Homogeneous Catalytic Oxidation of Olefins with Hydrogen Peroxide in the Presence of a Manganese-Substituted Polyoxomolybdate

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Abstract $[PMo_{11}Mn(H_2O)O_{39}]^{5-}$ is used as catalyst in the homogeneous oxidation of *cis*-cyclooctene, cyclohexene, styrene, and geraniol with H_2O_2 in acetonitrile. Oxidation of *cis*-cyclooctene gives only cyclooctene oxide; cyclohexene-1,2-diol is the main product for cyclohexene; styrene is preferentially oxidized to benzaldehyde; a TOF almost as high as 28800 h⁻¹ is reached for geraniol oxidation.

Keywords Polyoxomolybdate · Homogeneous catalysis · Oxidation · Hydrogen peroxide · Olefins

1 Introduction

Throughout the last decades, polyoxometalates (POMs) have received much attention, since POMs represent an important family of inorganic materials with a variety of structures and composition, with unique properties for potential applications in various fields from materials science to biology and medicine [1-6]. In particular, one of the most significant domains of interest is catalysis, owing to POMs properties such as oxidative stability, adjustable

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A. M. V. Cavaleiro CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal oxidation states, possible activation of various oxidants and inherent acidity [1]. POMs have been considered as soluble analogues of metal oxides and have found applications in oxidative and acid catalysis, both in homogeneous and heterogeneous systems [7–12].

The oxidation chemistry of organic compounds aims to create value-added functionalized derivatives starting from different types of substrates, from hydrocarbons to pharmaceuticals, or from terpenes to PAHs, for instance [13, 14]. Nowadays, green and sustainable chemistry has a great impact both in the laboratory and in industry. Aqueous hydrogen peroxide is considered as one of the most attractive oxidants both from the environmental and the economical perspective, triggering the search for efficient catalysts able to activate hydrogen peroxide, since oxidants such as manganese dioxide, chromic acid, potassium dichromate or selenium dioxide are known to produce large amounts of toxic wastes, particularly when applied on an industrial scale [14, 15].

In this context, most reported work on the oxidation of organic compounds like hydrocarbons and alcohols in the presence of polyoxometalates concern studies with Keggintype lacunary and transition metal-substituted polyoxotungstates (TMSP) or mixed vanadomolybdates [PMo_{12-r} $V_x O_{40}$ ^{*n*-} [7, 9, 16]. TMSP may be viewed as complexes of transition metal ions with lacunary Keggin or Dawson anions as ligands. The mono-substituted Keggin- and Dawson-type polyoxometalates have been compared with metalloporphyrins [7]. Other related species, like trisubstituted or sandwich-type anions, have the possibility of incorporating several transition metals in their structure. Despite the known differences in redox properties of polyoxotungstates versus polyoxomolybdates, the transition metal-substituted polyoxomolybdates and their catalytic properties have been scarcely investigated [16-26]. In

these reports, substituted polyoxomolybdates with, namely, Co^{II} , Mn^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Fe^{III} , Ru^{III} , Sb^{III} , were used together with several oxidants, such as, oxygen, iodobenzene diacetate and hydrogen peroxide. To the best of our knowledge, there is only one report in homogeneous oxidation with hydrogen peroxide, using $[PMo_{11}Mn(Br)O_{39}]^{5-}$, as catalyst for the isobutyraldehyde oxidation [20]. This same anion was used in the oxidation of cumene, oct-1-ene and cyclohexene but using oxygen as oxidant [17]. Recently, the use of $Cs_5[PMo_{11}M(H_2O)O_{39}]\cdot 6H_2O$ (Co, Mn, Ni) was reported as heterogeneous catalyst in solvent-free, liquid-phase oxidation of styrene, also with hydrogen peroxide [24, 25]. The same authors studied the oxidation of alcohols catalyzed by transition metal (Co, Mn, Ni) mono-substituted Keggin-phosphomolybdates under the same conditions [26].

Following our previous work on the use of manganese(III) substituted polyoxotungstates [27–31], in the present paper we report the oxidation of several model substrates with carbon–carbon double bonds in their structure, namely *cis*-cyclooctene (1), cyclohexene (2), styrene (3) and geraniol (4), with 30 % (w/w) aqueous H_2O_2 in acetonitrile, using the tetrabutylammonium (TBA) salt of a manganese(II) substituted Keggin-type POM, TBA₄H[PMo₁₁Mn(H₂O)O₃₉]·2H₂O (TBAPMo₁₁Mn), as homogeneous catalyst. As far as one can tell, with one exception [17], there are no references concerning the use of this catalyst in the oxidation of such substrates.

