

# A comparative study between Keggin-type tungstophosphates and tungstosilicates in the oxidation of cyclooctane with hydrogen peroxide

M. Salet S. Balula<sup>a,b</sup>, Isabel C.M.S. Santos<sup>a,b</sup>, Mário M.Q. Simões<sup>a</sup>,  
M. Graça P.M.S. Neves<sup>a</sup>, José A.S. Cavaleiro<sup>a</sup>, Ana M.V. Cavaleiro<sup>a,b,\*</sup>

<sup>a</sup> Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>b</sup> CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

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## Abstract

The tetrabutylammonium (TBA) salts of the Keggin-type polyoxotungstates  $[XW_{12}O_{40}]^{n-}$ ,  $[XW_{11}O_{39}]^{(n+4)-}$ ,  $[XW_{11}VO_{40}]^{m-}$  and  $[XW_{11}M^{III}(H_2O)O_{39}]^{p-}$ , X = P or Si and M = Fe or Mn, proved to be effective catalysts for the oxidation of cyclooctane with hydrogen peroxide, in acetonitrile, to the corresponding alkyl hydroperoxide, ketone, and alcohol. High turnover numbers and selectivity for cyclooctyl hydroperoxide were obtained, with values of cyclooctane conversion, after 9 h, between 13 and 96%, depending on the catalyst and reaction conditions. In general tungstosilicates were less active than tungstophosphates but presented higher selectivity for cyclooctyl hydroperoxide. Results obtained with  $H_2O_2$  near the stoichiometric ratio and in excess are compared. Excess of hydrogen peroxide afforded higher selectivity for cyclooctyl hydroperoxide.

In the presence of  $(TBA)_4[PW_{11}Fe(H_2O)O_{39}]$ , 74% of cyclooctane conversion and 80% of selectivity for cyclooctyl hydroperoxide were obtained after 2 h of reaction, using an excess of  $H_2O_2$ . In the same conditions, 100% of cyclooctyl hydroperoxide was obtained with  $(TBA)_4H_4SiW_{11}O_{39}$ , after 9 h (55% conversion). These results indicate that these are very promising systems for the oxidation of alkanes.

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## 1. Introduction

Oxidation of saturated hydrocarbons give rise to quite valuable compounds for organic synthesis, and such oxidative transformations have been extensively investigated over the last few decades [1,2]. In spite of the large number of catalytic systems proposed, low selectivities and conversions are frequently found [3]. A possible way to improve selectivity can be through the selective decomposition of alkyl hydroperoxides formed during the oxidation reactions. One of the targets of our recent research is the finding of Keggin-type polyoxotungstates that can afford good selectivity towards

formation of alkyl hydroperoxides in the catalytic oxidation of cycloalkanes [4–7].

Several catalysts have been described for the oxygenation of alkanes with *tert*-butyl hydroperoxide or hydrogen peroxide [1,2,8,9]. One of the first catalytic systems used to oxidize alkanes was the Fenton reagent, consisting of a  $Fe^{II}$  salt and  $H_2O_2$ , for which it was established that the real oxidant is the  $HO^\bullet$  radical [10]. Recent reviews deal with specific aspects of catalytic systems for the oxidation of alkanes involving transition metal ions [3,11–14]. The importance of alkane oxidation is shown by the large number of publications appearing annually on the subject, concerning a variety of catalytic systems.

A few reviews covering the recent literature on homogeneous oxidative catalysis with polyoxometalates have been

\* Corresponding author. Tel.: +351 234 370734; fax: +351 234 370084.  
E-mail address: [ana@dq.ua.pt](mailto:ana@dq.ua.pt) (A.M.V. Cavaleiro).

published [15–18]. In the particular case of alkane oxygenation only a few polyoxometalates have been studied as catalysts [2,15,16,18,19]. In 1999, we have shown that cyclohexyl hydroperoxide could be obtained in high yields from the oxidation of cyclohexane with hydrogen peroxide catalysed by some tungstophosphates, namely  $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$  [4]. The reaction took place in acetonitrile, at reflux, without need of any co-catalyst. This was, to our knowledge, the first report on the presence of cyclohexyl hydroperoxide in the products of polyoxometalate catalysed oxidation of cyclohexane. The results obtained prompted us to study the use of hydrogen peroxide, which is considered to be environmentally benign [8,9,20], in the oxidation of different cycloalkanes catalysed by a variety of polyoxotungstates.

