

Keggin-type polyoxotungstates as catalysts in the oxidation of cyclohexane by dilute aqueous hydrogen peroxide

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Abstract

Oxidation of cyclohexane by hydrogen peroxide in the presence of catalytic amounts of the Keggin-type heteropolytungstates $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{M}(\text{L})\text{O}_{39}]^{(7-m)-}$, M^{m+} = first row transition metal cation, $\text{L} = \text{H}_2\text{O}$ or CH_3CN , was found to produce cyclohexanol, cyclohexanone and, in certain cases, cyclohexyl hydroperoxide. The presence of the latter was demonstrated by negative chemical ionization GC-MS. The reactions were carried out in acetonitrile, using tetra *n*-butylammonium salts of the catalysts and aqueous 30% hydrogen peroxide as oxidant. The polyanions $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}]^{4-}$ showed higher catalytic activity and different selectivity for the oxidation of cyclohexane than did the corresponding Cu-, Co-, Mn- and Ni-substituted complexes. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Keggin-type heteropolyanions; Cyclohexane; Oxidation; Hydrogen peroxide; Hydroperoxide; Negative chemical ionisation

1. Introduction

The transformation of hydrocarbons into oxygenated derivatives has been extensively investigated over the last decades because such products are valuable intermediates for organic synthesis both in the laboratory and in industry [1–3]. Industrial oxidation processes are often not selective. This is the case for the catalytic oxidation of cyclohexane with air in the presence of cobalt or manganese salts to give cyclohexanone and cyclohexanol as main products, a reaction which may produce up to 100 other

compounds [4,5]. Thus, at present, one of the goals of studying metal complex catalysis is to find new efficient systems that oxidise organic compounds with high selectivity, preferably with cheap, environmentally friendly oxidants such as air or hydrogen peroxide.

As an oxidant, hydrogen peroxide has a high (47%) active oxygen content, is widely available and its by-product is water. Therefore, its chemistry is considered to be environmentally innocuous. Unfortunately, as with oxygen itself, this oxidant generally exhibits one of the most complex and minimally controllable oxidation chemistry of all the potentially attractive oxidants [6]. With respect to other oxidants, the

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major disadvantage of H_2O_2 is its instability with respect to decomposition into oxygen and water, a process that can be accelerated in the presence of metal complexes [7,8]. Most common first row transition metal ions in aqueous solution catalyse this decomposition of H_2O_2 [7,8].

Oxidation of hydrocarbons with hydrogen peroxide or molecular oxygen catalysed by transition metal polyoxometalates is potentially a method for obtaining value-added products from comparatively cheap starting materials [9,10]. In particular, transition metal mono-substituted Keggin-type heteropolytungstates, $[\text{XW}_{11}\text{MO}_{39}]^{(n-m)-}$ ($\text{X} = \text{P}, \text{Si}, \text{B}$), in which a transition metal cation, M^{m+} , is co-ordinated to the binding sites of lacunary heteropolyanions $[\text{XW}_{11}\text{O}_{39}]^{n-}$, have generated substantial interest as oxidative catalysts. This is because of their thermal and chemical stability and the range of possibilities for their modification without affecting the Keggin-type primary structure [11–13]. These metal-substituted heteropolytungstates bear many similarities to metal complexes of macrocyclic ligands as, for example, with metalloporphyrins and related species, because they possess rigid co-ordination sites surrounding a metal centre [14–16]. As well as the robust nature of the polyoxometalate ligands and their resistance to oxidation, the possibility of working with these species in both polar and nonpolar solvents [15,17] can lead to valuable applications in catalysis [9,10].

Some transition metal mono-substituted heteropolyanions have been used for catalytic oxidation of alkenes using hydrogen peroxide [10,18–20], molecular oxygen [21,22] or iodosylbenzene [10,23] and other oxygen donors. Also, they have been used for hydroxylation of alkanes with molecular oxygen [10,24] or with *tert*-butyl hydroperoxide [10,25,26]. In the present work, the use of the α -isomers of the heteropolytungstates $[\text{PW}_{11}\text{O}_{39}]^{7-}$ and $[\text{PW}_{11}\text{MO}_{39}]^{(7-m)-}$ (abbreviated PW_{11} and PW_{11}M , respectively) is reported for oxidation of cyclohexane with hydrogen peroxide.

