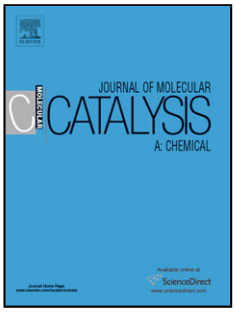

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Catalytic homogeneous oxidation of monoterpenes and cyclooctene with hydrogen peroxide in the presence of sandwich-type tungstophosphates $[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, M = Co^{II}, Mn^{II} and Fe^{III}

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Dedicated to Professor Georgiy B. Shul'pin on the occasion of his 70th birthday

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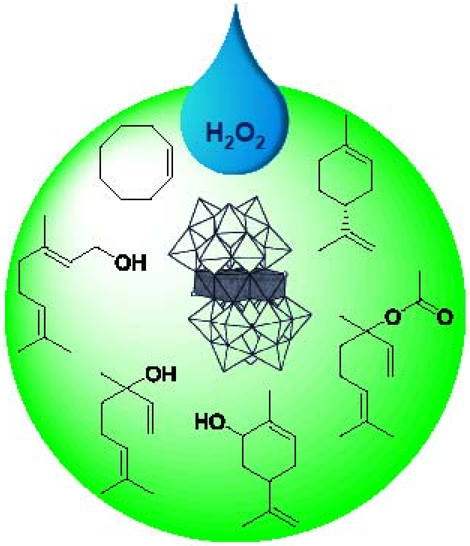
Graphical abstract



Highlights:

- Sandwich-type B-α-$[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$ (M = Co^{II}, Mn^{II}, Fe^{III}) polyoxometalates
- Oxidation of limonene, geraniol, linalool, carveol, and cyclooctene
- Oxidation with 30% (w/w) aqueous hydrogen peroxide, in acetonitrile
- The main/unique oxidation pathway for terpenoids and cyclooctene is epoxidation

Abstract

Catalytic efficiency of tetrabutylammonium salts of sandwich tungstophosphates B-α-$[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, M = Co^{II}, Mn^{II}, Fe^{III}, was studied in the oxidation of (*R*)-(+)-limonene, geraniol, linalool, linalyl acetate, carveol, and *cis*-cyclooctene with hydrogen peroxide, in acetonitrile. Oxidation of (*R*)-(+)-limonene gave limonene-1,2-diol as main product. Epoxidation of linalool takes place preferentially at the more substituted 6,7-double bond, the corresponding 6,7-epoxide reacting further, yielding furano- and pyrano-oxides, via intramolecular cyclization. Oxidation of linalyl acetate occurred preferentially at the more substituted 6,7-double bond for $Mn_4(PW_9)_2$, affording 6,7-epoxide at 82% selectivity. Linalyl acetate 1,2-epoxide was the major product with 51% and 77% selectivity for $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$, respectively. Oxidation of carveol occurred with very good conversions in the presence of $Mn_4(PW_9)_2$, $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$, yielding carvone and carveol 1,2-epoxide in similar amounts. Oxidation of *cis*-cyclooctene gave only the epoxide, while oxidation of geraniol at room temperature afforded 2,3-epoxygeraniol as the major product.

Keywords: sandwich-type polyoxometalates, monoterpenes, cyclooctene, oxidation

1. Introduction

Sandwich-type tungstophosphates having the general formula B-α-$[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, where M = 1st row transition metal, such as Mn, Fe, Co, Ni, Cu or Zn, have a molecular structure based on the linkage of two tri-lacunary Keggin sub-units B-α-$[PW_9O_{34}]^{9-}$ by a belt of four divalent metal ions (Fig. 1) [1-4]. The same structural unit is found for B-α-$[Fe_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ [5] or B-α-$[Mn_4(H_2O)_2(PW_9O_{34})_2]^{9-}$ and B-α-$[Mn_4(OH)_2(PW_9O_{34})_2]^{9-}$ [6], with trivalent Fe or mixed $Mn^{II}Mn^{III}$ belts, respectively. The presence of four 1st row transition metal centres in the belt of these anions [abbreviated as $M_4(PW_9)_2$] can be viewed as an advantage for their use in oxidative catalysis of organic compounds, when compared to other polyoxometalates (POMs) such as the transition metal monosubstituted Keggin-type anions. Hence, a number of reports have been published describing the use of some of these polyoxometalates as catalysts, namely in the oxidation with hydrogen peroxide of alkenes, alkanes and terpenes [5,7-17]. Examples of studies with other oxidants [18-19] or substrates [20-22] are also found.