A few reports have been published [21–23] concerning the oxidation of cyclooctane in the presence of polyoxotungstates (excluding photochemical processes), in which the main oxidation products were the corresponding ketone and alcohol. Formation of cyclooctyl hydroperoxide in the presence of polyoxotungstates was only reported in our previous paper on the oxidation of cyclooctane by  $\text{H}_2\text{O}_2$ , using borotungstates as catalysts [6]. In particular, reactions using  $[\text{BW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{6-}$  occurred with high conversion and selectivity for cyclooctyl hydroperoxide, with turnover numbers that reached 660 [6]. Other systems are known that afford cyclooctyl hydroperoxide in oxidations with  $\text{H}_2\text{O}_2$  catalysed by metal complexes [24–26], including one using a vanadium-containing molybdophosphate [27].

In the present work, we report the oxidation of cyclooctane by hydrogen peroxide, in acetonitrile, catalysed by several Keggin-type tungstophosphates or tungstosilicates, including transition metal substituted, lacunary and parent Keggin anions. A brief reference to the formation of cyclooctyl hydroperoxide in the presence of  $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$  was made before [5]. Results obtained using an excess of hydrogen peroxide and using a  $\text{H}_2\text{O}_2$ /substrate molar ratio near the stoichiometric value are described and compared. Using an excess of  $\text{H}_2\text{O}_2$ , 74% of cyclooctane conversion and 80% of selectivity for cyclooctyl hydroperoxide were obtained after 2 h of reaction with the compound  $(\text{TBA})_4[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]$  (TBA = tetrabutylammonium) and the highest selectivity for the hydroperoxide (100%) was obtained in the presence of  $(\text{TBA})_4\text{H}_4[\text{SiW}_{11}\text{O}_{39}]$ , after 9 h (55% conversion). This study, together with the previous one using related tungstoborates [6], reinforces the great potential of the Keggin-type polyoxotungstates in the homogeneous catalytic oxidation of alkanes.

## 2. Experimental

### 2.1. Reagents and methods

Acetonitrile (Panreac), 30% hydrogen peroxide (Riedel de-Häen), cyclooctane (Aldrich) and ceric sulphate (Aldrich) were used as received.

GC-MS analysis were performed using a Hewlett Packard 5890 chromatograph equipped with a mass selective detector (MSD) series II using helium as the carrier gas (35 cm/s) and a fused silica Supelco capillary column SPB-5 (30 m  $\times$  0.25 mm i.d.; 25  $\mu\text{m}$  film thickness). The chromatographic conditions were as follows: initial temperature: 80  $^\circ\text{C}$  (2 min); temperature rate: 20  $^\circ\text{C}/\text{min}$ ; final temperature: 220  $^\circ\text{C}$  (1 min); injector temperature: 250  $^\circ\text{C}$ ; detector temperature: 250  $^\circ\text{C}$ .

The total concentration of unused  $\text{H}_2\text{O}_2$  and hydroperoxide produced in solution was determined by titration using the ceric sulphate method [28]. An aliquot was accurately weighted, dissolved in diluted sulphuric acid and the peroxides titrated against 0.1N ceric sulphate solution, using ferroin as indicator. From the yields of hydroperoxide (and cyclooctanol and cyclooctanone) determined by gas chromatography, the amount of  $\text{H}_2\text{O}_2$  in solution and that used in the reaction could be determined.

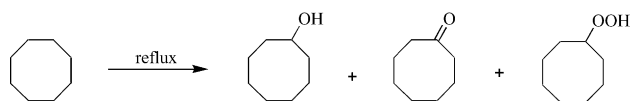
Cyclic voltammetry measurements were carried out as described previously [29]. Acetonitrile solutions (0.1 M  $\text{TBAClO}_4$ ) were prepared for TBA salts of  $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$  and  $[\text{SiW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$  (0.01 M) in the presence of 0.005 M of  $\text{H}_2\text{O}_2$ . The solutions were degassed with pure nitrogen for 5 min before use and blanketed with nitrogen gas during the voltammetric scans. The voltammetric measurements were made immediately after solution preparation and after 2 h, at room temperature, within the potential window +1000 to  $-2400$  mV, at 100 mV/s. Voltammograms were started near 1000 mV and run either in the positive or negative direction. The cathodic and anodic voltammetric peaks corresponding to the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  couples [29] were monitored.