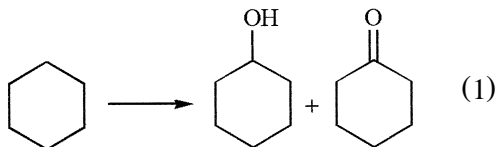
2. Results and discussion

The tetrabutylammonium (TBA) salts, $(\text{TBA})_4\text{H}_x[\text{PW}_{11}\text{M}(\text{L})\text{O}_{39}] \cdot n\text{H}_2\text{O}$, $\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{III}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$, $\text{L} = \text{H}_2\text{O}$ or absent, used in this work have been prepared previously [10]. Their synthesis generally involves metathetical exchange of a cation by addition of TBA bromide to an aqueous solution of the potassium or sodium salts of the heteropolyanion, which can be obtained in pure form by several methods [27,28]. Direct synthesis, without prior isolation of sodium or potassium salts, is possible and has been described in the preparation of the $\text{Mn}(\text{II})$ salt [29]. In the present work, the required compounds were made by direct synthesis, starting from an aqueous solution of the required anion prepared *in situ* [27], to which was added a solution of TBA bromide. This method is less time consuming and gives higher yields with no loss of purity, as determined by elemental and thermogravimetric analysis, infrared spectroscopy and powder X-ray diffraction methods. A single recrystallization from acetonitrile is usually sufficient for final purification. This method also gave good results for the synthesis of $(\text{TBA})_4\text{H}_3\text{-}[\text{PW}_{11}\text{O}_{39}]$, although the latter has now been prepared by a process which needs no recrystallization [30]. Dissolution of these TBA salts in acetonitrile may lead to partial replacement of any H_2O coordinated to M by a solvent molecule [15,17]. The extent of this replacement depends on the metal M and on the proportions of H_2O and CH_3CN . For this reason, the ligand L has been omitted from the formulae of the complexes.

The results discussed below were obtained for the oxidation of cyclohexane with hydrogen peroxide as a 30 wt.% solution in water, in the presence of a heteropolytungstate catalyst (PW_{11} or PW_{11}M). Although the heteropolyanions reported are described as the catalysts, it is possible that, in some cases, the active materials were different from the initial compounds put into the reaction mixtures. The nature of the

actual catalysts is under active investigation. Any excess of H_2O_2 used in these oxidation reactions was calculated on the basis that two mole proportions of H_2O_2 are necessary to produce one mole proportion of cyclohexanone or two mole proportions of cyclohexanol.

The results for oxidation of cyclohexane in acetonitrile with PW_{11}M ($\text{M} = \text{Cu}, \text{Co}, \text{Mn}$ or Ni) are summarised in Table 1. With any one of these four heteropolyanions as catalyst, only cyclohexanol and cyclohexanone were formed; no other products were detected by GC analysis (Eq. (1)).



For $\text{M} = \text{Cu}, \text{Co}$ or Mn , conversions of cyclohexane of between 5 and 11% were observed (entries 1–3). In the case of Ni , the conversion of cyclohexane rose to 20% (entry 4). With no catalyst present, the conversion was 1%. The ratio of cyclohexanol to cyclohexanone observed for these reactions varied from 1.7:1 for PW_{11}Cu to 0.25:1 for PW_{11}Ni .

Typical results with PW_{11} and PW_{11}Fe are listed in Table 2. Cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide were obtained (Eq. (2)). Generally, the conversion of cyclohexane into oxidised products was much more

efficient than was found for the catalysts listed in Table 1. With $\text{M} = \text{Fe}$, conversion of cyclohexane is more complete and becomes highly selective to the formation of hydroperoxide (entry 3). The lacunary heteropolyanion (PW_{11}) also gave cyclohexyl hydroperoxide (entry 9) but only as a minor product, cyclohexanone being the major one.

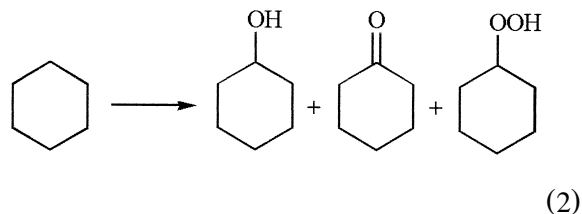


Fig. 1 shows the time course of reaction for the oxidation of cyclohexane with H_2O_2 catalysed by the Fe complex. Cyclohexyl hydroperoxide begins to appear from the very beginning of reaction and its yield is always greater than that of either cyclohexanol or cyclohexanone. When the reaction was left for more than 9 h under reflux, a much higher conversion was observed (96% after 10 h). Unfortunately, this extended reaction gave a very complex product mixture and there was a significant loss in selectivity.