Cyclooctene and cyclohexene are often used as model compounds to evaluate the possible use of a catalyst in alkene oxidation. Several polyoxometalates have already been used in the oxidation of *cis*-cyclooctene with H_2O_2, under homogeneous conditions, namely the sandwich $[M(PW_{11}O_{39})_2]^{10-}$ (M = Zr, Hf) [23], manganese containing POMs [24-26], sandwich-type tungstozincates $[WZnM_2(ZnW_9O_{34})_2]^{12-}$, M = Mn, Zn [27,28] and others [29,30]. A very recent paper describes the oxidation of these cycloalkenes with H_2O_2 in acetonitrile in the presence of the $M_4(PW_9)_2$ anions, with M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, and Zn^{II} [17]. Previous studies on the oxidation of *cis*-cyclooctene and/or cyclohexene by H_2O_2 in CH_3CN used the iron sandwich complexes, $[Fe^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [7] and $[Fe^{III}_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ [5], as well as the anion with M = Cu^{II} [11]. Also, $[Mn^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Co^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ were used in oxidations with iodosylbenzene [18] and *tert*-butylhydroperoxide + O_2 [19], respectively.

Limonene, geraniol, linalool and carveol are important natural compounds, which can be found in the essential oils of several plants [31,32]. These compounds, along with other monoterpenes, can be used as a source of epoxides, often starting materials for the synthesis of fragrances, flavours and therapeutically active substances [33,34]. A few recent reports are available concerning the use of $M_4(PW_9)_2$ polyoxometalates for the oxidation of geraniol or limonene with hydrogen peroxide in homogeneous and heterogeneous conditions, using acetonitrile as solvent [12,14,15]. In these studies, the heteropolyanions with M = Fe^{III} or Co^{II} were used. The oxidation of limonene with H_2O_2/1,2-dichloroethane in a biphasic media was also reported, for anions with M^{II} = Co, Zn, Cu, Mn [9,13]. Contrastingly, we could not find reports on the use of the $M_4(PW_9)_2$ anions in the oxidation of linalool or carveol.

The $M_4(PW_9)_2$ heteropolyanions have an M/W molar ratio higher than many metal substituted polyoxotungstates used as catalysts in oxidative catalysis, like the monosubstituted Keggin or Dawson anions or other sandwich-type polyoxometalates, such as the tungstozincates $[WZnM_2(ZnW_9O_{34})_2]^{12-}$, M = Mn^{II}, Zn^{II}, and others [8,27-29,35,36], what makes them interesting candidates for their application as catalysts in oxidative reactions. Following our previous experience in the use of the monosubstituted Keggin anions in oxidative catalysis with H_2O_2 in acetonitrile [15,24-26,36-39] and a few reported works with some $M_4(PW_9)_2$ anions [10-12,14,15], in the present work are presented the results of the use of the tetrabutylammonium (TBA) salts of sandwich-type tungstophosphate anions, $[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$, M = Co^{II}, Mn^{II} (n = 10) and Fe^{III} (n = 6), in the oxidation with hydrogen peroxide of some monoterpenes [(*R*)-(+)-limonene, geraniol, linalool, linalyl acetate, carveol] and cyclooctene.

2. Experimental section

2.1 Catalysts synthesis and reagents

$[(C_4H_9)_4N]_7H_3[Co_4^{II}(H_2O)_2(PW_9O_{34})_2]$, $[(C_4H_9)_4N]_7H_3[Mn_4^{II}(H_2O)_2(PW_9O_{34})_2]$

and $[(C_4H_9)_4N]_6[Fe_4^{III}(H_2O)_2(PW_9O_{34})_2]\cdot 4H_2O$ were synthesised as previously described [10,12,40]. Analytical and spectroscopic data were in agreement with those previously published [5,10,40]. All the reagents were of analytical grade and used as purchased.

2.2 Oxidation reactions with hydrogen peroxide

The reactions were typically carried out in air at 80ºC (except when indicated), in a stirred solution of the substrate (sub), catalyst (cat) and 30% (w/w) aqueous hydrogen peroxide (ox) in acetonitrile. The oxidation of geraniol was always carried out in the dark at room temperature. The amounts of the several components used in the reactions were dependent on the substrate and are presented in the results and discussion section.

The conversion and percentages of each compound in the reaction mixtures were determined by gas chromatography. Aliquots were withdrawn from the reaction mixture and injected directly into the GC-FID or GC-MS apparatus (both equipped with a fused silica capillary 5% phenyl 95% dimethylpolysiloxane column with 30 m × 0.25 mm i.d. and 0.25 μm film thickness) using helium as the carrier gas (35 cm/s). The chromatographic conditions for geraniol, limonene, linalool, carveol, and linalyl acetate were: initial temperature: 100ºC; temperature rate: 5ºC/min; final temperature: 220ºC (2 min); injector temperature: 250ºC; detector temperature: 250ºC; for cyclooctene: initial temperature: 80ºC (2 min); temperature rate: 20ºC/min; final temperature: 200ºC (2 min); injector temperature: 220ºC; detector temperature: 220ºC.