### 2.2. Catalyst synthesis

The following compounds were prepared by known procedures:  $(\text{TBA})_3\text{PW}_{12}\text{O}_{40}$  [30],  $(\text{TBA})_4\text{SiW}_{12}\text{O}_{40}$  [30],  $(\text{TBA})_4\text{H}_3\text{PW}_{11}\text{O}_{39}$  [4],  $(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}$  [4],  $(\text{TBA})_4\text{PW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}$  [29],  $(\text{TBA})_4\text{H}_4\text{SiW}_{11}\text{O}_{39}$  [29],  $(\text{TBA})_4\text{HSiW}_{11}\text{M}^{\text{III}}(\text{H}_2\text{O})\text{O}_{39}$ , M = Fe or Mn [29],  $(\text{TBA})_4\text{PW}_{11}\text{VO}_{40}$  [31] and  $(\text{TBA})_5\text{SiW}_{11}\text{VO}_{40}\cdot 1.5\text{H}_2\text{O}$  [31]. Characterization of these compounds has been described elsewhere [4,29,32–34].

### 2.3. Oxidation procedure

The reactions were typically carried out by heating a solution of 1 mmol of cyclooctane, 1.5  $\mu\text{mol}$  of the catalyst and 30%  $\text{H}_2\text{O}_2$  in 1.5 ml of acetonitrile, at reflux. Aliquots were withdrawn from the reaction mixture and injected directly into the GC-MS. The percentage of each compound in the reaction mixture was estimated directly from the corresponding chromatographic peak areas. Aliquots were taken from reaction mixtures, at regular intervals, for peroxide determination. The cyclooctyl hydroperoxide was identified by two different methods: (a) reduction with triphenylphosphine to



give cyclooctanol [2,13] and (b) GC-MS, using previous identification of cyclooctyl hydroperoxide mass spectrum [5].

The experiments with  $[XW_{11}O_{39}]^{n-}$ ,  $X = P, Si$  and  $PW_{11}Fe(H_2O)O_{39}]^{4-}$  (molar ratio  $H_2O_2/cyclooctane = 9.8$ ) were repeated under an atmosphere of nitrogen. The results were not significantly different from those obtained in air. A few experiments were performed in the presence of iodine, a well-known radical scavenger [35]. In these cases, the oxidation of cyclooctane did not occur.

### 3. Results and discussion

The studies of the oxidation of cyclooctane by hydrogen peroxide in acetonitrile were carried out in homogeneous phase, using tetrabutylammonium salts of the heteropolyanions  $[XW_{12}O_{40}]^{n-}$  ( $XW_{12}$ ),  $[XW_{11}O_{39}]^{(n+4)-}$  ( $XW_{11}$ ),  $[XW_{11}VO_{40}]^{m-}$  ( $XW_{11}V$ ),  $[XW_{11}M^{III}(H_2O)O_{39}]^{p-}$  ( $XW_{11}M$ ), where  $X = P$  or  $Si$  and  $M = Fe$  or  $Mn$ . Under the conditions used, three oxidation products were found (Scheme 1).

Results obtained in the cyclooctane catalytic oxidation with excess hydrogen peroxide (molar ratio  $H_2O_2/cyclooctane = 9.8$ ), including selectivity and turnover numbers, are summarized in Table 1. All the used salts catalysed the oxidation of cyclooctane with conversion between 49 and 96% after 9 h (conversion for both  $PW_{11}Fe$  and  $SiW_{11}Fe$  were approximately 96%, Fig. 1). Several catalysts originated 100% conversion after 12 h ( $PW_{11}Fe$ ,  $SiW_{11}Fe$ , and  $PW_{11}$ ). In the absence of the polyoxotungstates the oxidation of cyclooctane did not occur.