To evaluate the possible effect of either oxygen or light on the reaction catalysed by PW_{11}Fe , experiments were conducted, (a) under a nitrogen atmosphere and (b) in the dark (entries 4 and 5 of Table 2, respectively). When the oxida-

Table 1

Oxidation of cyclohexane by H_2O_2 catalysed by heteropolytungstates PW_{11}Cu , PW_{11}Co , PW_{11}Mn and PW_{11}Ni ^a

	H_2O_2 (mmol)	Heteropolyanion (mmol)	Conversion (%) ^b	Products (%) ^c		
				CyOH	CyONE	CyOH/CyONE
1	29.4	$(\text{TBA})_4\text{HPW}_{11}\text{CuO}_{39}$ (0.040)	11	7	4	1.7
2	39.2	$(\text{TBA})_4\text{HPW}_{11}\text{Co}(\text{H}_2\text{O})_{39} \cdot 2\text{H}_2\text{O}$ (0.038)	5	3	2	1.5
3	39.2	$(\text{TBA})_4\text{HPW}_{11}\text{Mn}(\text{H}_2\text{O})_{39} \cdot 3\text{H}_2\text{O}$ (0.038)	8	3	5	0.6
4 ^d	39.2	$(\text{TBA})_4\text{HPW}_{11}\text{Ni}(\text{H}_2\text{O})_{39} \cdot \text{H}_2\text{O}$ (0.039)	20	4	16	0.25

^aUnless otherwise stated, reactions were performed by stirring the substrate (18.5 mmol) in acetonitrile (10 ml) under reflux for 12 h.

^bBased on gas chromatographic peak areas.

^cExpressed as a percentage of the total products formed; CyOH = cyclohexanol; CyONE = cyclohexanone.

^dExperiment carried out with 9.3 mmol of substrate.

Table 2

Oxidation of cyclohexane by H_2O_2 catalysed by PW_{11} and $\text{PW}_{11}\text{Fe}^a$

	Heteropolyanion (mmol)	Time (h)	Conversion (%) ^b	Products (%) ^c		
				CyOH	CyONE	CyOOH
1 ^d	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.042)	12	0	–	–	–
2	no catalyst added	12	1	trace	trace	trace
3	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.042)	9	76	6	13	57
4 ^e	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.042)	8	73	6	11	56
5 ^f	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.043)	9	82	6	18	58
6 ^g	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.041)	21	1	trace	trace	trace
7 ^h	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.043)	10	16	1	2	13
8 ⁱ	$(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39} \cdot 2\text{H}_2\text{O}$ (0.041)	12	0	–	–	–
9	$(\text{TBA})_4\text{H}_3\text{PW}_{11}\text{O}_{39}$ (0.039)	12	35	8	21	6

^aUnless otherwise stated, reactions were performed by stirring the substrate (18.5 mmol) and H_2O_2 (30 wt.% solution in water; 39.2 mmol) in acetonitrile (10 ml) at 80°C.

^bBased on gas chromatographic peak areas.

^cExpressed as a percentage of the total products formed; CyOH = cyclohexanol; CyONE = cyclohexanone; CyOOH = cyclohexyl hydroperoxide.

^dNo H_2O_2 was added.

^eExperiment under a N_2 atmosphere.

^fExperiment carried out in the dark.

^gExperiment carried out at room temperature under a N_2 atmosphere, with 29.4 mmol of 30% H_2O_2 .

^hExperiment carried out at 60°C.

ⁱExperiment carried out with 18 mmol of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger.

tion was conducted under a N_2 atmosphere, a similar result to that in air was obtained (compare entry 4 with that of entry 3). Therefore, the possibility of auto-oxidation may be excluded. The dark reaction (entry 5) yielded 58% of cyclohexyl hydroperoxide after 9 h of reaction. In each case, after 10–12 h of reaction at 80°C, a rapid decrease in selectivity was observed. There was almost no reaction at room temperature (entry 6) and the conversion of cyclohexane was much less when the reaction was carried out at less than 80°C (16% of conversion after 10 h, entry 7).

