1961, p. 325.
- [41] P. Domingues, M.M.Q. Simões, A.M. Cardoso, A.M.V. Cavaleiro, J.A.S. Cavaleiro, R.A.W. Johnstone, A.J. Ferrer-Correia, *Rapid Commun. Mass Spectrom.* 13 (1999) 93.
- [42] D.H.R. Barton, F. Launay, V.N. Le Gloahec, T. Li, F. Smith, *Tetrahedron Lett.* 38 (1997) 8491.
- [43] C.M. Tourné, G.F. Tourné, S.A. Malik, T.J.R. Weakley, *J. Inorg. Nucl. Chem.* 32 (1970) 3875.
- [44] J.A. Gamelas, F.A.S. Couto, M.C.N. Trovão, A.M.V. Cavaleiro, J.A.S. Cavaleiro, J.D. Pedrosa de Jesus, *Thermochim. Acta* 326 (1999) 165.
- [45] I.C.M.S. Vieira, PhD Thesis, University of Aveiro, Portugal, 2005.
- [46] G.B. Shul'pin, G.V. Nizova, Y.N. Kozlov, L.G. Cuervo, G. Suss-Fink, *Adv. Synth. Catal.* 346 (2004) 317.
- [47] L.I. Kuznetsova, L.G. Detusheva, M.A. Fedotov, V.A. Likhonobov, *J. Mol. Catal. A: Chem.* 111 (1996) 81.
- [48] L.I. Kuznetsova, L.G. Detusheva, M.A. Kuznetsova, M.A. Fedotov, V.A. Likhonobov, *J. Mol. Catal. A: Chem.* 117 (1997) 389.
- [49] F. Gozzo, *J. Mol. Catal. A: Chem.* 171 (2001) 1.
- [50] D.T. Sawyer, *Coord. Chem. Rev.* 165 (1997) 297.
- [51] L. Moeini-Nombel, S. Matsuzawa, *J. Photochem. Photobiol. A: Chem.* 119 (1998) 15.