Oxidation of monoterpenes with hydrogen peroxide catalysed by Keggin-type tungstoborates

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Abstract

The Keggin-type anions $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$ and $[BW_{12}O_{40}]^{5-}$ were used for the first time as catalysts in studies of oxidation of monoterpenes by hydrogen peroxide. The oxidation of geraniol **1**, nerol **2**, (+)-3-carene **3**, thymol **4** and carvacrol **5** was examined. The reactions were carried out in acetonitrile, at room temperature (for **1** and **2**) or at reflux (for **3**, **4** and **5**). Compounds **1** and **2** were preferentially epoxidised at the C_2–C_3 double bond, whereas **3**, under controlled reaction conditions, could afford only the α-epoxide. The oxidation of **4** and **5** yielded a mixture of benzoquinones. For tetrabutylammonium salts, the Mn^{III} substituted anion was found to be a more efficient catalyst than $[BW_{12}O_{40}]^{5-}$. The infrared spectra of the recovered solids at the end of reaction showed that the Keggin anions were still present, but the electronic spectra of the manganese residues indicate that oxidation of Mn^{III} had taken place.

1. Introduction

The development of efficient catalysts for the selective oxidation of organic compounds in mild and environmental friendly conditions is an active field of research. An interesting line of study is the search for effective environmentally clean catalytic reactions to transform cheap natural compounds into valuable intermediates for organic synthesis both in the laboratory and in industry.

The use of Keggin-type polyoxometalates as catalysts in oxidative transformations, like epoxidation of olefins and hydroxylation of saturated hydrocarbons, has been well documented during the last decade [1–8]. In particular, transition metal substituted Keggin-type heteropolytungstates $[M(H_2O)XW_{11}O_{39}]^{(n-m)-}$ (X = P, Si, etc.), in which a transition metal cation, M^{m+}, is co-ordinated to the binding sites of a lacunary heteropolyanion $[XW_{11}O_{39}]^{n-}$, have been found to catalyse several types of oxidative reactions with a variety of oxidants and substrates [6–8]. The interest of these species, presenting a metal centre surrounded by a stable inorganic environment, for oxidative catalysis was noticed about 16 years ago [9,10] and was followed by a large surge of work. Most of this work is concerned with polyoxoanions having phosphorous or silicon as the heteroatom X [6–8].

We report here the use of the heteropolytungstate $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$ as catalyst in the oxidation

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reactions of the natural compounds geraniol **1**, nerol **2**, (+)-3-carene **3**, thymol **4** and carvacrol **5**, in acetonitrile, with hydrogen peroxide as the oxidant. The behaviour of the Mn^{III} substituted anion is also compared with that of the parent $[BW_{12}O_{40}]^{5-}$. Part of this work was briefly mentioned previously [11].

To our knowledge, catalytic studies using $[Mn^{III}-(H_2O)BW_{11}O_{39}]^{6-}$ and $[BW_{12}O_{40}]^{5-}$ in the conditions described here have not been reported before. Zhang and Pope have used the related anion $[Mn^{IV}-BW_{11}O_{40}H]^{6-}$ on the oxidation of cyclohexene and *cis*-stilbene with PhIO [12]. The epoxidations of 1-octene by the Ishii–Venturello system with $K_7[Mn^{II}(H_2O)BW_{11}O_{39}]$ and $H_5BW_{12}O_{40}$ as precursors were examined [13,14]. No other report of oxidative catalysis in the presence of Keggin-type tungstoborates could be found.

The anion $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$ is formed spontaneously in aqueous solution by oxidation with air of the related Mn^{II} heteropolyanion [15]. We have isolated solid compounds with the Mn^{III} anion and quaternary ammonium cations (tetrabutylammonium, TBA, hexadecyltrimethylammonium, HDTMA) to be used in the catalytic studies in acetonitrile. We have found that the chosen cation has influence on the course of reaction in the studied conditions.

