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Oxidation of cycloalkanes with hydrogen peroxide in the presence of Keggin-type polyoxotungstates

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Abstract

The catalytic homogeneous oxidation of cyclohexane and cyclooctane in acetonitrile with hydrogen peroxide in the presence of the tetrabutylammonium salts of Keggin-type polyoxotungstates $[XW_{11}O_{39}]^{n-}$ and $[XW_{11}MO_{39}]^{(n-m)-}$ (X = P, Si, B and M^{III} = Fe, Mn) afforded substantial amounts of the corresponding alkyl hydroperoxides. The cyclododecane oxidation reactions only gave rise to the alcohol and ketone. Under the used reaction conditions, high turnover numbers were obtained, reaching 614 in the cyclooctane oxidation after 9 h of reaction. These oxidation reactions appear to be radical processes, since they were totally inhibited in the presence of 2,6-di-*tert*-butyl-4-methylphenol or I_2, two well-known radical scavengers.

Keywords: Cyclohexane; Cyclooctane; Cyclododecane; Oxidation; Hydrogen peroxide; Polyoxotungstates; Polyoxometalates

1. Introduction

The transformation of hydrocarbons into oxygenated compounds has been extensively investigated over the last decades, because the products are valuable intermediates for organic synthesis [1–4]. The low selectivity is one problem related with these processes and, in the case of cyclohexane oxidation, the conversion is usually limited to 3–4% in order to achieve high selectivity to a ketone/alcohol mixture [5].

The Keggin anions and their derivatives have been used as catalysts for various types of oxidative reactions, like the epoxidation of alkenes and the hydroxylation of alkanes [6–9]. In particular, transition metal mono-substituted Keggin-type heteropolytungstates, α-$[XW_{11}MO_{39}]^{(n-m)-}$ (X = P, Si), in which a transition metal cation, M^{m+}, is coordinated to the binding sites of lacunary heteropolyanion α-$[XW_{11}O_{39}]^{n-}$, have generated great interest as oxidative catalysts. This is mainly due to their thermal and chemical stability and to the range of possibilities for their modification, without affecting the Keggin-type primary structure [10,11]. These metal-substituted heteropolytungstates bear many similarities with metal complexes of macrocyclic ligands like, for example, metalloporphyrins and related species, because they possess rigid coordination sites surrounding a metal centre [12]. Some transition metal mono-substituted polyoxotungstates have been used for catalytic oxidation of alkanes with molecular oxygen or with *tert*-butyl-hydroperoxide [7,8].

The use of aqueous hydrogen peroxide in the oxidation of organic substrates is considered to be very attractive from the point of view of synthetic organic chemistry, since diluted aqueous H_2O_2 is cheap, environmentally clean and easy to handle [13,14].

2. Objectives

We report here our recent studies on the oxidation of cyclohexane, cyclooctane and cyclododecane with aqueous hydrogen peroxide, in acetonitrile, catalysed by mono-substituted transition metal-substituted heteropolytungstates $[XW_{11}M(H_2O)O_{39}]^{(n-m)-}$ $[XW_{11}M]$ and the corresponding lacunary anions $[XW_{11}O_{39}]^{n-}$ $[XW_{11}]$ (X = P, Si, B and M = Mn^{III}, Fe^{III}), as tetrabutylammonium salts.

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Table 1
Oxidation of cyclohexane with H_2O_2 catalysed by polyoxotungstates[a]

	Catalyst (mmol)	Time (h)	Conversion (%)[b]	Turnover number[c]	Selectivity (%)[b]		
					Cyclohexanol ($C_6H_{11}OH$)	Cyclohexanone ($C_6H_{10}O$)	Cyclohexyl hydroperoxide $C_6H_{11}OOH$)
1	$PW_{11}Fe$ (0.042)	9	76	334	8	17	75
2[d]	$PW_{11}Fe$ (0.041)	21	1	–	Trace	Trace	Trace
3[e]	$PW_{11}Fe$ (0.043)	10	16	69	6	13	81
4[f]	$PW_{11}Fe$ (0.042)	8	73	322	8	15	77
5	PW_{11} (0.039)	12	35	166	23	60	17
6[g]	$FeCl_3{\cdot}6H_2O$ (0.52)	5	0	–	–	–	–
7	No catalyst	12	1	–	Trace	Trace	Trace

[a] Unless 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.