2 Experimental

2.1 Reagents and Methods

Acetonitrile (Panreac), 30 % (w/w) aqueous hydrogen peroxide (Riedel de-Haën), and *cis*-cyclooctene, cyclohexene, geraniol and styrene (Aldrich) were used as received. All other solvents used herein were obtained from commercial sources and used as received or distilled and dried using standard procedures. Compound TBA₃P- $Mo_{12}O_{40}$ (**TBAPMo**₁₂) was prepared as described elsewhere [20, 32].

Elemental analysis for P, Mo and Mn were performed by ICP spectrometry (Central Laboratory of Analysis, University of Aveiro) and C, H, N elemental analysis were performed on a Leco CHNS-932 apparatus. Weight loss was determined by thermogravimetric analysis performed between 30 and 700 °C at 5 °C/min on a TGA-50 Shimadzu thermobalance. Infrared absorption spectra were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets. Powder X-ray diffraction (XRD) was performed on powders deposited on silicon substrates, using a Philips X'Pert instrument operating with Cu-K α radiation ($\lambda = 1.54178$ Å) at 40 kV/50 mA. UV–Vis and diffuse reflectance spectra were registered on a Jasco V-560 spectrometer, using MgO as reference for diffuse reflectance. Magnetic susceptibilities were measured by the Evans method, at room temperature (r.t.), with a Sherwood Scientific Magnetic Susceptibility Balance MSB-MK I, calibrated with $[HgCo(NCS)_4]$ [33]. Diamagnetic corrections were taken from Meites [34].

The GC-MS analyses were performed on a Finnigan Trace GC-MS (Thermo Quest CE instruments) using helium as the carrier gas (35 cm/s) and a quartz liner injector; GC-FID analysis were performed using a Varian Star 3900 chromatograph and helium as the carrier gas (35 cm/s) and a quartz liner injector. Fused silica capillary columns of the DB-5 type (30 m; 0.25 mm i.d.; 25 µm film thickness) were used in both cases. The chromatographic conditions were as follows: for styrene, initial temperature (90 °C); temperature rate (5 °C/min until 140 °C, then 50 °C/min); final temperature (250 °C); injector temperature (250 °C); detector temperature (270 °C); for cis-cyclooctene, initial temperature (80 °C); temperature rate (20 °C/min); final temperature (220 °C); injector temperature (250 °C); detector temperature (250 °C); for cyclohexene, initial temperature (70 °C); temperature rate (15 °C/min); final temperature (220 °C); injector temperature (250 °C) detector temperature (270 °C); for geraniol, initial temperature (100 °C); temperature rate (5 °C/min until 150 °C, then 15 °C/min); final temperature (220 °C); injector temperature (250 °C); detector temperature (250 °C).

2.2 Synthesis of TBA₄H[PMo₁₁Mn(H₂O)O₃₉] \cdot 2H₂O (TBAPMo₁₁Mn)

The compound was prepared by an adaptation of a described procedure for TBA₄[PW₁₁Mn(H₂O)O₃₉] [35]. Firstly, Na2MoO4·2H2O·(41 mmol, 10 g) and Na2HPO4 (3 mmol, 0 39 g) were dissolved in 20 mL of water, and heated for 10 min at 80-90 °C. After cooling, the pH was adjusted to 4.8 by adding, slowly and with stirring, HCl 6 M [35]. To this solution were added (at 90 °C with vigorous stirring) two aqueous solutions prepared with MnSO₄·H₂O (3 mmol, 0.51 g, in 4 mL) and K₂S₂O₈ (2 mmol, 0.41 g, in 4 mL), respectively. The resulting solution was maintained at the same temperature (90 °C) for approximately 2 h and then an aqueous solution of TBABr (20 mmol, 5 mL) was added. The immediate formation of a solid was observed, which was filtered, washed with water, ethanol and ethyl ether, and dried in a vacuum desiccator. Anal. found (%): Mo, 38.9; P, 1.17; Mn, 1.95; C, 28.0; H, 5.35, N, 2.10. Calcd. for C₆₄H₁₅₁MnMo₁₁N₄PO₄₂ (%): Mo, 37.8; P, 1.11; Mn, 1.97; C, 27.6; H, 5.20, N, 2.01. Total weight loss found: 37.9 %; calcd: 36.0 %. FT-IR (cm⁻¹): 1059(m), 1039(m), 938(s), 874(m), 821(s), 755 (s), 499(w). FT-Raman (cm⁻¹): 958, 940, 885, 597, 234. Magnetic moment at r.t.: 5.36 μ_B.