It is well established that the chemical transformation of abundant and cheap natural products can make available other more valuable compounds [16–21]. Compounds **1** to **5** are examples of monoterpenes, which can be found in the essential oils of several plants [22]. They represent different structural types and different courses of oxidative reactions can be expected. Also, certain epoxides are often starting materials for the synthesis of fragrances, flavours and therapeutically active substances [23]. Under the conditions used in our studies **1** and **2** are preferentially epoxidised at the C_2–C_3 double bond, providing a possible example of hydroxyl-directed epoxidation of olefins. Oxidation of **3** in the appropriate conditions give rise only to the α-isomer of 3,4-epoxycarane with a moderate conversion (Scheme 1). The reaction of **4** and **5** yielded primarily a mixture of benzoquinones (Scheme 2). To our knowledge, no previous studies on the oxidation of the chosen substrates in the presence of Keggin-type metal substituted polyoxotungstates have been reported before.
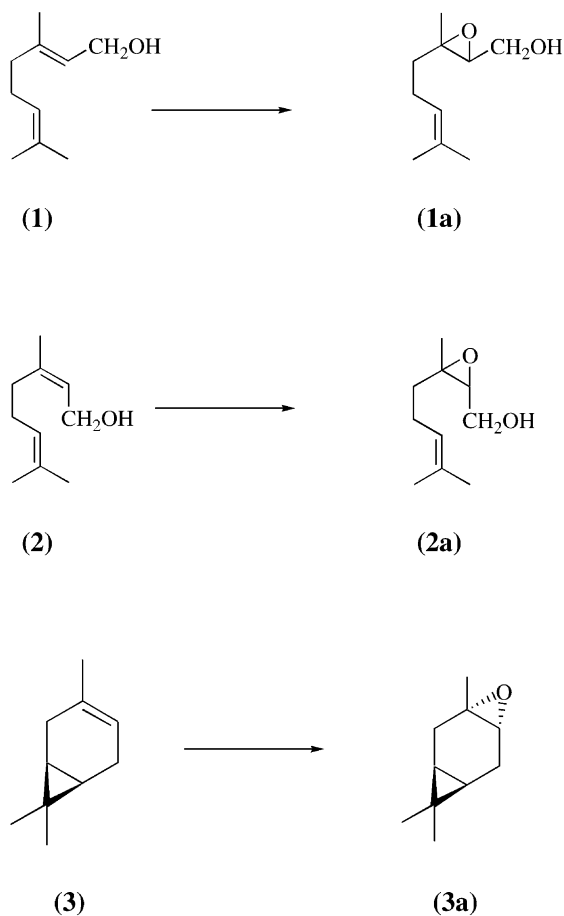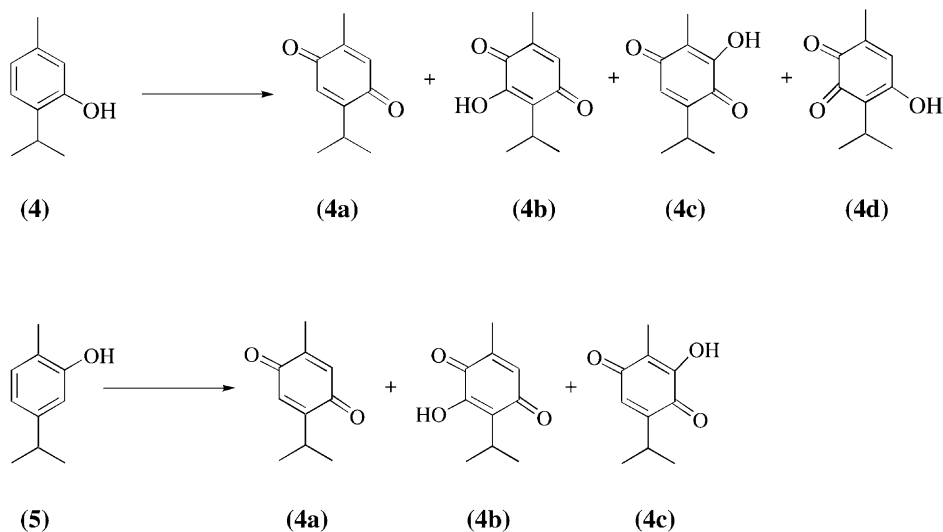

Scheme 1.

2. Experimental

2.1. Reagents and methods

Hydrogen peroxide (30 wt.% solution in water) was purchased from Riedel-de-Haën. Geraniol, nerol, thymol, carvacrol and (+)-3-carene were purchased from Aldrich. All chemicals and solvents were used as received or distilled and dried using standard procedures.

Elemental analysis for W and Mn were performed by ICP spectrometry (University of Aveiro, Central Laboratory of Analysis) and C, H, N elemental analysis was performed on a Leco CHNS-932. Hydration water contents were determined by thermogravimetric analysis on a TGA-50 Shimadzu thermobalance.

Electronic absorption spectra (visible and near infrared) were recorded on a Jasco V-560 spectropho-

Scheme 2.

tometer, using solutions $5 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. Diffuse reflectance spectra were registered on a Shimadzu 3100 spectrophotometer, using MgO as reference. Infrared absorption spectra were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets. X-ray powder diffraction patterns and magnetic moments at room temperature were obtained as described elsewhere [24].

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); GC-FID was performed using a Varian Star 3400CX chromatograph and hydrogen as the carrier gas (55 cm/s). In both cases fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm i.d.; 25 μm film thickness) were used. The chromatographic conditions were as follows: initial temperature: 60 °C ((+)-3-carene), 100 °C (geraniol, nerol, thymol and carvacrol); temperature rate: 5 °C/min (geraniol, nerol and (+)-3-carene), 20 °C/min (thymol and carvacrol); final temperature: 220 °C; injector temperature: 220 °C; detector temperature: 230 °C.