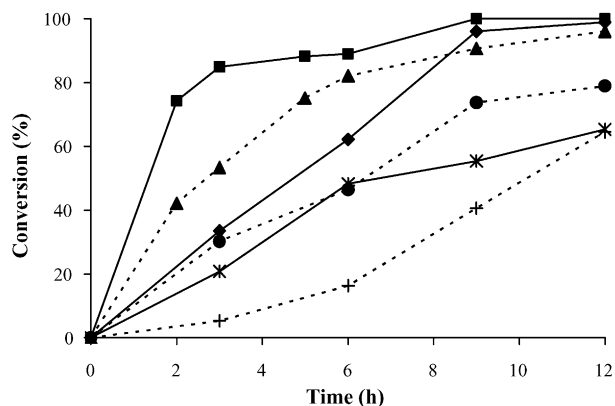


Fig. 1. Time course of cyclooctane oxidation in the presence of  $PW_{11}Fe$  [ $\blacksquare$ ] 9.8 mmol  $H_2O_2$ ; ( $\blacktriangle$ ) 2.0 mmol  $H_2O_2$ ],  $SiW_{11}Fe$  [ $\blacklozenge$ ] 9.8 mmol  $H_2O_2$ ; ( $\bullet$ ) 2.0 mmol  $H_2O_2$ ] and  $SiW_{11}$  [ $\times$ ] 9.8 mmol  $H_2O_2$ ; (+) 2.0 mmol  $H_2O_2$ ]. Substrate: 1 mmol; catalyst: 1.5  $\mu$ mol; acetonitrile: 1.5 ml; temperature: reflux.

Comparing the performance of the different salts at different reaction times, it could be seen that the highest conversion was always observed in the presence of  $PW_{11}Fe$  (Fig. 1). In fact, the results obtained with this catalyst were quite remarkable, as 74% of cyclooctane conversion and 80% of selectivity for cyclooctyl hydroperoxide were produced after 2 h of reaction.

Reactions performed with 9.8 mmol of oxidant *per* mmol of substrate afforded mainly cyclooctyl hydroperoxide and cyclooctanone as products after 9 h. The former was always the major product, reaching 100% in the case of  $SiW_{11}$  as catalyst (Table 1). In these conditions no cyclooctanol was detected, except in the presence of the  $SiW_{11}V$  and  $SiW_{11}Fe$ . Although tungstosilicates showed to be less active than tungstophosphates they were more selective to the cyclooctyl hydroperoxide.

Results obtained with the molar ratio  $H_2O_2/cyclooctane$  equal to 2.0 are presented in Table 2. Conversions after 9 h

Table 1  
Oxidation of cyclooctane with 9.8 mmol of  $H_2O_2$  catalyzed by several polyoxotungstates at 80 °C, after 9 h of reaction<sup>a</sup>

| Catalyst     | Conversion <sup>b,c</sup> (%) | Turnover number <sup>d</sup> | $H_2O_2$ used (%) | Selectivity (%) <sup>b</sup> |               |                |
|--------------|-------------------------------|------------------------------|-------------------|------------------------------|---------------|----------------|
|              |                               |                              |                   | $C_8H_{14}O$                 | $C_8H_{15}OH$ | $C_8H_{15}OOH$ |
| $PW_{12}$    | 70 (71)                       | 469                          | 44                | 37                           | 0             | 63             |
| $SiW_{12}$   | 49 (57)                       | 329                          | 29                | 19                           | 0             | 81             |
| $PW_{11}$    | 74 (100)                      | 497                          | 26                | 37                           | 0             | 63             |
| $SiW_{11}$   | 55 (65)                       | 369                          | 66                | 0                            | 0             | 100            |
| $PW_{11}Fe$  | 89 <sup>e</sup> (100)         | 593                          | 97                | 26                           | 0             | 74             |
| $SiW_{11}Fe$ | 62 <sup>e</sup> (100)         | 414                          | 62                | 30                           | 8             | 62             |
| $PW_{11}Mn$  | 70 (75)                       | 465                          | 43                | 22                           | 0             | 78             |
| $SiW_{11}Mn$ | 70 (79)                       | 464                          | 74                | 13                           | 0             | 87             |
| $PW_{11}V$   | 87 (94)                       | 580                          | 99                | 23                           | 0             | 77             |
| $SiW_{11}V$  | 69 (70)                       | 460                          | 38                | 14                           | 10            | 76             |
| No catalyst  | –                             | –                            | –                 | –                            | –             | –              |

<sup>a</sup> Reaction conditions: catalyst, 1.5  $\mu$ mol; solvent,  $CH_3CN$  (1.5 ml); cyclooctane, 1 mmol.

<sup>b</sup> Based on the gas chromatographic peak areas.

<sup>c</sup> The values in parentheses correspond to the conversion after 12 h.

<sup>d</sup> Mol of total products/mol of catalyst used.

<sup>e</sup> Results obtained after 6 h.