2.3 General Oxidation Procedure

The oxidation reactions of *cis*-cyclooctene (1), cyclohexene (2), styrene (3) and geraniol (4) (Table 1) were carried out in acetonitrile, in a closed 5 mL reaction

vessel equipped with a magnetic stirrer, using H_2O_2 (30 wt. % aqueous solution) as oxidant. The oxidation reactions of 1, 2 and 3 were performed at 80 °C whereas the oxidation reactions of 4 were done at r.t. and protected from light.

Table 1 Results obtained for the oxidation of olefins with H2O2 catalysed by PM011Mn

Substrate	TON ^a	Conversion (%)	Selectivity (%)				
	_	_					
PMo ₁₁ Mn ^b	426	71	100				
PMo ₁₂ ^b	252	42	100				
Without catalyst	-	7	100				
	_	_	O 2a	ОН 2b		OH 2d	OH OH 2e
PMo ₁₁ Mn ^c	142	71	6	15	16	15	48
PMo ₁₂ ^c	22	11	0	0	0	25	75
Without catalyst	-	2	100	0	0	0	0
	_	_	Ja Ba	3b		HO O J	О ОН
PMo ₁₁ Mn ^d	220	66	75	5	7	9	4
PMo ₁₂ ^d	13	4	100	0	0	0	0
Without catalyst	_	0	0	0	0	0	0
	_	_	4a			O CH ₂ OH	
PMo ₁₁ Mn ^e	183	91	95			5	
PMo ₁₁ Mn ^f	652	65	96			4	
PMo ₁₂ ¹ Without catalyst	133	13	100			0	

^a Turnover number (mol of products per mol of catalyst)

^b Reaction conditions: catalyst (5.0 μmol), CH₃CN (1.5 mL), substrate (3.0 mmol), 30 wt % H₂O₂ (3.3 mmol), 6 h at 80 °C

^c Reaction conditions: catalyst (5.0 μmol), CH₃CN (1.5 mL), substrate (1.0 mmol), 30 wt % H₂O₂ (3.0 mmol), 6 h at 80 °C

^d Reaction conditions: catalyst (3.0 μmol), CH₃CN (3.0 mL), substrate (1.0 mmol), 30 wt % H₂O₂ (4.0 mmol), 6 h at 80 °C

 e Reaction conditions: catalyst (5.0 μmol), CH_3CN (1.5 mL), substrate (1.0 mmol), 30 wt % H_2O_2 (1.0 mmol), 2 h at r.t. and in the absence of light

 $^{\rm f}$ Reaction conditions: catalyst (1.0 μ mol), CH₃CN (1.5 mL), substrate (1.0 mmol), 30 wt % H₂O₂ (1.0 mmol), 2 h at r.t. and in the absence of light





The typical procedure was as follows: to the substrate (1.0) or 3.0 mmol) and the catalyst (1.0, 3.0 or 5.0 µmol) in acetonitrile (1.0 or 3.0 mL), aqueous 30 % (w/w) H₂O₂ (1.0, 3.0, 3.3 or 4.0 mmol of H_2O_2) was added and the resulting solution stirred for the allotted time. Aliquots were taken directly from the reaction mixture and injected into the GC-FID or GC-MS equipments, using helium as the carrier gas and a quartz liner injector, for analysis of the starting materials and products. The triphenylphosphine test [36] was also used to verify the potential formation of cyclohexene hydroperoxide. However, this hydroperoxide was not detected during cyclohexene oxidation under the present conditions. The oxidation of cyclohexene was also tested i) under an argon atmosphere in a closed reactor, and ii) using 1 mmol of iodine as a radical trap. Blank reactions were performed for all the substrates in all the conditions tested.

3 Results and Discussion

The oxidative reactions of compounds 1-4 with H_2O_2 were performed in acetonitrile in the presence of catalytic amounts of **TBAPMo₁₁Mn**. The use of tetra-alkylammonium salts guarantees the adequate solubility in organic solvents [7, 8].