2.2. Synthesis of catalysts

$(\mathrm{TBA})_4\mathrm{H}_2[\mathrm{Mn}(\mathrm{H}_2\mathrm{O})\mathrm{BW}_{11}\mathrm{O}_{39}]\cdot\mathrm{H}_2\mathrm{O}$ (**I**): an aqueous solution of the anion $[\mathrm{Mn}(\mathrm{H}_2\mathrm{O})\mathrm{BW}_{11}\mathrm{O}_{39}]^{6-}$ was prepared by following a published procedure [15]. Three aqueous solutions were prepared and mixed as described [15]: (A) KMnO_4 (0.38 mmol) and HNO_3 (3.28 mmol) in 10 cm³; (B) $\mathrm{Mn}(\mathrm{CH}_3\mathrm{COO})_2$ (1.63 mmol, 10 cm³); (C) $\mathrm{Na}_2\mathrm{WO}_4\cdot2\mathrm{H}_2\mathrm{O}$ (22 mmol) and $\mathrm{H}_3\mathrm{BO}_3$ (8.08 mmol) in 10 cm³, pH adjusted to 6.3. The resulting solution was extracted with tetrabutylammonium bromide in $1,2\text{-}\mathrm{C}_2\mathrm{H}_4\mathrm{Cl}_2$ (18 mmol, 20 cm³). After separation, the organic solvent was evaporated and the resulting oil re-dissolved in the minimum amount of acetonitrile. An orange solid was precipitated by slow addition of water, filtered, washed and dried in a desiccator under vacuum. Yield, 88%. Anal. Found: W, 55.2; Mn, 1.5; C, 21.97; H, 4.18, N, 1.69; hydration $\mathrm{H}_2\mathrm{O}$, 0.5. Calc.: W, 54.4; Mn, 1.5; C, 21.67; H, 4.01, N, 1.51; hydration $\mathrm{H}_2\mathrm{O}$, 0.5. IR (cm⁻¹): 990(m), 948(vs), 896(vs), 828(vs), 750(s, sh), 526(m). $\mu = 4.86\mu_\mathrm{B}$.

$(\mathrm{HDTMA})_4\mathrm{H}_2[\mathrm{Mn}(\mathrm{H}_2\mathrm{O})\mathrm{BW}_{11}\mathrm{O}_{39}]\cdot10\mathrm{H}_2\mathrm{O}$ (**II**): an aqueous solution of the anion $[\mathrm{Mn}(\mathrm{H}_2\mathrm{O})\mathrm{BW}_{11}\mathrm{O}_{39}]^{6-}$ was prepared as described above. To this solution (30 cm³) an excess of (HDTMA)Br in water (8 mmol, 15 cm³) was added dropwise, with stirring, at 80–85 °C. The orange solid formed was collected, washed with water and dried in vacuum. Yield, 92%. Anal. Found: W, 48.6; Mn, 1.3; C, 22.61; H, 4.38; N, 1.44; hydration $\mathrm{H}_2\mathrm{O}$, 4.4. Calc.: W, 49.7; Mn, 1.4;

C, 22.44; H, 4.76; N, 1.38; hydration H_2O, 4.4. IR (cm^{-1}): 987(m), 941(vs), 892(vs), 798(vs), 763(s, sh), 526(m). $\mu = 4.94\mu_B$.

$(TBA)_4H[BW_{12}O_{40}]\cdot 7H_2O$ (**III**): this compound was prepared following a published procedure [25]. Anal. Found: C, 19.16; H, 3.85; N, 1.46; hydration H_2O, 3.5. Calc.: C, 19.44; H, 4.05; N, 1.42; hydration H_2O, 3.2. Infrared spectra agreed with reported values [25].

2.3. Oxidation procedure

Reactions were performed as described below. In all cases, at regular intervals, an aliquot was taken directly from the reaction mixture with a microsyringe and directly injected into the GC or GC–MS equipment for analysis of starting materials and products. Reaction products reported here were identified as described elsewhere [19,20,26]. The percentage of each compound in the reaction mixtures was estimated directly from the corresponding peak area.

2.3.1. Geraniol 1, nerol 2 and (+)-3-carene 3

A typical oxidation procedure was as follows: the chosen catalyst $(5.06 \times 10^{-3}\,mmol)$, substrate (0.34 mmol), H_2O_2 (30 wt.% solution in water diluted in CH_3CN, 1:10) and acetonitrile (1.5 ml) were placed in a round bottom flask, and the mixture stirred at room temperature, in the dark, (**1** and **2**) or at reflux (**3**). At the end of all reactions a drop of solution was taken and put on a KBr pellet, to obtain an IR spectra. At the end of some reactions catalysed by $(TBA)_4H_2[Mn(H_2O)BW_{11}O_{39}]\cdot H_2O$ the resulting solutions were left to evaporate at room temperature in an evacuated desiccator to recover the catalyst and the obtained solids were analysed by infrared and visible spectroscopy.

