Photocatalyzed Oxidation of Cyclohexene and Cyclooctene with $(nBu_4N)_4W_{10}O_{32}$ and $(nBu_4N)_4W_{10}O_{32}$/Fe^{III}[*meso*-Tetrakis(2,6-dichlorophenyl)-porphyrin] in Homogeneous and Heterogeneous Systems

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Photoexcitation of $(nBu_4N)_4W_{10}O_{32}$ is a suitable mean of oxidizing cyclohexene and cyclooctene with O_2 at room temperature and pressure. This process can be carried out in homogeneous solution as well as using the decatungstate in a dispersed form after its heterogenisation on silica. Cyclohexene and cyclooctene are mainly oxidized to the corresponding hydroperoxides as a consequence of primary photoprocesses which lead to the formation of allylic radicals. The presence of the Fe^{III}[*meso*-tetrakis(2,6-dichlorophenyl)porphyrin] chloride as cocatalyst strongly affects the photocatalytic properties of $(nBu_4N)_4W_{10}O_{32}$, playing a key role in the allylic-hydroperoxide dependent oxidation of the cycloalkenes. In the photooxidation of cyclohexene, the porphyrin increases the photocatalytic efficiency of the decatungstate in terms of total turnover number and catalyses the decomposition of cyclohexenyl hydroperoxide with the selective formation of cyclohex-2-en-1-ol. On the other hand, its presence during the photoinduced oxidation of cyclooctene favours the formation of cyclooctene epoxide by addition of ROO· and RO· radicals to the double bond. In the case of cyclooctene, the heterogenisation of the decatungstate on the solid support also affects the chemoselectivity of the photocatalytic process in the absence of the iron porphyrin complex.

Introduction

The catalytic oxidation of hydrocarbons at room temperature and atmospheric pressure using environmentally friendly reagents, such as O_2, is an important goal both in fine and industrial chemistry.[1] In this challenging field, a number of groups are investigating polyoxometallates as catalysts with a noticeable activity in the oxidation of numerous organic compounds.[2] Their heterogenisation with solid matrices is attracting more and more interest[3] because the support makes them more easily handled and recycled than in homogeneous solution and, moreover, it can play a fundamental role in controlling both the efficiency and the selectivity of the catalytic process. In this framework, we have recently reported that photoexcitation of $(nBu_4N)_4W_{10}O_{32}$ supported on silica induces the oxidation of cyclohexane by O_2.[4] In particular we pointed out that the $(nBu_4N)_4W_{10}O_{32}/SiO_2$ system is a very promising photocatalyst for synthetic purposes, because its efficiency is comparable to that of the semiconductor TiO_2, with the advantage that it does not cause any oxidative mineralisation of the substrate.

We examine here the photocatalytic properties of $(nBu_4N)_4W_{10}O_{32}$ **1** and $(nBu_4N)_4W_{10}O_{32}/SiO_2$ **2** in the oxidation of cyclohexene and cyclooctene. We have chosen these two substrates as representative unsaturated hydrocarbons which are expected to present different oxidation mechanisms under aerobic conditions.[5] As part of our continuing interest in composite systems based on the use of polyoxotungstates and iron porphyrins,[6] we have also investigated the photocatalytic properties of **1** and **2** in the presence of Fe^{III}[*meso*-tetrakis(2,6-dichlorophenyl)porphyrin] chloride [Fe(TDCPP)Cl] as cocatalyst. In this case, we are interested in verifying the possible role of the porphyrin complex in governing the oxidation product distribution through its well-known mechanisms.[7] The bulky substituents in the *ortho* positions of the porphyrin *meso*-aryl groups provide a steric protection of the aromatic ring against a rapid oxidative degradation of the complex during both thermal[8] and photochemical catalytic processes.[9]

Results and Discussion

EPR Spin Trapping Investigation

In this section we report the results obtained during photoexcitation of **1** and **2** in the presence of phenyl *tert*-butyl nitrone, which is known to trap radicals to give more stable nitroxides.[10] Although the trapping process is not quantitative, in many instances the captured radical can be identified by the parameters obtained from the EPR spectrum. Using this technique, we revealed the radical species formed during the oxidation of cyclohexane[6a] and cyclohexylamine[11] photocatalysed by complex **1**.