Blank reactions: a) with H_2O_2 but without catalyst; b) with catalyst but without H_2O_2 were performed for the conditions studied. Conversion values attained in the blank reactions were in the range of 0 - 7%.

The assessment of the stability of catalysts was performed as follows: a drop of the reaction mixture was dried on a KBr pellet and the infrared spectrum measured. These experiments were performed in the oxidation of cyclooctene (ox/cat = 600), and of geraniol (ox/cat = 1500).

2.3 Instrumentation and methods

Electronic absorption and FTIR spectra, C, H, N elemental analysis and thermogravimetric analyses were obtained as previously described [26,41]. The reaction products were identified by GC-MS, based on the mass spectra interpretation and by comparison with the library of the equipment.

3. Results and discussion

The oxidation of the monoterpenes (*R*)-(+)-limonene, geraniol, linalool, linalyl acetate, and carveol, and of cyclooctene in the presence of the Mn-, Co- or Fe-containing sandwich polyoxotungstates was studied with 30% (w/w) aqueous hydrogen peroxide as oxidant.

3.1. Oxidation of (R)-(+)-limonene

(*R*)-(+)-Limonene (**1**) is a monoterpene with a exocyclic and an endocyclic double bond. The oxidation occurred at these double bonds and at the allylic position of the six member ring, although with different selectivities, as summarized in Scheme 1 and Table 1.

The (*R*)-(+)-limonene oxidation with H_2O_2 in the presence of sandwich-type anions was performed at 80ºC using sub/cat = 333 and ox/sub = 2. After 2 h of reaction, the best conversions were obtained with $Fe_4(PW_9)_2$ (89%) and $Co_4(PW_9)_2$ (86%), followed by $Mn_4(PW_9)_2$ with 68% conversion. Conversion increased slowly up to 7 hours of reaction, reaching 98% and 94% with $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$, respectively. Typically, five products were observed (Scheme 1). The reactions seem to indicate that epoxidation at the cyclohexene double bond is the main pathway, since the selectivity for limonene 1,2-epoxide (**2**) and limonene glycol (limonene-1,2-diol, **3**) together varies between 56% and 73%. Moreover, diol **3** was obtained as the main product for all the catalysts, with selectivity between 50-62%. The limonene diepoxide (**4**) was the second most abundant product formed for $Fe_4(PW_9)_2$ (30% selectivity) and $Co_4(PW_9)_2$ (20% selectivity), while for $Mn_4(PW_9)_2$ the amount of **4** paralleled the amount of limonene 1,2-epoxide (**2**). The opening of the epoxide ring of **2** is possibly the reason for the predominance of diol **3**. Carveol (**5**) and carvone (**6**), resulting from allylic oxidation at the six member ring, were obtained as minor products. In comparison with results previously published, obtained in comparable conditions, but with a higher ox/sub molar ratio [15], it was found that lowering the ox/sub molar ratio to 2 did not affect the conversion obtained.

3.2. Oxidation of monoterpenoid allylic alcohols (geraniol, linalool, carveol)

Geraniol (**7**) and linalool (**9**) are isomeric acyclic monoterpenoid allylic alcohols with two C-C double bonds with different reactivity. Geraniol was oxidized with H_2O_2 at room temperature, whereas linalool needed higher temperatures. The results obtained for the catalytic oxidation of these compounds are summarized in Table 2.

The results presented here for the oxidation of geraniol (**7**) in the presence of the Co and Fe sandwich-type catalysts are comparable to those already found in the literature [12,15]; however, to our knowledge, no studies using the $Mn_4(PW_9)_2$ anion had been published so far. The Mn, Co, and Fe heteropolyanions, under the conditions used here, showed analogous performance; moreover, the 97% conversion for the cobalt heteropolyanion and the 94% selectivity for 2,3-epoxide (**8**) are very interesting, since were obtained with less amount of oxidant than those previously published [15]. In fact, the main product was always 2,3-epoxygeraniol (**8**), obtained with more than 99% of selectivity for $Fe_4(PW_9)_2$ or $Mn_4(PW_9)_2$ (Table 2). It should be noted that a very small decrease in 2,3-epoxide (**8**) selectivity was observed for all the catalysts, as the reaction proceeds. Actually, after 3 hours of reaction the selectivity for **8** was always 100% [at 44% of conversion for $Mn_4(PW_9)_2$, 58% for $Co_4(PW_9)_2$, and 65% for $Fe_4(PW_9)_2$] although lowering into 94% selectivity after 5 hours with $Co_4(PW_9)_2$ only. The selective formation of 2,3-epoxygeraniol (**8**) as the major product is commonly observed in studies with related sandwich-type POMs [11,28,42] or transition metal substituted Keggin-type anions [12,15,36,38,43].