2.3.2. Thymol 4 and carvacrol 5

A typical oxidation procedure was as follows: the chosen catalyst (0.012 mmol), substrate (3 mmol) and 30 wt.% H_2O_2 (1 ml, 9.8 mmol) were placed in a round bottom flask and acetonitrile (5 ml) was added. The resulting mixture was stirred at reflux temperature. Recover and identification of the catalyst at the end of reaction were performed as described above.

2.4. Titration of hydrogen peroxide

At regular intervals samples were taken from reaction mixtures and the titration of hydrogen peroxide was carried out by the ceric sulphate method [27]. An aliquot was accurately weighed, quickly dissolved in diluted sulphuric acid and the peroxide titrated against 0.1 N ceric sulphate solution, using ferroin as indicator.

3. Results

The oxidative reactions of compounds **1** to **5** with H_2O_2 were performed in the presence of catalytic amounts of polyoxometalates (**I**), (**II**) or (**III**). The use of tetra-alkylammonium salts of the desired heteropolyanion to ensure adequate solubility in organic solvents is a common procedure in catalytic studies with this type of polyoxometalates [6–8]. In the cases of transition metal substituted Keggin-type anions the addition of TBABr to an aqueous solution of the heteropolyanion (prepared in situ or using a soluble salt) has been found to precipitate the TBA salt in some cases, namely salts of $[M(H_2O)PW_{11}O_{39}]^{(7-m)-}$ [28], but has not a general application. In the work described here the precipitation of the TBA salt of the undecatungstoboromanganate(III) anion did not occur rapidly (it was obtained in very low yield after some weeks). Extraction of the anion with TBA into 1,2-dichloroethane followed by evaporation of the organic solvent, dissolution of the resulting oil in acetonitrile and precipitation with water [29] was a more efficient process for preparation of this compound. However, the salt with HDTMA could be prepared by direct precipitation.

The prepared compounds were found to be crystalline by powder X-ray diffraction. Infrared spectra showed the characteristic pattern of heteropolyanions with the Keggin structure [25]. The spectra of the manganese containing compounds were almost indistinguishable from that of the parent $[BW_{12}O_{40}]^{5-}$ anion. The presence of Mn^{III} in compounds (I) and (II) was confirmed by the presence of a band near 470–480 nm on the reflectance spectra of the solids and by the value of their magnetic moments at room temperature (4.86 and $4.94\mu_B$, respectively). Dissolution of the TBA salt in acetonitrile may lead to partial replacement of the

water molecule co-ordinated to manganese, possibly in small extent, as the band of the visible spectra of the anion in solution is observed at 480 nm in water (K^+ salt) and at 460 nm in acetonitrile. The HDTMA salt is not appreciably soluble in pure acetonitrile, but was found to dissolve in mixtures of acetonitrile and alcohols (CH_3OH, C_2H_5OH, and others).

3.1. Epoxidation of geraniol 1 and nerol 2

Geraniol and nerol are allylic alcohols that offer several possible places of oxidative attack, namely at the two double bonds, at the allylic carbon centres, and at the carbon of the CH_2OH group. It was found by GC analysis of the reaction mixture that, in the presence of catalytic amounts of compounds (**I**), (**II**) or (**III**), the oxidation of geraniol and nerol, at room temperature, with diluted H_2O_2, afforded the 2,3-epoxide as the main product (Table 1). With compound (**II**) the conversion of the substrates is lower than with (**I**) or (**III**). Conversion and selectivity observed in the presence of compound (**I**) does not change significantly with time between 1 and 7 h of reaction, as shown in Fig. 1 for the case of geraniol. This figure also shows that in the presence of catalyst (**III**) conversion reaches 94% only after 7 h of reaction. The similarity of geraniol and nerol reactivity is not unexpected and had been observed before [20].

The concentration of H_2O_2 present in solution during geraniol and nerol oxidative reactions was monitored, for the molar ratio H_2O_2/substrate = 3. In the case of catalyst (**I**) only 8% of the initial H_2O_2 was present after 60 min (Fig. 2). Therefore the efficiency of usage of H_2O_2 was approximately 35%. In similar conditions, with catalyst (**III**), 45–48% of the added H_2O_2 was still present after 7 h. In this case, the efficiency of usage of H_2O_2 was approximately 60%. This difference was attributed to the influence of the manganese on the decomposition of H_2O_2. The effect of manganese centres on the dismutation of hydrogen peroxide had been studied before for other polyoxometalates [30].

Preliminary experiments were carried out to test the possibility of catalyst re-use. At the end of the reaction (after 1 h, 96% of conversion), using catalyst (**I**), more geraniol and H_2O_2 were added to the same reaction mixture, and the products analysed in the same conditions as before. This procedure was repeated two more times. The total conversion of geraniol and the selectivity for 2,3-epoxygeraniol did not change significantly in each one of the four cycles.