Oxidation of cyclohexane by H_2O_2 catalysed by PW_{11}Fe appears to be a radical process because addition of 2,6-di-*tert*-butyl-4-methylphenol, a radical scavenger, inhibited the formation of any product of cyclohexane oxidation (entry 8).

The decomposition of H_2O_2 during reaction was monitored by titration of aliquots with ceric sulphate (Fig. 2). Decomposition of H_2O_2 was rapid and complete in the presence of PW_{11}Cu (< 60 min) and PW_{11}Mn (< 240 min). In the

case of PW_{11}Co , the rate of decomposition of H_2O_2 was only moderate and 25% of the added hydrogen peroxide was present after 6 h. Both PW_{11}Ni and PW_{11}Fe were even gentler in that,

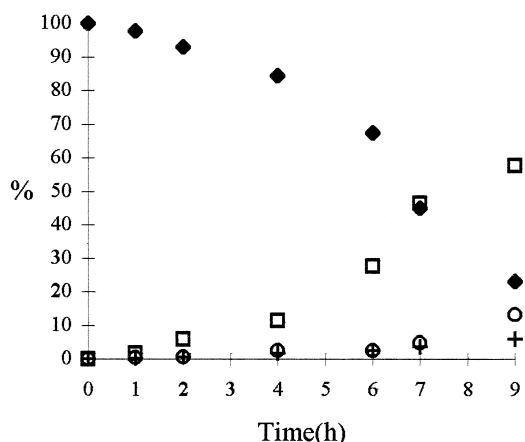


Fig. 1. Time course of the oxidation of cyclohexane with H_2O_2 catalysed by $(\text{TBA})_4\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})_{39} \cdot 2\text{H}_2\text{O}$. (◆) Cyclohexane, (+) Cyclohexanol, (○) Cyclohexanone, (□) Cyclohexyl hydroperoxide. Substrate (18.5 mmol); catalyst (0.042 mmol); H_2O_2 30% (29.4 mmol at the beginning and more 9.8 mmol after 6 h of reaction); acetonitrile (10 ml); 9 h stirring at 80°C.

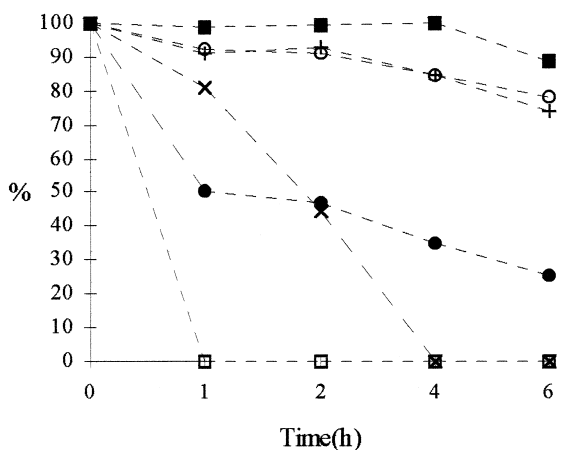


Fig. 2. Time dependence of the concentration of $\text{H}_2\text{O}_2 + \text{CyOOH}$ in the presence of: (■) PW_{11} (0.040 mmol); (+) PW_{11}Fe (0.039 mmol); (○) PW_{11}Ni (0.039 mmol); (●) PW_{11}Co (0.040 mmol); (×) PW_{11}Mn (0.039 mmol); (□) PW_{11}Cu (0.039 mmol); (cyclohexane, 18.5 mmol; H_2O_2 30%, 29.4 mmol; acetonitrile, 10 ml; 80°C).

after 6 h, about 60–80% of the original hydrogen peroxide remained. As described earlier, decomposition of H_2O_2 was virtually absent in the presence of the unmetallated PW_{11} heteropolyanion [31]. At the end of reactions, the total of unused H_2O_2 and hydroperoxide produced was estimated by titration with ceric sulphate. From the yields of hydroperoxide (and cyclohexanol and cyclohexanone) determined by gas chromatography, the amount of H_2O_2 used in the reaction could be determined. For the active PW_{11}Fe , PW_{11} catalysts, the efficiency of usage of H_2O_2 was very high and approaching 100%.

The decomposition of H_2O_2 in the presence and absence of cyclohexane was also examined. Decomposition was generally faster in the absence of cyclohexane than in its presence. Except for PW_{11}Cu , cyclohexane appears to suppress or minimize the undesirable decomposition of H_2O_2 .