[b] Based on the gas chromatographic peak areas.

[c] mmol of products/mmol of catalyst.

[d] Experiment carried out at room temperature.

[e] Experiment carried out at 60 °C.

[f] Experiment under a N_2 atmosphere.

[g] Experiment carried out with 29.4 mmol of 30% H_2O_2.

3. Experimental

Tetrabutylammonium salts of the required polyoxotungstates were prepared by known procedures [15–17]. Reaction conditions used in the catalytic studies are presented in Tables 1–3. Aqueous hydrogen peroxide (30 wt.%) was used and added at the beginning of each reaction. For the products analysis, FID gas chromatography and GC–MS (capillary column: DB-5, 30 m × 0.25 mm i.d., 0.25 μm film thickness) were used.

The chromatographic conditions were as follows: for cyclohexane oxidation reactions, initial temperature (40 °C, 4 min), temperature rate (10 °C/min), final temperature (200 °C, 2 min), injector temperature (220 °C), detector temperature (230 °C); for cyclooctane oxidation reactions, initial temperature (80 °C, 2 min), temperature rate (20 °C/min), final temperature (220 °C, 2 min), injector temperature (250 °C), detector temperature (250 °C); for cyclododecane oxidation reactions, initial temperature (120 °C), temperature rate (10 °C/min), final temperature (230 °C, 10 min), injector temperature (250 °C), detector temperature (250 °C). The conversion and selectivity values were based on the chromatographic peak areas. In the case of cyclooctane, the conversion values were checked by addition of an internal standard (chlorobenzene) at the end of the reaction. Identical results were obtained by the two methods.

For determination of H_2O_2, the sample was dissolved in dilute sulphuric acid (cooled with ice) and the peroxides were titrated against 0.1N ceric sulphate solution, using ferroin as the indicator [18].

Cyclohexanone, cyclohexanol, cyclooctanone, cyclooctanol, cyclododecanone and cyclododecanol were identified by FID gas chromatography by comparison with authentic standards and by gas chromatography–mass spectrometry. The cyclohexyl and the cyclooctyl hydroperoxides were identified by GC–MS with methane negative ion ionisation and tandem mass spectrometry [19]. Other possible reaction products detectable by GC were not observed. In the case of cyclohexane, the absence of carboxylic acids as possible products in the final reaction mixture was confirmed. This was carried out by attempted esterification with diazomethane.

Table 2
Oxidation of cyclooctane with H_2O_2 catalysed by polyoxotungstates[a]

	Catalyst	Time (h)	Conversion (%)[b]	Turnover number[c]	Selectivity (%)[b]		
					Cyclooctanone ($C_8H_{14}O$)	Cyclooctanol ($C_8H_{15}OH$)	Cyclooctyl hydroperoxide ($C_8H_{15}OOH$)
1	$PW_{11}Fe$	9	92	614	35	7	58
2	$PW_{11}Mn$	12	93	620	47	10	43
3	PW_{11}	12	80	534	48	7	45
4	$SiW_{11}Fe$	12	79	527	44	9	47
5	$SiW_{11}Mn$	12	89	594	52	25	23
6	SiW_{11}	12	63	420	60	9	31

[a] Reaction conditions—catalyst: 1.5 μmol; cyclooctane: 1 mmol; H_2O_2: 2 mmol; reflux in acetonitrile (1.5 ml).

[b] Based on the gas chromatographic peak areas.

[c] mmol of products/mmol of catalyst.