3.2. Epoxidation of (+)-3-carene 3

The main product of oxidation of (+)-3-carene in the presence of catalyst (**I**), at reflux temperature, was the α-isomer of 3,4-epoxicarane **3a**, which was obtained with a selectivity between 62 and 100%, depending on the oxidant/substrate molar ratio used.

Table 1
Oxidation of geraniol and nerol with H_2O_2 in the presence of all catalysts after 3 h[a]

Substrate	Catalyst	H_2O_2/substrate molar ratio	Conversion (%)[b]	2,3-Epoxide yield (%)	2,3-Epoxide selectivity (%)
Geraniol	(**I**)	1	0	0	0
	(**I**)	2	33	25	75
	(**I**)	3	96	83	86
	(**II**)	3	25	21	85
	(**III**)	3	80	70	87
	None	3	0	0	0
Nerol	(**I**)	1	0	0	0
	(**I**)	2	43	33	76
	(**I**)	3	96	73	76
	(**II**)	3	17	13	79
	(**III**)	3	82	62	76
	None	3	0	0	0

[a] Reactions were carried out at room temperature and protected from light in acetonitrile ($1.5 \, cm^3$) with 0.34 mmol of substrate, 5.06×10^{-3} mmol of catalyst, using H_2O_2 (30 wt.%) diluted in CH_3CN (1:10).
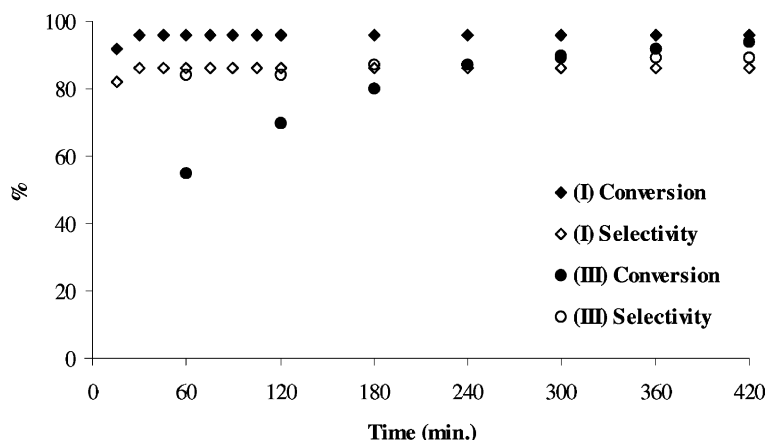[b] Based on gas chromatographic peak areas.

Fig. 1. Oxidation of geraniol with H_2O_2 in the presence of catalyst (**I**) and catalyst (**III**). Reactions were carried out at room temperature in acetonitrile ($1.5\,cm^3$) with 0.34 mmol of substrate, 5.06×10^{-3} mmol of catalyst, and using H_2O_2 (30 wt.%) diluted in CH_3CN (1:10), with molar ratio H_2O_2/substrate = 3.

The conversion of (+)-3-carene increased with the amount of hydrogen peroxide added but this was accompanied by a decrease in selectivity for the α-epoxide (Table 2). When the molar ratio H_2O_2/substrate is larger than six, several products were formed (each one in minor quantities), and their identification was not attempted. The reaction time did not have a noticeable influence on the obtained results, as no significant variation was observed for reaction times between 2 and 5 h.

In the presence of compound (**II**) no oxidation products were detected during the first 5 h of reaction, and this is presumably due to its low solubility in the reaction media.
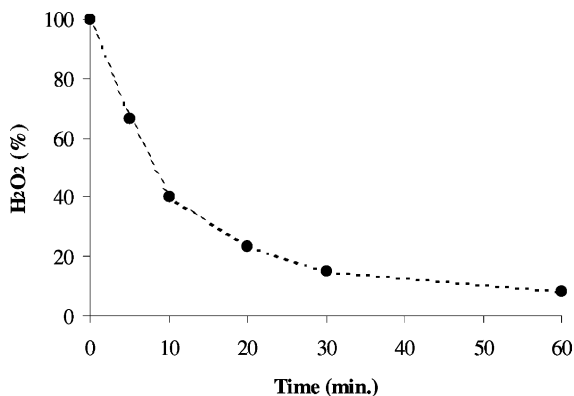

Fig. 2. Fraction of initial H_2O_2 present in solution during the oxidation of geraniol in the presence of catalyst (**I**) with molar ratio H_2O_2/substrate = 3.

At reflux temperature, the main product of oxidation of (+)-3-carene in the presence of compound (**III**) was also the α-3,4-epoxicarane **3a**, which was obtained with a selectivity between 50 and 65%, depending on the oxidant/substrate molar ratio used. Longer times of reaction were again necessary in the presence of catalyst (**III**) than of (**I**) to obtain similar values of conversions.