A most striking property of cyclohexyl hydroperoxide is its stability in comparison with other hydroperoxides. Cyclohexyl hydroperoxide has been isolated from aerial oxidation of cyclohexane [32] and has been prepared by

slow addition of Grignard reagents to oxygen at -70°C [33,34]. Its stability is worth noting because this is a secondary peroxide and as such could be expected to undergo ready dehydration. At 70°C , cyclohexyl hydroperoxide was not decomposed in benzene solution after 270 h; it apparently decomposes only slowly at 150°C [32]. When reduced with aqueous solution of ferrous sulphate, it is converted into 62.3 mol% of cyclohexanol and 37.4 mol% of cyclohexanone. Reduction with hydrogen in the presence of platinum oxide produces substantially pure cyclohexanol in high yield [32].

Cyclohexanone and cyclohexanol were identified unambiguously by FID gas chromatography by comparison with authentic standards and by gas chromatography-mass spectrometry. An additional compound having m/z 116 as its molecular ion during GC-MS was suspected of being cyclohexyl hydroperoxide, although it has been stated that this compound totally decomposes during gas chromatography [35,36]. The hydroperoxide was identified by several methods: (1) in a reaction typical of a hydroperoxide, it was reduced with triphenylphosphine [37] to give cyclohexanol and, (2) GC-MS with methane negative ion ionization and tandem mass spectrometry provided an identification. The negative ion spectrum showed peaks at m/z 115, m/z 99, m/z 46 and m/z 33, which were identified as the $[\text{M}-\text{H}]^-$ and fragment ions $\text{C}_6\text{H}_{11}\text{O}^-$, CH_2O_2^- and HO_2^- , respectively. Tandem mass spectrometry of the $[\text{M}-\text{H}]^-$ ion at m/z 115 gave two decomposition products at m/z 99 (loss of O^-) and m/z 33 (O_2H^-), reinforcing the conclusions presented above.

3. Experimental

Elemental analyses for P, W and M were performed by ICP spectrometry (University of Aveiro, Central Laboratory of Analysis). Hydration water contents were determined by thermogravimetric analysis on a Mettler M3 ther-

mobalance equipped with a TC 10A microprocessor.

3.1. Catalysts synthesis (general procedure)

$(\text{TBA})_4\text{H}_x[\text{PW}_{11}\text{M}(\text{H}_2\text{O})\text{O}_{39}] \cdot n\text{H}_2\text{O}$: an aqueous solution of the anion $[\text{PW}_{11}\text{M}(\text{H}_2\text{O})\text{O}_{39}]^{(n-m)-}$ was prepared by mixing Na_2HPO_4 (9.1 mmol), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (100 mmol) and the nitrate salt of M (12 mmol) in 200 ml of water and adjusting the pH to 4.8, as described [27]. An aqueous solution of TBA bromide (45 mmol) in 20 ml was added dropwise, with stirring, at 80–85°C. The solid which formed was filtered off and recrystallized from acetonitrile. In this recrystallization some insoluble material is separated and the salt precipitated by addition of water (1:1). In the case of the iron-substituted compound, a few drops of nitric acid were added to the acetonitrile solution so as to turn the solution from green to yellow (conversion of the dimeric to monomeric anion).

$(\text{TBA})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$: this was prepared similarly, except for the addition of the salt of M.

$(\text{TBA})_4\text{H}[\text{PW}_{11}\text{CuO}_{39}]$: to a solution of $\text{K}_5[\text{PW}_{11}\text{Cu}(\text{H}_2\text{O})\text{O}_{39}] \cdot n\text{H}_2\text{O}$ [27] (10^{-3} mol in 50 ml) at 70°C was added slowly an excess of TBA bromide (5×10^{-3} mol in 25 ml). After filtration of the solid product, the precipitate was washed with water and absolute ethanol.

The following compounds were prepared:

$\alpha\text{-}[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Mn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 3\text{H}_2\text{O}$. Anal. Found: W, 51.5; P, 0.80; Mn, 1.28; C, 21.02; H, 4.01; N, 1.41; hydration H_2O , 1.3. Calcd.: W, 53.6; P, 0.82; Mn, 1.46; C, 20.36; H, 4.09; N, 1.48; hydration H_2O , 1.43.