Both **1** and **2** were irradiated in a CH_3CN/cyclohexene (6:1) mixture containing phenyl *tert*-butyl nitrone (1×10^{-3} $mol \cdot dm^{-3}$) inside the cavity of an EPR spectrometer. The spectrum obtained is shown in Figure 1. It consists of a triplet of doublets with hyperfine coupling constants ($a_N =$

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13.7 G and a_H = 2.1 G) which can be assigned to the adducts between the spin trap and cyclohexenyl radicals.[10] This spectrum remained the same even when an analogous irradiation was performed under anaerobic conditions. We can therefore conclude that it is not due to the trapping of cyclohexenylperoxo radicals, which are known to form a paramagnetic adduct with very similar hyperfine coupling constants.[12] The trapping of cyclohexenyl radicals is in agreement with the results of other authors who proposed that the dimeric species obtained in analogous experiments under anaerobic conditions originated from the coupling of these allylic radicals.[13]

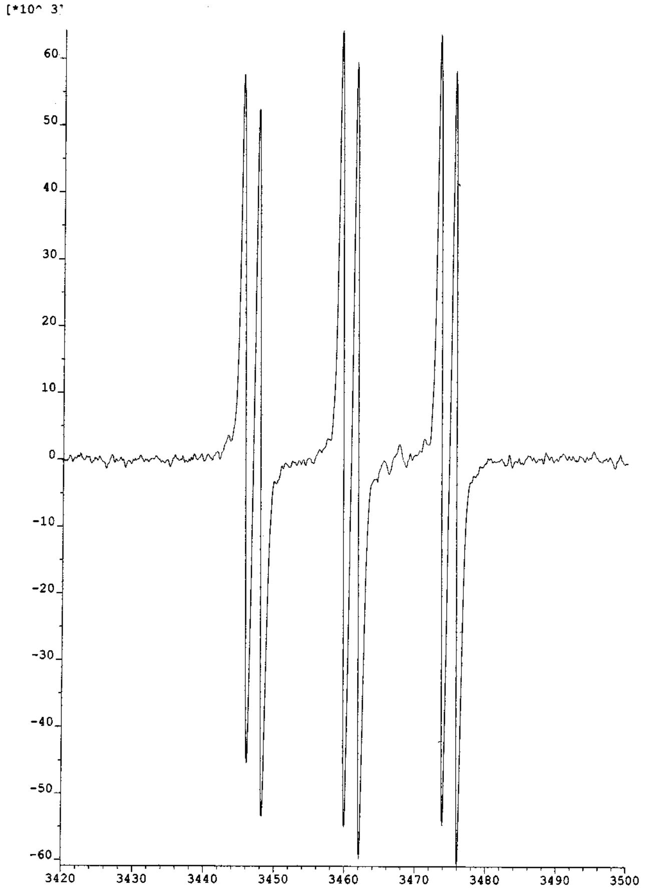
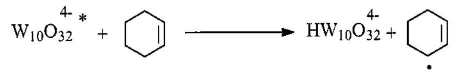


Figure 1. EPR spectrum obtained during irradiation ($\lambda > 320$ nm) of an aerated cyclohexene/CH_3CN (1:6 v/v) solution of $W_{10}O_{32}^{4-}$ (1×10^{-3} mol·dm^{-3}) in the presence of phenyl *tert*-butyl nitrone (1×10^{-3} mol·dm^{-3})

The detection of allylic radicals indicates that the photoinduced oxidation of cyclohexene occurs according to the mechanisms already proposed for the oxidation of other hydrocarbons and alcohols.[14] In particular, compound **1** in the photogenerated excited state is able to abstract a hydrogen from the cycloalkene to produce allylic radicals according to Equations 1 and 2. These radical species can be trapped by phenyl *tert*-butyl nitrone giving a paramagnetic nitroxide stable enough to be detected by EPR spectroscopy (Equation 3).

We failed to detect any EPR signals on irradiating **1** or **2** in CH_3CN/cyclooctene (6:1), indicating that the photoinduced oxidation of cyclooctene (Equation 2), although possible, does not give a steady state concentration of allylic radicals that is sufficiently high to obtain an observable paramagnetic adduct with phenyl *tert*-butyl nitrone. The different behaviour of the two investigated cycloalkenes can be explained by taking into account that cyclooctene is much less reactive than cyclohexene in hydrogen-abstraction processes. In particular, the relative rate constants differ by a factor of 17, depending mainly on the degree of reorganization required to give a planar allylic radical.[5]

$$W_{10}O_{32}^{4-} \xrightarrow{h\nu} W_{10}O_{32}^{4-\,*} \qquad [1]$$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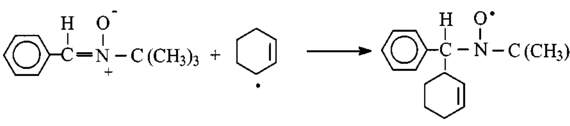
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Photocatalyzed Oxygenations with $(nBu_4N)_4W_{10}O_{32}$ and $(nBu_4N)_4W_{10}O_{32}/SiO_2$