3.3. Oxidation of thymol 4 and carvacrol 5

Thymol and carvacrol are *p*-menthane type aromatic monoterpenes. Oxidative reactions performed in the presence of compound (**I**) (**II**) or (**III**), at reflux temperature, afforded mixtures of several benzoquinones. Four major oxidation products were found, namely 2-isopropyl-5-methyl-1,4-benzoquinone (thymoquinone) **4a**, 2-hydroxy-3-isopropyl-6-methyl-1,4-benzoquinone **4b**, 2-hydroxy-6-isopropyl-3-methyl-1,4-benzoquinone **4c** and 4-hydroxy-3-isopropyl-6-methyl-1, 2-benzoquinone **4d** (Scheme 2). Conversion values were in the 35–40% range after 3 h and did not increase with extra reaction time, in the case of catalyst (**I**) and (**II**). Using catalyst (**III**), it was only possible to convert 20% of the carvacrol after 9 h of reaction. Oxidation of carvacrol **5** provided mainly mixtures of **4b** and **4c**, with a small amount of thymoquinone **4a**. Conversion and yield of the different products obtained with catalyst (**II**) are shown in Fig. 3. Similar results were obtained with (**I**). Oxidation of thymol

Table 2
Oxidation of (+)-3-carene with H_2O_2 at reflux[a]

Catalyst	H_2O_2/substrate molar ratio	Conversion (%)[b]	α-3,4-Epoxycarane yield (%)	α-3,4-Epoxycarane selectivity (%)
(I)[c]	5	21	21	100
(I)[c]	6	37	37	100
(I)[c]	7	76	47	62
(III)[d]	5	67	44	65
(III)[d]	6	75	38	50
None[d]	6	0	0	0

[a] Reactions were carried out in acetonitrile (1.5 cm^3) with 0.34 mmol of substrate, 5.06×10^{-3} mmol of catalyst, using H_2O_2 (30 wt.%) diluted in CH_3CN (1:10).

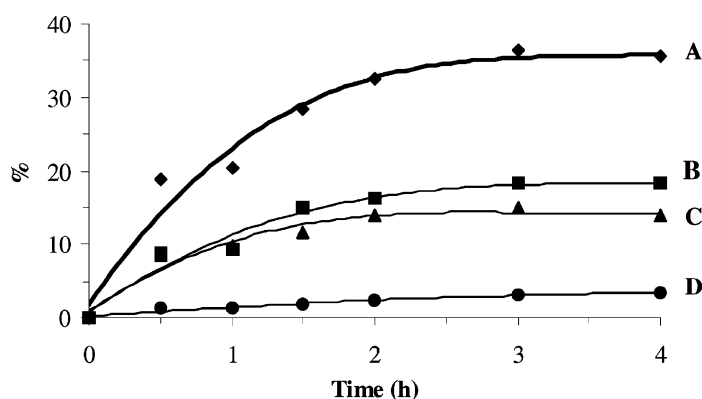[b] Based on gas chromatographic peak areas.

[c] After 2 h.

[d] After 6 h.

Fig. 3. Oxidation of carvacrol with H_2O_2 in the presence of the HDTMA salt of $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$. (A) Conversion; (B) compound 4b; (C) compound 4c; (D) compound 4a. Reaction conditions: 0.012 mmol of catalyst; 3 mmol of substrate; 1 ml 30 wt.% H_2O_2 (9.8 mmol); 5 ml of acetonitrile; reflux temperature.

in the presence of (**I**) (**II**) or (**III**) yielded mixtures of all the products **4a–d**; thymoquinone was again produced only in small amounts.

3.4. Stability of the catalysts

In order to assess the stability of the catalysts, the solids recovered at the end of the reactions, after evaporation of the solvent, were analysed by spectroscopic techniques. This study was performed for some reactions catalysed by $(TBA)_4H_2[Mn(H_2O)BW_{11}O_{39}] \cdot H_2O$ and $(TBA)_4H[BW_{12}O_{40}] \cdot 7H_2O$. The infrared spectra of the obtained residues showed that the Keggin unit was still present (Fig. 4). These spectra cannot be used to distinguish the TBA salt of the Mn^{III} anion (or even the correspondent Mn^{IV} [29])
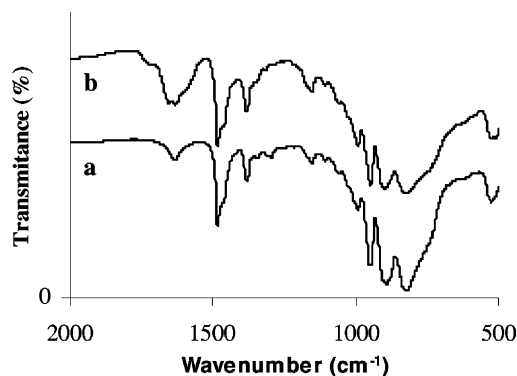