$\alpha\text{-}[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot 2\text{H}_2\text{O}$. Anal. Found: W, 53.3; P, 0.81; Co, 1.49; C, 20.23; H, 3.92; N, 1.36; hydration H_2O , 0.9. Calcd.: W, 53.8; P, 0.82; Co, 1.57; C, 20.44; H, 4.05; N, 1.49; hydration H_2O , 0.96.

$\alpha\text{-}[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{Ni}(\text{H}_2\text{O})\text{O}_{39}] \cdot \text{H}_2\text{O}$. Anal. Found: W, 53.0; P, 0.81; Ni, 1.53; C,

20.97; H, 3.97; N, 1.62; hydration H_2O , 0.5. Calcd.: W, 54.0; P, 0.83; Ni, 1.57; C, 20.54; H, 4.01; N, 1.50; hydration H_2O , 0.48.

$\alpha\text{-}[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}[\text{PW}_{11}\text{CuO}_{39}]$. Anal. Found: W, 54.6; P, 0.80; Cu, 1.56; C, 21.04; H, 3.97; N, 1.43. Calcd.: W, 54.5; P, 0.83; Cu, 1.71; C, 20.71; H, 3.94; N, 1.51.

$\alpha\text{-}[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{PW}_{11}\text{Fe}(\text{H}_2\text{O})\text{O}_{39}] \cdot 2\text{H}_2\text{O}$. Anal. Found: W, 53.6; P, 0.88; Fe, 1.48; C, 20.15; H, 3.90; N, 1.35; hydration H_2O , 0.8. Calcd.: W, 53.8; P, 0.82; Fe, 1.49; C, 20.46; H, 4.02; N, 1.49; hydration H_2O , 0.96.

$\alpha\text{-}[(\text{C}_4\text{H}_9)_4\text{N}]_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$. Analysis in agreement with literature values [30].

3.2. Methods and reagents

For analysis of the products of cyclohexane oxidation, FID gas chromatography (GC; Carlo Erba 6130; capillary column: DB-5, 30 m \times 0.25 mm i.d., hydrogen as carrier gas) and gas chromatography-mass spectrometry (GC-MS; Hewlett Packard 5890-MSD 5970 operating in the electron ionisation mode at 70 eV; capillary column: DB-5, 30 m \times 0.25 mm i.d., helium as carrier gas) with injector at 200°C and oven increasing temperature (40–220°C) were used.

Negative CI mass spectra and tandem mass spectra were acquired with a VG AutoSpecQ (Micromass, UK). Methane was used as the CI reagent gas at pressures of 5×10^{-4} mbar. The source temperature was maintained at 220°C. Samples were introduced via the GC probe. Tandem mass spectra were acquired by selecting the desired ion and colliding it at 8 kV with sufficient Ar in the collision cell as to reduce the selected ion intensity by approximately 50%. The resulting product ions were measured. Data acquisition was carried out with a VG OPUS 2.1C system, interfaced to the mass spectrometer by a VG SIOS unit.

For determination of H_2O_2 , the sample was dissolved in dilute sulphuric acid cooled with ice and the peroxides were titrated against 0.1 N ceric sulphate solution, using ferroin as indicator [38].

The following commercially available reagents were used without further purification: 2,6-di-*tert*-butyl-4-methylphenol (Sigma, 99%), acetonitrile (Lab-Scan, HPLC grade), cyclohexane (Riedel de Haën, Pro Analysis), H₂O₂ (Riedel de Haën, 30 wt.% solution in water), cyclohexanone and cyclohexanol (Merck, Pro Analysis).

3.3. General oxidation procedure

A typical oxidation procedure was as follows. The chosen heteropolytungstate (0.038–0.043 mmol), cyclohexane (2 ml, 18.5 mmol) and H₂O₂ (30 wt.% solution in water, 3 ml, 29.4 mmol) were placed in a two-necked flask and acetonitrile (10 ml) added. The resulting mixture was stirred and heated at 80°C. After 6 h stirring, more H₂O₂ (30 wt.% solution, 1 ml, 9.8 mmol) was added. At regular intervals, an aliquot was taken directly from the reaction mixture by a microsyringe and injected into the GC or GC-MS for analysis of starting material and products.

The same oxidation procedure was carried out for the determination of just the decomposition of H₂O₂ itself in the reaction mixture. At regular intervals, an aliquot taken directly from the reaction mixture was weighed and titrated against ceric sulphate.

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