The epoxidation of linalool (**9**) takes place preferentially at the more substituted 6,7-double bond, but the corresponding non-allylic 6,7-epoxide (**9a**) reacts further, yielding the furano- and pyrano-oxides (**10**) and (**11**) (Schemes 3 and 4), in a relative molar ratio furano/pyrano ring of 1.8-2.5 after 5 h of reaction, via an intramolecular cyclization [44,45].

According to Hutchings [45], the furano-oxide is the kinetically favoured product. Moreover, the formation of 5-membered heterocycles is known to be preferred over 6-membered heterocycles, although the 6-membered ring has the lower strain energy [45]. No preferential allylic-hydroxyl assisted epoxidation of linalool (**9**) seems to occur under the present reaction conditions. This may be due to the steric situation around the hydroxyl group, hindering the formation of (**9b**). Moreover, linalool diepoxide (**12**) was formed in minor amounts, probably by over-epoxidation of (**9a**). Reactions performed at 80ºC lead to higher conversions [91%, 81%, and 60% for $Fe_4(PW_9)_2$, $Mn_4(PW_9)_2$, and $Co_4(PW_9)_2$, respectively] than those at 60ºC (43%, 48%, and 23% for $Fe_4(PW_9)_2$, $Mn_4(PW_9)_2$, and $Co_4(PW_9)_2$, respectively). So far, to our knowledge, no studies on the oxidation of linalool with H_2O_2, using POMs as catalysts, were published. Yet, there are reports on the oxidation of linalool catalysed by peroxotungstophosphates [44,46] or a peroxotungstoborate [46].

The oxidation of linalyl acetate (**13**) occurred preferentially at the more substituted 6,7-double bond only for $Mn_4(PW_9)_2$, thus affording the 6,7-epoxide (**14**) at 82% selectivity. The other products were 1,2-epoxide (**15**) and aldehyde (**16**) resulting from the cleavage of the 6,7-double bond. Interestingly, the selectivity changed enormously when $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$ were used instead. Actually, **15** was the major product with 51% and 77% selectivity with $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$, respectively. Aldehyde (**16**) was formed as the second most abundant product for $Fe_4(PW_9)_2$, since only 1% of **14** was registered. Since the rearrangement of the 6,7-epoxide (**14**) cannot occur here, due to the protection of the hydroxyl group of linalool by the acetate group, maybe 6,7-epoxide (**14**) is an intermediate for the formation of **16**, as observed earlier for other olefins [39,47].

The oxidation of carveol (**5**) with hydrogen peroxide occurred with excellent conversions in the presence of the Mn, Co, and Fe heteropolyanions (Table 2), yielding carvone (**6**) and 1,2-epoxide (**17**) in similar amounts after 3 hours of reaction at 80ºC. The 8,9-epoxide (**18**) was always a minor product. Carveol (**5**) and carvone (**6**) were observed as minor products in the allylic oxidation of limonene (**1**) (Table 1), the ketone **6** probably resulting from the oxidation of **5**, whereas epoxides **17** and **18**, resulting from the epoxidation of **5**, were not detected in the oxidation of limonene (**1**). Moreover, the epoxide ring opening of **17** was not observed (contrarily to what happens with limonene, where **2** gives rise to large amounts of **3**, consequently the putative triol was not formed under the present conditions. The less substituted C_8-C_9 double bond seems to be less reactive for epoxidation than the endocyclic C_1-C_2 double bond, and the presence of the hydroxyl group in the allylic position seems to favour the epoxidation at C_1-C_2, as happened for geraniol.

3.3. Oxidation of cis-cyclooctene

Since limonene (**1**) gave rise to somewhat high percentages of allylic oxidation resulting products, **5** and **6**, and in order to assess the selectivity of the present system for epoxidation, relatively to allylic oxidation, the oxidation of *cis*-cyclooctene with hydrogen peroxide was also studied in the presence of $Mn_4(PW_9)_2$, $Co_4(PW_9)_2$, and $Fe_4(PW_9)_2$. 1,2-Epoxycyclooctane was always obtained with 100% selectivity, so the allylic oxidation did not occur under the present conditions. The conversion profile obtained for *cis*-cyclooctene oxidation at 80ºC is illustrated in Figure 2.

In a recent study, Farsani *et al.* described the oxidation of *cis*-cyclooctene with H_2O_2 in acetonitrile in the presence of similar Mn, Fe and Co sandwich tungstophosphates [17]. Nevertheless, their tetrabutylammonium salts of the Co and Mn sandwich heteropolyanions had different cation/anion ratios and, thus, different chemical formula. Additionally, the reaction conditions involved higher catalyst amount (lower sub/cat ratios) and lower substrate concentration [17]. The results presented here correspond to higher conversion and selectivity than those already published [17], independently of the used temperature, for the cobalt and manganese heteropolyanions, and at similar temperature in the case of the iron heteropolyanion.