Fig. 4. Infrared spectra of the manganese substituted polyoxoanion before (a) and after (b) catalysis.
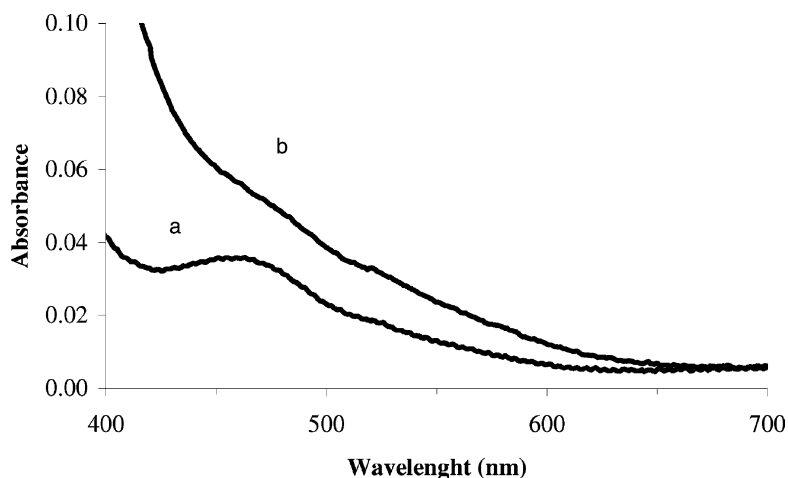
Fig. 5. Visible spectra of catalyst (**I**), in conditions of the geraniol oxidation (molar ratio H_2O_2/substrate $= 3$), before (a) and 30 min after (b) H_2O_2 addition. Spectra obtained at 60 or 120 min after H_2O_2 addition coincide with curve (b).

from that of the parent $[BW_{12}O_{40}]^{5-}$, because they are very similar. Nevertheless the obtained solids had different colours, being dark orange when reactions were performed in the presence of the Mn anion or white when $[BW_{12}O_{40}]^{5-}$ was used.

Fig. 5 shows the visible spectra of catalyst (**I**) obtained before and during a catalytic experiment of geraniol oxidation. In the presence of H_2O_2 the d–d band around 460 nm, characteristic of Mn^{III}, disappeared and the obtained spectra corresponded to that of the Mn^{IV} heteropolyanions already reported [29,31]. The observed alterations were thus interpreted as corresponding to the oxidation of Mn^{III} to Mn^{IV}. Also the electronic spectra of the residues obtained after catalysis suggested that the manganese centre had not reverted to the Mn^{III} state.

4. Discussion

Transition metal substituted Keggin-type heteropolytungstates having boron as the heteroatom have been neglected from the point of view of oxidative catalysis. In general they offer no evident advantage over similar anions with P and Si and they are often more difficult to synthesise in pure form. Zhang and Pope have studied the oxidation of cyclohexene and *cis*-stilbene, with PhIO as oxidant, in the presence of several heteropolytungstates substituted with

manganese, including a high valent Mn^{IV} monosubstituted Keggin tungstoborate [12]. The difference of conditions used precludes any comparison with the study described here.

Keggin type polyoxotungstates have been used as catalyst precursors in epoxidation studies by the Ishii–Venturello and related systems [5,8]. Both $K_7[Mn^{II}(H_2O)BW_{11}O_{39}]$ and $H_5[BW_{12}O_{40}]$ were examined as catalyst precursors in the oxidation of 1-octene, but epoxide formation was found to be very low [13] or even zero [14], respectively, in conditions where $H_3[PW_{12}O_{40}]$ and $Na_7[PW_{11}O_{39}]$ had a much better performance. These facts suggested that the boron polyoxotungstates could be more stable in the presence of H_2O_2 than the phosphorous analogues and seemed to rule out the formation of polyperoxotungstates in solution, at least in the conditions of this study, in which diluted H_2O_2 was used. In our studies, the recover of the catalysts at the end of the reactions and the absence of an induction period on the time course of reactions seems to indicate that the degradation of the studied heteropolyanions to form tungsten peroxocomplexes is not probable.

What seemed to be alteration of the polyoxotungstate catalyst in the presence of H_2O_2 followed by recover of the initial structure after evaporation of solvents has been reported before [32] and, thus, a change of structure during the catalytic reactions cannot be ruled out. The low concentration of the polyoxome-

talates in solution and the presence of a paramagnetic centre were not favourable to the use of common spectroscopic techniques to monitor the state of the catalysts in reaction conditions. However, visible spectra indicated that Mn(IV) was present during catalysis, what may imply that manganese was stabilized in that oxidation state by the intact polyoxometalate.