Table 2

Oxidation of cyclooctane with 2.0 mmol of H<sub>2</sub>O<sub>2</sub> catalyzed by several polyoxotungstates at 80 °C, after 9 h of reaction<sup>a</sup>

| Catalyst             | Conversion <sup>b,c</sup> (%) | Turnover number <sup>d</sup> | H <sub>2</sub> O <sub>2</sub> used (%) | Selectivity (%) <sup>b</sup>     |                                   |                                    |
|----------------------|-------------------------------|------------------------------|--|----------------------------------|-----------------------------------|------------------------------------|
|                      |                               |                              |  | C <sub>8</sub> H <sub>14</sub> O | C <sub>8</sub> H <sub>15</sub> OH | C <sub>8</sub> H <sub>15</sub> OOH |
| PW <sub>12</sub>     | 34 (49)                       | 227                          | 36                                     | 49                               | 10                                | 41                                 |
| SiW <sub>12</sub>    | 34 (67)                       | 227                          | 36                                     | 37                               | 11                                | 52                                 |
| PW <sub>11</sub>     | 44 (79)                       | 293                          | 50                                     | 42                               | 8                                 | 50                                 |
| SiW <sub>11</sub>    | 41 (66)                       | 273                          | 48                                     | 35                               | 6                                 | 59                                 |
| PW <sub>11</sub> Fe  | 75 <sup>e</sup> (96)          | 500                          | 100                                    | 37                               | 6                                 | 57                                 |
| SiW <sub>11</sub> Fe | 46 <sup>e</sup> (79)          | 307                          | 93                                     | 39                               | 9                                 | 52                                 |
| PW <sub>11</sub> Mn  | 67 (89)                       | 447                          | 82                                     | 53                               | 10                                | 37                                 |
| SiW <sub>11</sub> Mn | 66 (89)                       | 440                          | 91                                     | 60                               | 14                                | 26                                 |
| PW <sub>11</sub> V   | 26 (87)                       | 173                          | 58                                     | 46                               | 13                                | 41                                 |
| SiW <sub>11</sub> V  | 13 (53)                       | 87                           | 48                                     | 41                               | 11                                | 48                                 |
| No catalyst          | –                             | –                            | –                                      | –                                | –                                 | –                                  |

<sup>a</sup> Reaction conditions: catalyst, 1.5 μmol; solvent, CH<sub>3</sub>CN (1.5 ml); cyclooctane, 1 mmol.<sup>b</sup> Based on the gas chromatographic peak areas.<sup>c</sup> The values in parentheses correspond to the conversion after 12 h.<sup>d</sup> Mol of total products/mol of catalyst used.<sup>e</sup> Results obtained after 6 h.

were generally lower when compared with those in Table 1, with the highest values obtained in the presence of PW<sub>11</sub>Fe (Fig. 1). The main products were again cyclooctyl hydroperoxide and cyclooctanone. Cyclooctanol was always detected in the products in low yields during the course of the reactions. The ratio cyclooctyl hydroperoxide/cyclooctanone, calculated after 9 h of reaction, varied between 0.4 and 1.7, being smaller than 1 for reactions with PW<sub>12</sub>, PW<sub>11</sub>V, PW<sub>11</sub>Mn and SiW<sub>11</sub>Mn. Under these conditions, the lowest selectivity for the hydroperoxide was observed for the XW<sub>11</sub>Mn polyoxoanions and the highest selectivity for SiW<sub>11</sub>.

The comparison between the results obtained with 2.0 and 9.8 mmol of H<sub>2</sub>O<sub>2</sub> per mol of substrate (Tables 1 and 2) indicates that, in most cases, an improvement in the selectivity for cyclooctyl hydroperoxide occurred when a larger amount of oxidant was used (Fig. 2).

Fig. 3 represents the yield of all products during cyclooctane oxidation in the presence of PW<sub>11</sub>Fe. The yield of cyclooctyl hydroperoxide decreased after 6 h of reaction, and the yield of cyclooctanone was simultaneously raised. In re-

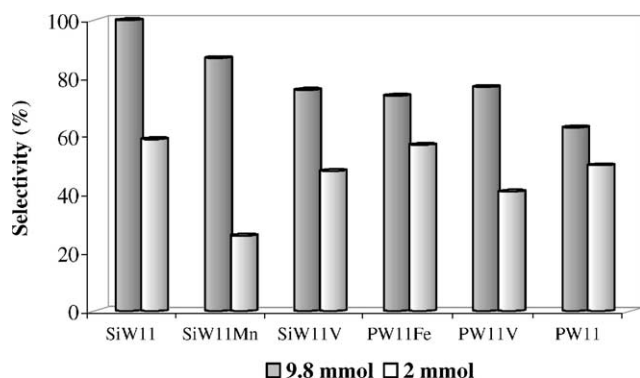


Fig. 2. Selectivity for cyclooctyl hydroperoxide formation with 2.0 or 9.8 mmol of H<sub>2</sub>O<sub>2</sub> after 9 h in cyclooctane oxidation reactions. Substrate: 1 mmol; catalyst: 1.5 μmol; acetonitrile: 1.5 ml; temperature: reflux.