3.4. Catalysts stability

Previous reports on the stability of these sandwich-type heteropolyanions in the presence of H_2O_2, under catalysis conditions, showed that $Fe_4(PW_9)_2$ is stable under conditions of deficiency of H_2O_2, at room temperature [5]. However, for the reactions of cyclooctane oxidation performed at 80 ºC, with ox/cat molar ratio above 1330, all the three catalysts, $Co_4(PW_9)_2$, $Mn_4(PW_9)_2$, and $Fe_4(PW_9)_2$, were found to decompose into the monosubstituted Keggin heteropolyanions ($XW_{11}M$), being the degradation of the manganese sandwich heteropolyanion more extensive than that of the analogous cobalt anion [10]. A different situation was observed here, where catalysts' recovery was carried out for the reactions of *cis*-cyclooctene performed at 80ºC with ox/cat = 600 and for those of geraniol oxidation performed at room temperature with ox/cat = 1500. The infrared spectra of the solids recovered at the end of the reactions, after evaporation of the solvent, suggested that the catalysts are stable under the reaction conditions studied, as exemplified for $Mn_4(PW_9)_2$ in the oxidation of *cis*-cyclooctene (Figure 3).

Oxidations of organic substrates with hydrogen peroxide in the presence of metal-substituted Keggin-type polyoxometalates may occur by different pathways [37,42,48]. Studies performed in our laboratory with metal substituted Keggin anions in conditions similar to those used in this work have shown that the reactions with H_2O_2 could occur via radical or non-radical processes, possibly depending on the reactivity of the substrates and reaction conditions. Overall, the oxidation of cycloalkanes, alkylbenzenes and similar compounds catalysed by $XW_{11}M$ anions occurs probably through a radical process [10,37,49-54], being completely inhibited in the presence of a radical scavenger, whereas the oxidation of *cis*-cyclooctene [26,55], styrene [39], anthracene [37] and geraniol [12] do not seem to involve radicals. Also, more than one route may occur simultaneously, as found for the oxidation of cyclohexene with H_2O_2 in the presence of $[PMo_{11}Mn^{II}(H_2O)O_{39}]^{5-}$ [26]. This reaction yielded cyclohexene-1,2-diol (resulting from the epoxide ring opening) as the major product together with some products of allylic oxidation. The latter could be eliminated using a radical scavenger, but this did not inhibit completely the reaction, and the former was always the main product [26].

Observing the oxidation products obtained for the diverse substrates, it can be proposed that the reactions described in 3.2 and 3.3 are possibly of a non-radical nature, due to the predominance of the formation of epoxides and/or their derivatives and to the absence of allylic oxidation. The occurrence of allylic oxidation observed for limonene is possibly an indicative of a radical process, which, as mentioned above for cyclohexene and referred previously by Casuscelli et al [56], may not be the only mechanism.

The activation of H_2O_2 in the non-radical processes catalysed by the sandwich-type $M_4(PW_9)_2$ occurs possibly through the formation of a peroxo or hydroperoxo complex centred at the metal M, which reacts with the double bonds, originating an epoxide through the heterolytic oxygen transfer from the oxidant to the substrate, as commonly proposed in the literature [24,42,48]. It should be noted that only two of the four metal atoms M of the anions belt (those initially bound to water, see Fig. 1) are possibly available for coordination with hydrogen peroxide. As mentioned for other cases [43,57], the activation of the H_2O_2 may occur both at the tungsten and at the substituting-metal, but this does not alter significantly the possible mechanism. The preferential epoxidation of geraniol at the C2–C3 position has been explained by the formation of a complex involving the polyoxometalate, the oxidant and the substrate, which may coordinate to the metal center or interact with the polyoxometalate through the OH group [24,42,43].

Radical species resulting from the homolytic breakage of the O–O bond of hydrogen peroxide are expected to occur in the presence of transition metals with consecutive oxidation states, like Mn$^{II/III}$, Co$^{II/III}$, Fe$^{II/III}$ [58,59]. Fenton and Fenton-like mechanisms may occur through the formation of HO• radicals, as proposed for the reactions of cyclooctane with H_2O_2 catalyzed by iron or manganese polyotungstates [52], but other species have been proposed in other studies, like, for example, a POM-Ti^{IV}–O• species [48], and it is not possible to advance a suggestion.