The results here discussed show that both $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$ and $[BW_{12}O_{40}]^{5-}$ are catalytically active for oxidations with H_2O_2. The main products obtained were basically the same, suggesting related reactions course. Formation of a tungsten-peroxo intermediate, without destruction of the polyanion, as proposed by Neumann and Juwiler [33] is a likely possibility to explain the action of the $[BW_{12}O_{40}]^{5-}$ anion. If TBA salts are compared it is clear that when Mn^{III} is present the catalyst is more effective (higher conversion/selectivity and/or shorter reaction times). In this case, oxidation of the Mn^{III} was observed, what seems to indicate that manganese is functioning as a catalytic centre. There is no reason to think that the manganese is the only catalytic centre and it is possible that the tungsten/oxygen framework also take part in the oxidative catalysis.

The oxidation of the three different types of monoterpenes with H_2O_2 studied in this work provided different results. Acyclic compounds **1** and **2** were epoxidised at room temperature, in the dark, affording the 2,3-epoxide with high regioselectivity and conversion. Selective formation of the 2,3-epoxide had been observed in the presence of some metal catalysts [34,35] and also of the sandwich-type polyoxometalate $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ [33]. Some of these systems also employ H_2O_2, with conversions above 90%, but in most cases they involve the use of chlorinated solvents. Different behaviour has been reported with other Mn^{III} catalysts, like some metalloporphyrins, that yield several products [20] or Mn^{III}(salen) complexes, that provide mainly the 6,7-epoxide [36]. Geraniol and nerol present two double bonds, both trisubstituted, but the electron density of the $C_2–C_3$ double bond is significantly lowered by the inductively electron-accepting hydroxyl group in comparison with the $C_6–C_7$ double bond [37]. In many reported cases the regioisomeric product distribution seems to be dominated by the relative electron density of the two double bonds, that favours epoxidation at the $C_6–C_7$ position [20,37]. When preferential epoxidation at the $C_2–C_3$ position has been found, this has been explained by the formation of a complex involving the metal centre, the oxidant and the substrate, that may co-ordinate through the OH group [34,35,37].

Formation of such type of complexes does not seem very likely in the case of the Keggin type anions studied in this work, as none of the metals present (Mn or W) have more than one coordinative position available. However, it seems that we have here a new example of hydroxyl-directed epoxidation. The possible association of the substrate to the anion by hydrogen bonding in the close proximity of any metal centre, instead of direct coordination, might lead to a mechanism similar to those proposed for other systems in selective 2,3-epoxidation of geraniol [34,35].

Selective epoxidation of (+)-3-carene was obtained in the presence of $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$ with moderate conversion. In this case the α-epoxide was obtained preferentially to the β-epoxide and no allylic oxidation was observed. Results with $[BW_{12}O_{40}]^{5-}$ were less interesting. Epoxidation of (+)-3-carene in the presence of some manganese(III) porphyrins with H_2O_2 has been described, but complex mixtures of oxidation products were obtained [20]. Again this shows that the polyoxoanion framework must have influence on the course of reaction observed.

The third type of oxidative reactions studied was performed with the aromatic monoterpenes thymol and carvacrol. In this case, complex mixtures of products were obtained, showing that the Keggin-type anions studied offer no advantage in the catalysis of these reactions, namely in comparison with the Mn^{III} porphyrins [19].

Compound (**I**) could be used as catalyst in all reactions, as it was found to be freely soluble in acetonitrile. Compound (**II**) was soluble in acetonitrile solutions of substrates **1**, **2**, **4** and **5**, but not in similar solutions of **3**. The different cations have an obvious influence on the course of the studied reactions, possibly due to anion–cation interactions in solution.

5. Conclusions

The anions $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$ and $[BW_{12}O_{40}]^{5-}$ were used for the first time in studies of oxidative catalysis of monoterpenes with H_2O_2.

This catalytic method of epoxidation occurs in mild conditions and the use of a versatile, cheap and environmental friendly oxidant should probably make it useful among catalytic methods for catalytic epoxidation. In the case of TBA salts, the Mn^{III} substituted anion has provided better results than the $[BW_{12}O_{40}]^{5-}$.

Geraniol **1** and nerol **2** oxidation reactions gave rise mainly to 2,3-epoxygeraniol **1a** and 2,3-epoxynerol **2a**, respectively, with conversions that can reach 96%, with 86% selectivity, depending on reaction conditions. The oxidation reactions of (+)-3-carene **3** to the α-epoxide **3a**, in the presence of $[Mn^{III}(H_2O)BW_{11}O_{39}]^{6-}$, occurred under moderate conversion with 100% selectivity. When higher conversions were obtained, this was accompanied by a loss in the selectivity.

The oxidation reactions of aromatic monoterpenes **4** and **5** are less selective than the epoxidation reactions of **1**, **2** and **3** and mixtures of benzoquinones were obtained in moderate conversion.

Acknowledgements

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