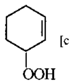
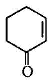
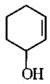
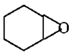
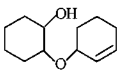
The EPR experiments show that under photolytic conditions, the decatungstate is able to initiate the oxidation of cyclohexene through allylic hydrogen abstraction (Equations 1 and 2). It is clear that for efficient catalytic cycles to be observed, the polyoxotungstate in its original form should be easily restored after the primary photoreduction. It has already been reported that **1** and **2** in their oxidised states can be regenerated by O_2, which, in turn, undergoes a reductive activation process[14c,15] with a pseudo first-order rate constant of about 150 s^{-1}.[6b] On this basis, we have investigated the possibility of inducing the photocatalytic oxidation of cyclohexene to stable products in the presence of O_2.

In typical experiments, **1** (2×10^{-4} mol·dm^{-3}) was irradiated in a CH_3CN/cyclohexene (6:1) mixture saturated with O_2, and **2** (20 g·dm^{-3}) as a powder suspension in the same dispersing medium. The selected excitation wavelength range ($300 < \lambda < 370$ nm) and the amounts of photocatalysts were chosen so that the maximum absorption of the incident light was the same in the two systems. Table 1 reports the distribution of the oxidation products and the overall turnover values after two hours irradiation.

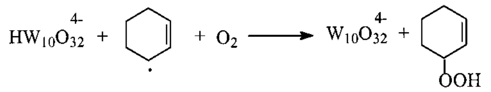
Photoexcitation of **1** in the homogeneous phase leads to the oxidation of cyclohexene to the corresponding allylic hydroperoxide as the main product (about 90% of the overall oxidized cycloalkene). In agreement with literature data on the photocatalysed oxidation of alkanes in the presence of decatungstates and O_2, we propose that the hydroperoxide is formed according to Equation 4.[14c]

In agreement with previous evidence,[16] we also observed the formation of cyclohex-2-en-1-ol and cyclohex-2-en-1-one during irradiation. On the basis of literature data regarding alkane photooxidation with **1**,[6,14c] we propose that

Table 1. Photocatalytic properties[a] of $(n\mathrm{Bu_4N})_4\mathrm{W_{10}O_{32}}$ **1** and $(n\mathrm{Bu_4N})_4\mathrm{W_{10}O_{32}/SiO_2}$ **2** in CH_3CN/cyclohexene (6/1), in the presence of 760 Torr of O_2, with and without Fe(TDCPP)Cl

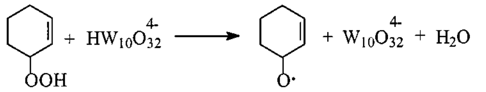
Photocatalyst	Total turnover [b]	 [c] (%)	 [f] (%)	 [f] (%)	 (%)	 (%)
1+ hν	123	89	7.5	1.8	0.7	1.0
1/Fe(TDCPP)Cl + hν [d]	185	59	24	15	0.9	1.1
1/Fe(TDCPP)Cl + hν + dark [e]	215	40	27	30	1.2	1.8
2 + hν [g]	25	89	6.4	1.9	1.2	1.5
2/Fe(TDCPP)Cl + hν [d, g]	43	73	16	9	0.8	1.2
2/Fe(TDCPP)Cl + hν + dark [e]	52	48	29	20	1.4	1.6

[a] 3 ml of CH_3CN/cyclohexene 6:1 containing **1** ($2\mathrm{x}10^{-4}$ mol· × dm^{-3}, 0.6 μmol of irradiated polyoxotungstate) or **2** (20 g·dm^{-3}, 1.93 μmol of irradiated polyoxotungstate) were irradiated for 120 minutes at 22 ± 1°C. Excitation wavelengths: $300<\lambda<370$ nm. Light intensity: 15 mW × cm^{-2}. The error calculated on the basis of the obtained concentration data is ±5%. – [b] μmol of oxidised cyclohexene/μmol of decatungstate. – [c] Total peroxides are determined with the iodometric method; however, considering that cyclohexene exhibits a higher reactivity than acetonitrile and on the basis of literature data,[14c] we can approximate that the allylic hydroperoxide is the main component. – [d] Initial concentration of Fe(TDCPP)Cl: 2×10^{-5} mol × dm^{-3}. – [e] 180 minutes after light interruption. – [f] The reported values are corrected for the thermal decomposition of hydroperoxide inside the chromatographic column (see Experimental section). – [g] The photocatalyst has been used for four consecutive cycles, leading to similar values within the experimental error.



[4]

the formation of these products occurs mainly according to Equations 5–9 which involve the decatungstate both in its excited state and in its photoreduced form.