4. Conclusions

Sandwich-type tungstophosphates of general formula B-α-$[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$ (M = Co^{II}, Mn^{II}, Fe^{III}) were evaluated as catalysts for the oxidation of (*R*)-(+)-limonene, geraniol, linalool, linalyl acetate, carveol, and *cis*-cyclooctene with 30% aqueous H_2O_2, in acetonitrile. The oxidation of (*R*)-(+)-limonene gave limonene-1,2-diol as the dominant product. Thus, for limonene the main pathway was the epoxidation of the endocyclic double bond, followed by the epoxide ring opening affording limonene-1,2-diol. The epoxidation of linalool takes place preferentially at the more substituted 6,7-double bond, but the corresponding 6,7-epoxide reacts further, yielding the furano- and pyrano-oxides, in a relative molar ratio furano/pyrano ring of 1.8-2.5 after 5 h of reaction, via an intramolecular cyclization. The oxidation of linalyl acetate occurred preferentially at the more substituted 6,7-double bond only for $Mn_4(PW_9)_2$, thus affording the 6,7-epoxide at 82% selectivity. Interestingly, the selectivity changed enormously when $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$ were used instead. Actually, 1,2-epoxide was the major product with 51% and 77% selectivity with $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$, respectively. The oxidation of carveol occurred with very good conversions in the presence of $Mn_4(PW_9)_2$, $Co_4(PW_9)_2$ and $Fe_4(PW_9)_2$, yielding carvone and carveol 1,2-epoxide at similar amounts. Carveol 8,9-epoxide was always a minor product. The oxidation of *cis*-cyclooctene gave only the epoxide, thus without allylic oxidation, while the oxidation of geraniol at room temperature afforded the 2,3-epoxygeraniol as the major product.

Acknowledgments

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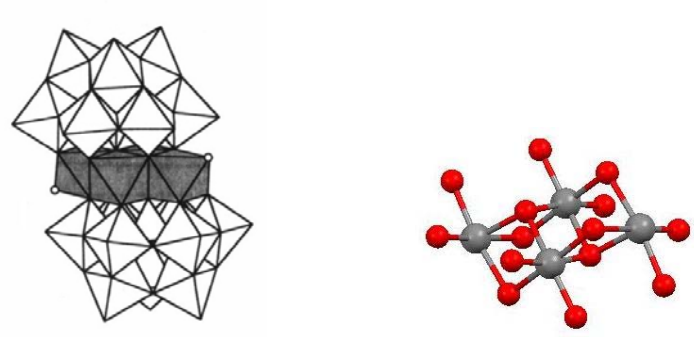


(A) (B)

Fig. 1 (A) Structure of the complex B-α-$[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$. Each dashed octahedron represents a MO_6 group and the open circles correspond to oxygen atoms of co-ordinating water molecules. (B) Belt of metal ions (grey) bound to oxygen atoms of the $[PW_9O_{34}]^{9-}$ ligands (red). Coordinated water not shown.

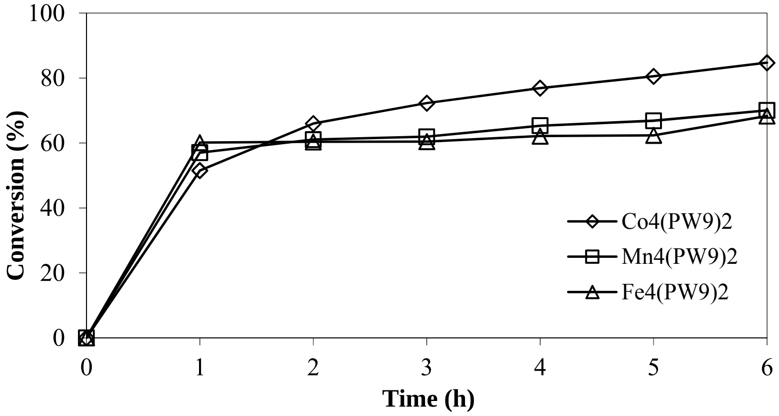


Fig. 2. Cyclooctene (3 mmol) oxidation catalysed by sandwich-type POMs (5 μmol), with 1.5 mL of CH_3CN at 80ºC and in the presence of H_2O_2 30% (3 mmol).