Table 3
Oxidation of cyclododecane with H_2O_2 catalysed by Fe substituted polyoxotungstates[a]

	Catalyst (mmol)	Time (h)	H_2O_2 (mmol)	Conversion (%)[b]	Turnover number[c]	Selectivity (%)[b]	
						Cyclododecanone ($C_{12}H_{22}O$)	Cyclododecanol ($C_{12}H_{23}OH$)
1[d]	$PW_{11}Fe$ (0.005)	7	6	49	98	44	39
2	$BW_{11}Fe$ (0.005)	12	6	15	30	67	33
3	$SiW_{11}Fe$ (0.005)	12	6	21	42	53	47
4	$BW_{11}Fe$ (0.0015)	12	4	27	180	76	24
5	$SiW_{11}Fe$ (0.0015)	12	4	9	60	54	46
6[e]	$BW_{11}Fe$ (0.0015)	9	2	55	366	63	37

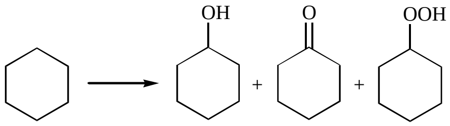
[a] Unless otherwise stated, reactions were performed by stirring the catalyst, the substrate (1 mmol) and H_2O_2 (30 wt.% solution in water) in acetonitrile (5 ml) at 80 °C.

[b] Based on the gas chromatographic peak areas.

[c] mmol of products/mmol of catalyst.

[d] After 24 h of reaction, the chromatogram showed several peaks, although $C_{12}H_{22}O$ and $C_{12}H_{23}OH$ were the major ones.

[e] Reaction carried out in 3 ml of acetonitrile.



Scheme 1.

4. Results

Typical results obtained in the oxidation of cyclohexane with H_2O_2 in the presence of PW_{11} and $PW_{11}Fe$ are summarised in Table 1 [15]. With these catalysts, cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide were obtained as the reaction products (Scheme 1). The best conversion of cyclohexane, accompanied by a highly selective formation of cyclohexyl hydroperoxide, which appeared from the very beginning of the reaction (Fig. 1), was obtained with $PW_{11}Fe$ at 80 °C (entry 1). From Table 1, it can also be observed that almost no reaction occurred at room temperature (entry 2) and a low conversion (16% after 10 h) was found when the reaction was carried out at 60 °C (entry 3).

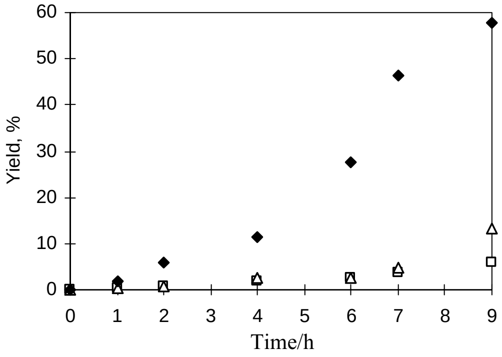


Fig. 1. Time course of the oxidation of cyclohexane with H_2O_2 catalysed by $PW_{11}Fe$ (0.005 mmol). Reaction was performed by stirring the substrate (18.5 mmol) and H_2O_2 (30 wt.% solution in water; 39.2 mmol) in acetonitrile (10 ml) at 80 °C. Yield of: (□) cyclohexanol, (△) cyclohexanone and (◆) cyclohexyl hydroperoxide.

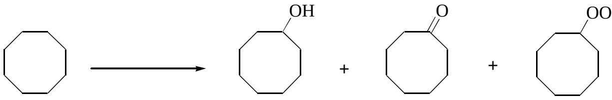
To evaluate the possible effect of oxygen on the reaction catalysed by $PW_{11}Fe$, experiments were performed under a nitrogen atmosphere (entry 4). Under this condition or under normal air working conditions similar results were obtained (compare entries 4 and 1). Therefore, the possibility of auto-oxidation may be excluded. When the reaction was carried out with an iron salt ($FeCl_3$), no reaction products were obtained (entry 6).