The prepared salt was characterized by chemical analysis. thermogravimetry, infrared, Raman and Uv/Vis spectroscopy, powder DRX and r.t. magnetic moment determination. The method used in this work for the synthesis of TBAP-Mo₁₁Mn was different from those reported for TBA salts of the $[PMo_{11}Mn(L)O_{39}]^{n-}$ anions $(L = CH_3CN, Br^- \text{ or } H_2O)$ [20, 37, 38]), but the characterization data (Sect. 2) agrees well with what has been published and are in agreement with the proposed formula. FT-IR spectra (Fig. 1-I) and FT-Raman spectra (Fig. 1-II) show the characteristic patterns of metal-substituted heteropolyanions with the Keggin structure in the region between 600 and $1,100 \text{ cm}^{-1}$ [39]. The former is identical to that reported by Combs-Walker and Hill for $[PMo_{11}Mn(CH_3CN)O_{39}]^{5-}$ in the same region [38]. The Raman spectrum presents strong bands at 958 and 940 cm⁻¹ and compares well with that reported for potassium salts [39]. The compound used in this work was found to be crystalline by powder X-ray diffraction (Fig. 1-III), crystallizing with a cubic lattice, as reported by Coronado et al. [37]. TBAPMo11Mn is isostructural with related $TBA_4H[PM_{11}M'(H_2O)O_{39}]$ salts, M = Mo, W and M' = 1st row transition metal [37, 40].

The presence of Mn^{II} in the compound was confirmed by the value of its magnetic moment at r.t. (5.36 μ_B) [34] and by the absence of d-d bands in the electronic spectra. The diffuse reflectance spectrum showed only the bands characteristic of the Keggin-type polyoxomolybdates, at 213 and 278 cm⁻¹, attributed to Mo \leftarrow O charge transfer between atoms in O-Mo-O bridges [38]. When dissolved in acetonitrile, the **TBAPMo**₁₁**Mn** visible spectrum (identical to that reported in [38]) is very similar to that obtained in the solid state, and no d-d band is observed.

 $[PMo_{11}Mn(H_2O)O_{39}]^{5-}$ The polyoxometalate (PMo11Mn) was found to be catalytically active in the oxidation of all the substrates 1-4 in the conditions used in this work (Table 1). For comparison, **TBAPM012** was also tested in the oxidation of all the substrates (Table 1), showing much less activity than PMo₁₁Mn, except in the epoxidation of cis-cyclooctene, for which the yield observed when PMo11Mn was replaced by PMo12 was about 42 % after 6 h. In the presence of PMo11Mn, ciscyclooctene was selectively oxidized to the corresponding epoxide, without the production of any by-product, at 80 °C, for a substrate/catalyst molar ratio (S/C) of 600 and H₂O₂/substrate near 1. The reaction has a rapid evolution reaching 44 % of conversion after 1 h, and 71 % of conversion after 6 h of reaction (TON = 426) (Fig. 2).

The oxidation of cyclohexene was performed with an excess of H_2O_2 because when a stoichiometric $H_2O_2/sub-$ strate molar ratio was used low conversion values (less than 10 % after 6 h of reaction) were obtained. For $H_2O_2/sub-$ substrate = 3 the conversion was 65 % after 3 h and 71 % after 6 h (Fig. 2). The major product was 1,2-cyclohexanediol (Table 1; Fig. 3), which is probably due to the epoxide ring opening; the corresponding hydroxyketone was also formed, possibly due to overoxidation of the diol. The epoxide was always a minor product. It is known that cyclohexene oxide is a very reactive epoxide, since the steric influence of the cyclohexane ring promotes ring opening of the epoxide, whereas cyclooctene oxide is one of the most stable epoxides known, since every reaction of



Fig. 2 Conversion vs time profile for the oxidation of olefins in the presence of **PMo₁₁Mn**. Reaction conditions indicated in Table 1

the epoxide group is retarded by the steric hindrance of the cyclooctane ring [41]. Some allylic oxidation was also observed with the formation of cyclohex-2-en-1-ol and the cyclohex-2-en-1-one. These two products are usually obtained when a radical mechanism is involved, typically



Fig. 3 Selectivity profile for the oxidation of cyclohexene in the presence of $PMo_{11}Mn$. Products and reaction conditions indicated in Table 1



Fig. 4 Selectivity profile for the oxidation of styrene in the presence of $PMo_{11}Mn$. Products and reaction conditions indicated in Table 1



Fig. 5 Time course for the oxidation of geraniol in the presence of $PMo_{11}Mn$ using 1.0 mmol of H_2O_2 ; substrate: 1.0 mmol; acetonitrile: 1.5 mL; at r.t. and in the absence of light; catalyst: 5.0 µmol (*filled triangle*) or catalyst: 1.0 µmol (*filled circle*)



Fig. 6 Visible spectra of **TBAPMo₁₁Mn** at the beginning (without H_2O_2) (t = 0 min) and during the reaction (t = 20-120 min). Reaction conditions: geraniol, 1.0 mmol; catalyst, 1.0 µmol; acetonitrile, 1.0 mL; aqueous 30 % (w/w) H_2O_2 , 1.0 mmol; r.t.

from an autoxidation pathway [17]. In order to confirm this, reactions in the presence of I_2 , a well-known radical scavenger, were done and no cyclohex-2-en-1-ol and cyclohex-2-en-1-one were obtained. Moreover, the major product was again 1,2-cyclohexanediol with 69 % selectivity. Additional tests, carried out under an argon atmosphere, provided the same results as in air, suggesting that the oxygen needed for the autoxidation pathway was provided by the H_2O_2 and nor by atmospheric O_2 . This type of behaviour was already observed for tungsten polyoxometalates during our previous works [27, 29, 30, 42].