actions with excess hydrogen peroxide, a decrease of cyclooctyl hydroperoxide yield was also observed (but only after 9 h of reaction) for all catalysts except PW<sub>11</sub>, SiW<sub>11</sub> and SiW<sub>11</sub>Fe. Thus, the results reported in Table 1 for most catalysts correspond to conditions in which the yields of cyclooctyl hydroperoxide are at their maximum. In certain cases (PW<sub>11</sub>Mn, PW<sub>11</sub>V, SiW<sub>11</sub>Mn), cyclooctanol was detected in the products after 12 h. When 2.0 mmol of H<sub>2</sub>O<sub>2</sub> per mol of substrate were used, the lowering of the yield of cyclooctyl hydroperoxide, as shown in Fig. 3, was not observed for most catalysts. The decreasing of the yield of cyclooctyl hydroperoxide, with simultaneous increases of the yields of cyclooctanone or of this compound and cyclooctanol have been reported previously [22,36,37].

The concentration of H<sub>2</sub>O<sub>2</sub> in solution was monitored during the course of reactions. For reactions with excess H<sub>2</sub>O<sub>2</sub>, in the presence of PW<sub>11</sub>Fe, fairly rapid decomposition of H<sub>2</sub>O<sub>2</sub> accompanied the oxidative reaction (Fig. 4a). For anions like SiW<sub>11</sub>, the decomposition of unused H<sub>2</sub>O<sub>2</sub> was also complete after 12 h, but the oxidant vanished from solution more slowly than in the case of the iron anion. In all cases the catalysts favoured the decomposition of hydrogen peroxide,

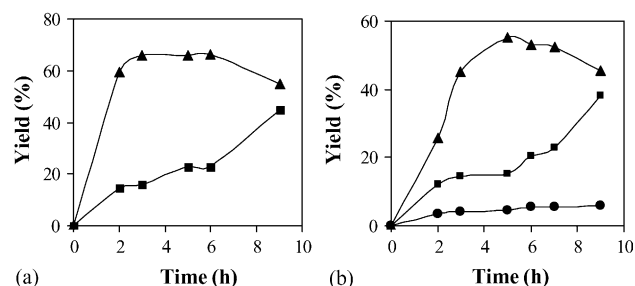


Fig. 3. Yield of all the products during cyclooctane oxidation in the presence of PW<sub>11</sub>Fe with (a) 9.8 mmol and (b) 2.0 mmol of H<sub>2</sub>O<sub>2</sub>; (▲): cyclooctyl hydroperoxide; (■): cyclooctanone; (●): cyclooctanol. Substrate: 1 mmol; catalyst: 1.5 μmol; acetonitrile: 1.5 ml; temperature: reflux.

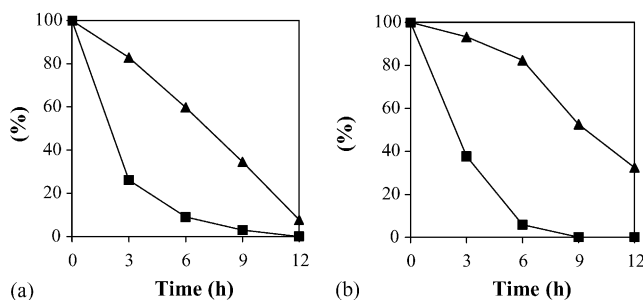


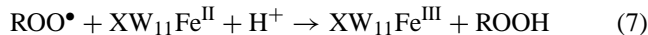
Fig. 4. Fraction of the initial H<sub>2</sub>O<sub>2</sub> present in solution during the cyclooctane oxidation in the presence of (a) 9.8 mmol H<sub>2</sub>O<sub>2</sub> and (b) 2.0 mmol H<sub>2</sub>O<sub>2</sub> [PW<sub>11</sub>Fe (■) and SiW<sub>11</sub> (▲)]. Substrate: 1 mmol; catalyst: 1.5 μmol; acetonitrile: 1.5 ml; temperature: reflux.

which in their absence is only about 33% after 12 h. For reactions performed with H<sub>2</sub>O<sub>2</sub>/cyclooctane = 2.0 the amount of H<sub>2</sub>O<sub>2</sub> in solution also decreased more rapidly in the presence of PW<sub>11</sub>Fe than of SiW<sub>11</sub> (Fig. 4b) but the decomposition of H<sub>2</sub>O<sub>2</sub> was not so extensive. In this case, after 9 h, between 15 and 35% of the initial H<sub>2</sub>O<sub>2</sub> was decomposed in the presence of the metal substituted anions and 4–8% in the presence of XW<sub>12</sub> or XW<sub>11</sub>.