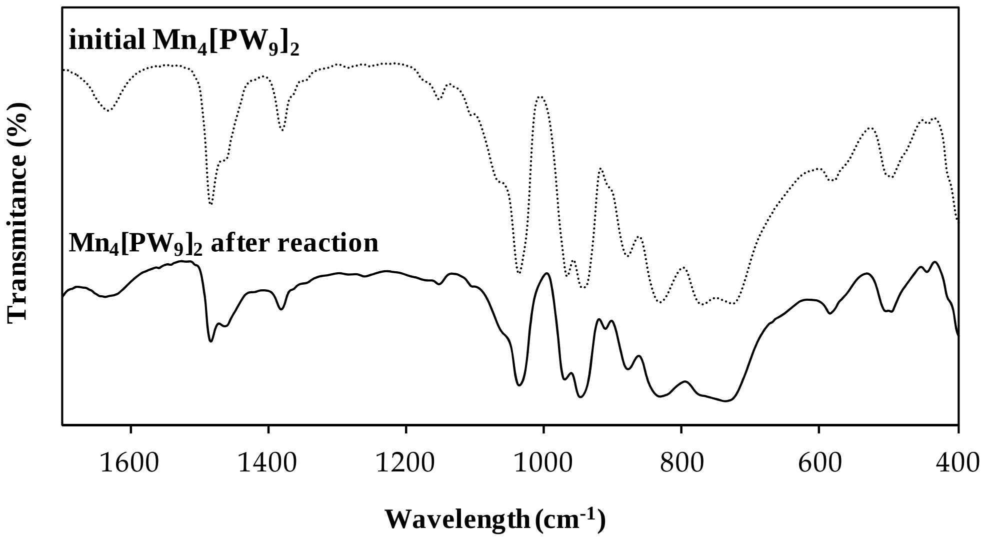
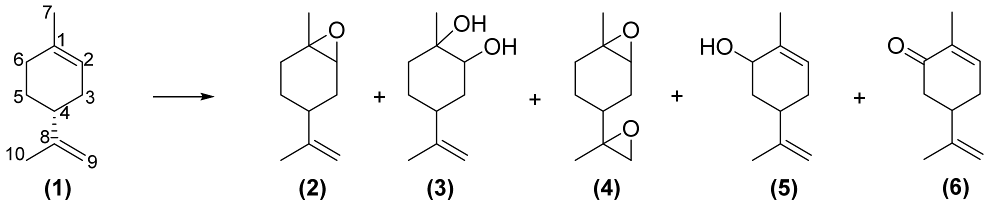
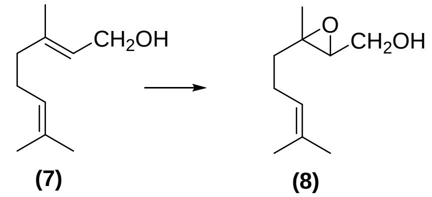


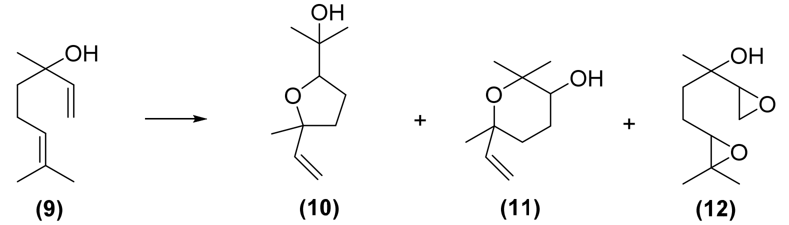
Fig. 3. The infrared spectra of the initial $Mn_4(PW_9)_2$ catalyst and the recovered solid after catalysis.



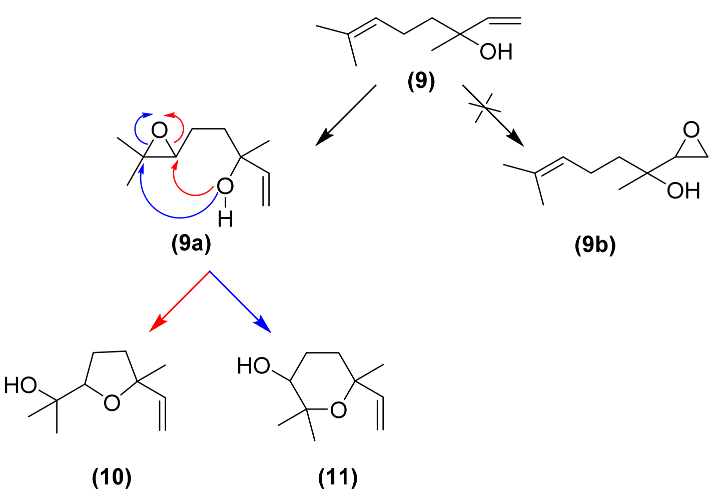
Scheme 1. Oxidation of limonene by hydrogen peroxide catalysed by $M_4(PW_9)_2$ heteropolyanions



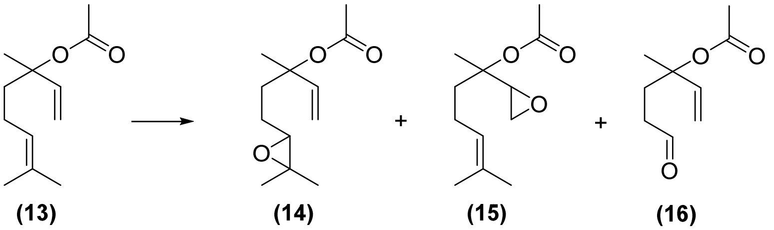
Scheme 2. Oxidation of geraniol by hydrogen peroxide catalysed by $M_4(PW_9)_2$ heteropolyanions