Styrene is preferentially oxidized to benzaldehyde (75 % selectivity), through the cleavage of the vinylic double bond, although minor products were also observed (Table 1). The oxidation of styrene in the presence of other transition metal-substituted POMs was already reported, benzaldehyde being commonly obtained [43], but this is the first report for this **PMo**₁₁**Mn** catalyst. In this case the major product is also benzaldehyde (Fig. 4). The conversion profile for styrene is similar to those of *cis*-cyclooctene and cyclohexene, reaching almost the same conversion after 6 h; however, styrene oxidation shows the slowest kinetic profile (Fig. 2).

Geraniol is an allylic alcohol that offers several places of potential oxidative attack, namely at the two double bonds, at the allylic carbon centres, and at the carbon bonded to the hydroxyl group. In the presence of catalytic amounts of **PMo₁₁Mn** the oxidation of geraniol with H₂O₂, at r.t., affords the 2,3-epoxide as the main product with high selectivity (Table 1). The diepoxide was found as the only minor product. When using a S/C = 200 the reaction is very fast and 88 % of conversion is achieved after 15 min of reaction (Fig. 5). This corresponds to a TON of 176 and a TOF of 705 h⁻¹. At S/C = 1000, conversion after 15 min is 60 % (TON = 605 and TOF = 2420 h⁻¹).



Scheme 1 Major pathway for the formation of the epoxidation products

In both cases, leaving the reaction for 2 h has almost no influence on the obtained conversion and selectivity (Table 1). Moreover, when S/C = 1000 was used, as can be observed in Fig. 5, after only 1 min of reaction 48 % of geraniol conversion was reached, which corresponds to 480 TON and 28755 h^{-1} TOF.

When preferential epoxidation of geraniol at the C_2-C_3 position occurs, this has been explained by the formation of a complex involving the metal centre, the oxidant and the substrate, that may coordinate through the OH group [44, 45] or by the possible association of the substrate to the anion by hydrogen bonding in the close proximity of any metal centre [28]. Selective formation of the 2,3-epoxide in the oxidation of geraniol with H_2O_2 was observed before in the presence of some metal substituted polyoxotungstates [46, 47].

The visible spectra of $PMo_{11}Mn$ at the beginning, throughout, and at the end of the reactions were compared in solution (Fig. 6). No alterations were seen in the visible region of the spectra, indicating that Mn(II) is present during all the reaction time as the major species. At the end of the reaction, a drop of the reaction mixture was dried on a KBr pellet and the infrared spectrum measured in order to assess the stability of the catalyst. This FTIR spectrum (Fig. 1-Ib) of **PMo₁₁Mn** has the same pattern as the starting material. This and the absence of an induction period on the course of the reactions seem to indicate that the degradation of the present heteropolyanion is not likely.

The **PMo₁₁Mn** catalyst as was possible to see during this work, led to several kinds of products, through radical and non-radical mechanisms. Using all the information obtained with the stability studies of the catalyst and the products obtained with the several substrates we propose a major pathway for the formation of the epoxidation products (Scheme 1), in accordance to Fig. 6, thus centred on Mn(II) and involving a ligand exchange [48, 49].

4 Conclusions

This paper presents the first utilization of the Keggin-type $\mathbf{PMo_{11}Mn}$ in oxidative catalysis of unsaturated organic compounds using hydrogen peroxide as oxidant. The TBA salt of this POM was synthesized by a procedure adapted from the literature. $\mathbf{PMo_{11}Mn}$ was tested as homogeneous catalysts in the oxidation of *cis*-cyclooctene, cyclohexene, styrene, and geraniol with aqueous 30 % (w/w) H₂O₂. Globally, this catalyst shows a good performance for the oxidation of these substrates, reaching reasonable TON. In particular, $\mathbf{PMo_{11}Mn}$ shows excellent activity for geraniol oxidation, reaching 48 % of conversion, after 1 min of reaction, for S/C = 1000, giving rise to a TOF almost as

high as 28800 h^{-1} for this reaction. High selectivity (95 %) for 2,3-epoxygeraniol was found in the case of geraniol.

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