By comparing the cyclooctane oxidation after 12 h of reaction, in the presence of 2.0 and 9.8 mmol of H<sub>2</sub>O<sub>2</sub>, in some cases, like for the SiW<sub>11</sub> and PW<sub>11</sub>Fe catalysts, nearly the same conversions were achieved. This means that the system using 2.0 mmol of H<sub>2</sub>O<sub>2</sub> per mmol of substrate is more efficient than the system with 9.8 mmol. In fact, the efficiency of use of H<sub>2</sub>O<sub>2</sub> is higher than 90% for SiW<sub>11</sub> when 2.0 mmol were used, against 10% of efficiency in the case of 9.8 mmol added. In the case of PW<sub>11</sub>Fe, nearly 70% of efficiency was registered for the use of H<sub>2</sub>O<sub>2</sub> (2.0 mmol) against 14% when 9.8 mmol were used. The only advantage of using a higher concentration of H<sub>2</sub>O<sub>2</sub> seemed to be the higher selectivity observed for the formation of cyclooctyl hydroperoxide.

Taking into account the results described in this work, it is clear that, even if the reaction mechanisms are radical in nature, the details must vary, depending on the catalyst and reaction conditions. This is the result of the existence of several possible concurrent reactions, namely, the hydroperoxidation or hydroxylation of cyclooctane, the decomposition of cyclooctyl hydroperoxide and the dismutation of H<sub>2</sub>O<sub>2</sub>, catalysed by metals like Fe or Mn. Also, in view of the results obtained with XW<sub>11</sub> and XW<sub>12</sub> anions, it is highly probable that in the presence of XW<sub>11</sub>M anions activation of H<sub>2</sub>O<sub>2</sub> may occur simultaneously at W and M.

When excess of H<sub>2</sub>O<sub>2</sub> was used, extensive hydroperoxidation was obtained. In the presence of the iron catalysts, it was assumed that the formation of hydroperoxide occurred by a Fe(III) initiated generation of HO• [9], as described recently for several iron complexes in acetonitrile [19] and resumed in Eqs. (1)–(7) (R = C<sub>8</sub>H<sub>15</sub>).



Eqs. (1) and (2) account for the reduction of iron (III) in the polyoxometalates in the presence of H<sub>2</sub>O<sub>2</sub> in acetonitrile [9,38,39]. This reduction was confirmed in this work by cyclic voltammetry for SiW<sub>11</sub>Fe and PW<sub>11</sub>Fe. This reaction does not occur in aqueous solution [40]. This result parallels that reported by Paczesniak and Sobkowiak for Fe(ClO<sub>4</sub>)<sub>3</sub> [41]. The molecular oxygen necessary to obtain ROO• (Eq. (5)) may possibly be originated, at least partially, in situ from H<sub>2</sub>O<sub>2</sub> (e.g., from Eq. (2) and from HOO• dismutation [9]). Others have suggested that some systems with excess H<sub>2</sub>O<sub>2</sub>, involving iron complexes, can produce their own O<sub>2</sub>-atmosphere [12,42]. This would explain why the yield of hydroperoxide was higher when an excess of hydrogen peroxide was used, and would agree with the fact that when some reactions (molar ratio H<sub>2</sub>O<sub>2</sub>/cyclooctane = 9.8) were performed under N<sub>2</sub> the same catalytic results were obtained. Formation of cyclooctanol and cyclooctanone may be explained considering also other reactions of the Fenton's process [9,12].

A similar mechanism could possibly explain the results obtained with other catalysts. The generation of HO• and HOO• in the presence of a vanadomolybdophosphate was recently proposed [27]. In this case, the first step was assumed to be the coordination of a hydrogen peroxide molecule to V(V), followed by the formation of a V(IV) polyoxometalate and HOO•. The HO• radicals were then generated by a reaction similar to that of Eq. (3), with reoxidation of vanadium.