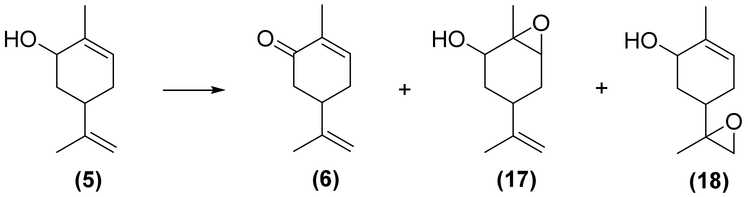
Scheme 3. Oxidation of linalool by hydrogen peroxide catalysed by $M_4(PW_9)_2$ heteropolyanions



Scheme 4. Linalool 6,7-epoxide (**9a**) intramolecular cyclization into five and six member heterocyclic rings



Scheme 5. Oxidation of linalyl acetate by hydrogen peroxide catalysed by $M_4(PW_9)_2$ heteropolyanions



Scheme 6. Oxidation of carveol by hydrogen peroxide catalysed by $M_4(PW_9)_2$ heteropolyanions

Table 1. Oxidation of (*R*)-(+)-limonene with hydrogen peroxide catalysed by sandwich-type tungstophosphates[(a)].

Catalyst	Time (h)	Conversion (%)	TON[(b)]	Selectivity[(c)] (%)				
				(**2**)	(**3**)	(**4**)	(**5**)	(**6**)
$Mn_4(PW_9)_2$	2	68	227	23	50	20	3	4
$Co_4(PW_9)_2$	2	86	287	5	62	20	4	9
$Fe_4(PW_9)_2$	2	89	297	0	56	30	5	9
$Mn_4(PW_9)_2$	7	80	267	21	53	19	2	5
$Co_4(PW_9)_2$	7	98	327	5	62	20	4	9
$Fe_4(PW_9)_2$	7	94	313	3	54	26	4	13

(a) Reaction conditions: sub = 1 mmol; cat = 3 μmol; CH_3CN = 1.5 mL; 2 mmol of H_2O_2 30%; 80ºC; (b) mol of converted substrate per mol of catalyst; (c) product numbering indicated on Scheme 1.

Table 2. Oxidation of geraniol, linalool, linalyl acetate, and carveol with hydrogen peroxide catalysed by sandwich-type tungstophosphates$^{(a)}$.

Catalyst	Substrate	Temp (ºC)	Time (h)	Conversion (%)	TON	Selectivity$^{(c)}$ (%)		
						(**8**)		
Mn$_4$(PW$_9$)$_2$	geraniol	RT$^{(b)}$	5	90	300	>99		
Co$_4$(PW$_9$)$_2$	geraniol	RT$^{(b)}$	5	97	323	94		
Fe$_4$(PW$_9$)$_2$	geraniol	RT$^{(b)}$	5	87	290	>99		
						(**10**)	(**11**)	(**12**)
Mn$_4$(PW$_9$)$_2$	linalool	60	5	48	160	64	30	6
Co$_4$(PW$_9$)$_2$	linalool	60	5	23	77	65	30	5
Fe$_4$(PW$_9$)$_2$	linalool	60	5	43	143	70	28	2
Mn$_4$(PW$_9$)$_2$	linalool	80	5	81	270	62	36	2
Co$_4$(PW$_9$)$_2$	linalool	80	5	60	200	66	26	8
Fe$_4$(PW$_9$)$_2$	linalool	80	5	91	300	61	36	3
						(**14**)	(**15**)	(**16**)
Mn$_4$(PW$_9$)$_2$	linalyl acetate	80	6	40	133	82	15	3
Co$_4$(PW$_9$)$_2$	linalyl acetate	80	6	44	147	39	51	10
Fe$_4$(PW$_9$)$_2$	linalyl acetate	80	6	48	160	1	77	22
						(**6**)	(**17**)	(**18**)
Mn$_4$(PW$_9$)$_2$	carveol	80	3	99	330	45	45	6
Co$_4$(PW$_9$)$_2$	carveol	80	3	98	327	49	44	2
Fe$_4$(PW$_9$)$_2$	carveol	80	3	99	330	51	46	2

(a) Reaction conditions: sub = 1 mmol; cat = 3 µmol; CH$_3$CN = 1.5 mL; 3 mmol of H$_2$O$_2$ 30%; (b) RT = room temperature, protected from light; (c) product numbering indicated on Schemes 2-6.