The oxidation of cyclohexane in the presence of the lacunary heteropolyanion PW_{11} afforded cyclohexanone as the main product, followed by cyclohexanol and cyclohexyl hydroperoxide as the minor ones (entry 5). For both $PW_{11}Fe$ and PW_{11}, the efficiency of H_2O_2 utilisation was very high, approaching 100%.

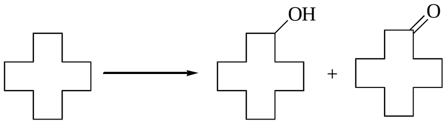
When the oxidation of cyclohexane with hydrogen peroxide was carried out in the presence of $BW_{11}Fe$, the same products were obtained. With this catalyst, turnover numbers higher than 1000, high efficiency of H_2O_2 utilisation (65%) and formation of cyclohexyl hydroperoxide as the main product were found [20].

The oxidation of cyclooctane with hydrogen peroxide in the presence of the P and Si polyoxotungstates afforded also the corresponding alcohol, ketone and hydroperoxide (Scheme 2). The results showing the selectivity and the turnover numbers obtained for the cyclooctane oxidation are summarised in Table 2.

All catalysts gave rise to high percentages of conversion, between 63 and 93%, reaching turnover numbers higher than 600 for $PW_{11}Fe$ and $PW_{11}Mn$. In the course of the reactions it was found that all three products appeared from the beginning of the reaction. The best selectivity for the cyclooctyl hydroperoxide was obtained with $PW_{11}Fe$



Scheme 2.



Scheme 3.

(entry 1). With catalysts $PW_{11}Mn$, PW_{11} and $SiW_{11}Fe$, almost identical selectivity for the cyclooctanone and the cyclooctyl hydroperoxide was obtained (entries 2–4). The cyclooctanone was obtained as the main product when $SiW_{11}Mn$ and SiW_{11} were used (entries 5 and 6). It is worth mentioning that these results on the oxidation of cyclooctane seem to be very promising when compared with others recently published, in which the same products were obtained, but with much lower turnover numbers [21,22]. Results obtained with the boron polyoxotungstates were presented elsewhere [20].

Cyclododecane oxidation with hydrogen peroxide gave rise only to the corresponding alcohol and ketone (Scheme 3) in the conditions tested (Table 3). $PW_{11}Fe$ originated 49% of cyclododecane conversion after 7 h, against 15 or 21% in the case of $BW_{11}Fe$ or $SiW_{11}Fe$, after 12 h, respectively, for a substrate/catalyst ratio = 200. In the case of a higher ratio substrate/catalyst (666), $BW_{11}Fe$ showed 27% of conversion, whereas $SiW_{11}Fe$ gave only 9%. The best result was obtained with $BW_{11}Fe$ for the ratio substrate/catalyst = 666, using 3 ml of acetonitrile. In these conditions, 55% of conversion and 366 turnovers were obtained, after 9 h of cyclododecane oxidation. As far as we know, there are no previous reports on the use of polyoxotungstates and hydrogen peroxide in the oxidation of cyclododecane.

We have also observed that in the presence of 2,6-di-*tert*-butyl-4-methylphenol or I_2, well-known radical scavengers, no products were obtained during the oxidation of the cycloalkanes studied. This result indicates that we are in the presence of radical processes.

5. Conclusions

The oxidation of cyclohexane with H_2O_2 was efficiently catalysed by some Keggin-type polyoxotungstates providing substantial amounts of cyclohexyl hydroperoxide with high percentages of conversion, in acetonitrile, at 80 °C. The same type of products were formed when cyclooctane was oxidised in the presence of the studied polyoxotungstates. The conditions were tested to get high turnover numbers, reaching 614 after 9 h for cyclooctane oxidation reaction. Cyclododecane gave only alcohol and ketone in the conditions tested. Oxidation of cycloalkanes with hydrogen peroxide catalysed by the polyoxotungstates tested appeared to be a radical process, because addition of known radical scavengers inhibited the formation of any product of cycloalkane oxidation.

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