In the case of the XW<sub>11</sub> and XW<sub>12</sub> anions, where no other metal but tungsten exists, the activation of H<sub>2</sub>O<sub>2</sub> could possibly occur at the W atoms through a sequence of reaction similar to that described for vanadium polyoxomolybdates [27]. The formation of peroxide (or hydroperoxide) complexes with the Keggin or related structures having the peroxo group coordinated to W has been assumed before to explain catalytic results [43–46]. These type of complexes has rarely been structurally characterized [47]. Formation of peroxotungstocomplexes from reaction of PW<sub>11</sub> and PW<sub>12</sub> with H<sub>2</sub>O<sub>2</sub> cannot be excluded [9,16], but those species have not yet been described as radical generators. Further studies are certainly needed to clarify the reaction mechanisms in the presence of this group of polyoxotungstates.

Comparing the catalytic results presented in this work with a few studies known for the cyclooctane oxidation in homogeneous, non-photochemical, systems with polyoxotungstates, higher turnovers numbers were obtained in the presence of all catalysts reported here than when the anions [PW<sub>11</sub>Co(H<sub>2</sub>O)O<sub>39</sub>]<sup>5-</sup> [21,22] and [Mn<sub>2</sub>ZnW(ZnW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>12-</sup> [23] were used. Moreover, the

formation of cyclooctyl hydroperoxide was not described in those reports. As far as we know, Shul'pin and co-workers were the only researchers to report the formation of cyclooctyl hydroperoxide when using  $\text{H}_2\text{O}_2$  as oxidant [24,25,27,36], namely with vanadium containing phosphomolybdates as catalysts [27].

Recently, our group reported the oxidation of cyclooctane with  $\text{H}_2\text{O}_2$  using several borotungstates as catalysts [6]. The turnover numbers and the selectivity obtained for cyclooctyl hydroperoxide with  $\text{PW}_{11}\text{Fe}$ , in this work, are quite similar to those with  $\text{BW}_{11}\text{Fe}$  [6]. However, the tungstosilicate catalysts showed higher selectivity for cyclooctyl hydroperoxide, when compared with tungstoborates and tungstophosphates. This is well illustrated by the system using 9.8 mmol of  $\text{H}_2\text{O}_2$  per mmol of substrate in the presence of  $\text{SiW}_{11}$ , which reached 100% selectivity for cyclooctyl hydroperoxide.

#### 4. Conclusion

The Keggin-type tungstophosphates and tungstosilicates studied in this work proved to be active catalysts for the oxidation of cyclooctane with hydrogen peroxide, using acetonitrile as the solvent, at reflux. With this system, high conversion (between 49 and 96%, after 9 h, when excess  $\text{H}_2\text{O}_2$  was used) and turnover numbers were obtained. The products of oxidation were cyclooctanone, cyclooctyl hydroperoxide and cyclooctanol (this was never above 15% of the total products obtained and was even not detected in some reactions). No co-catalysts were necessary.

High selectivity for cyclooctyl hydroperoxide accompanied reactions performed with excess of hydrogen peroxide ( $\text{H}_2\text{O}_2/\text{cyclooctane} = 9.8$ ). In general, in this condition, tungstosilicates showed to be less active than tungstophosphates but presented higher selectivity for cyclooctyl hydroperoxide. Thus, in the presence of  $\text{PW}_{11}\text{Fe}$ , 74% of cyclooctane conversion and 80% of selectivity for cyclooctyl hydroperoxide were obtained, after 2 h of reaction and with  $\text{SiW}_{11}$ , the results were 100% of cyclooctyl hydroperoxide and 55% conversion after 9 h.

The outcome of the reactions with different catalysts certainly reflects the different structure (namely the presence or absence of first row transition metals) and stability of the anions. Some of the used tungstophosphates may decompose in the presence of  $\text{H}_2\text{O}_2$  [16]. Nevertheless, the overall results obtained do not distinguish clearly this possibility. The study of the stability of the different catalysts in acetonitrile will be presented elsewhere.

Two additional interesting points may be stressed after analysis of the obtained results. One is related to the use of tungstosilicates as oxidative catalysts. Tungstosilicates are generally much less used than tungstophosphates in oxidative catalysis [15,16], but the results here presented indicate the possibility of using them as selective agents in the preparation of hydroperoxides. The second remark is about the fact that

the catalytic action of Keggin-type polyoxotungstates in the oxidation of alkanes seems not to depend only on the presence of a substituting transition metal, as fairly good results were obtained with lacunary or parent anions. Similar results were observed in our study with tungstoborates [6].

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