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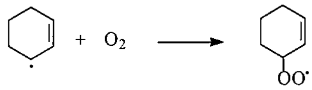

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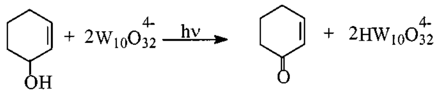

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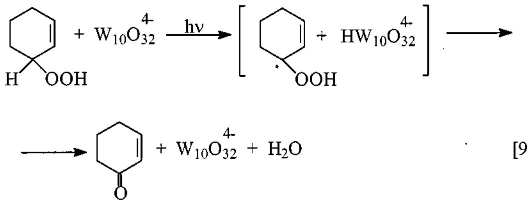


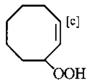
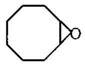
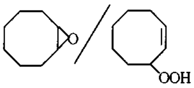
[9]

The possibility that the allylic hydroperoxide undergoes a secondary disproportionation or reactions with the cycloalkene without the involvement of the photoexcited decatungstate can be excluded since the total turnover number and the product distribution did not show any appreciable change when irradiation is interrupted. This statement is in agreement with the conclusion of a previous paper concerning the oxidation of cyclohexene by hydroperoxides in the presence of polyoxoanions.[17] Another possible reaction leading to the formation of allylic oxidation products is the well-known direct photochemistry of hydroperoxides.[18] However this possibility can be ruled out by taking into account the fact that the chosen amount of decatungstate avoids any possible light absorption by the hydroperoxide. Finally, we have to consider that some possible autooxidation reactions may give the observed traces of cyclohexene epoxide. Thus, the hydroxy ether reported in the last column of Table 1 can originate from the opening of the epoxide ring as a consequence of a nucleophilic attack by cyclohex-2-en-1-ol, favoured by the presence of protons. Despite a significant reduction in the turnover values, the use of the heterogeneous photocatalyst **2** does not cause any significant change in the nature and distribution of the oxidation products of cyclohexene.

The absence of any EPR signals during irradiation of **1** or **2** in the presence of cyclooctene is in agreement with the low tendency of this cycloalkene to release allylic hydrogen atoms and, therefore, to form hydroperoxides according to Equation 4. On the other hand, even small amount of hydroperoxides are sufficient to initiate radical chain processes under aerobic conditions leading to the autooxidation of cyclooctene. This process is well-known to occur via addition of ROO• or RO• radicals to the double bond and is largely responsible for cyclooctene epoxide formation.[5]

In line with the above accepted mechanism, Table 2 shows that irradiation of **1** or **2** in a CH_3CN/cyclooctene mixture (6:1) saturated with O_2 leads to the formation of allylic hydroperoxide and cyclooctene epoxide, although with turnover values significantly lower than those obtained during the photooxidation of cyclohexene. It is worth noting that, contrary to what was observed with cyclohexene, heterogenisation of the decatungstate on the solid support affects the chemoselectivity of the photocatalytic process by increasing the epoxide/hydroperoxide concentration ratio.

Table 2. Photocatalytic properties[a] of $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{W}_{10}\mathrm{O}_{32}$ **1** and $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ **2** in $\mathrm{CH}_3\mathrm{CN}$/cyclooctene (6:1), in the presence of 760 Torr of O_2, with and without Fe(TDCPP)Cl

	Turnover [b]		
Photocatalyst	 [c]		
1 + hν	5.8	1.9	0.3
1/Fe(TDCPP)Cl + hν [d]	3	4.9	1.6
1/Fe(TDCPP)Cl + hν + dark [e]	1	8.1	8.1
2 + hν [f]	1	2.3	2.3
2/Fe(TDCPP)Cl + hν [d, f]	0.1	4.0	40
2/Fe(TDCPP)Cl + hν + dark [e]	<0.03	4.2	>140

[a] 3 ml of $\mathrm{CH}_3\mathrm{CN}$/cyclooctene (6:1) containing **1** (2×10^{-4} mol·dm^{-3}, 0.6 μmol of irradiated polyoxotungstate) or (**2**) (20 g·dm^{-3}, 1.93 μmol of irradiated polyoxotungstate) were irradiated for 120 minutes at 22 ± 1°C. Excitation wavelengths: $300<\lambda<370$ nm. Light intensity: 15 mW × cm^{-2}. Reported values are ±5%. – [b] μmoles of formed product/μmoles of irradiated decatungstate. – [c] Because of the lower reactivity of cyclooctene, we were forced to verify the amount of peroxide, deriving from $\mathrm{CH}_3\mathrm{CN}$, formed during irradiation. We observed that it was negligible with respect to that obtained from cyclooctene. – [d] Initial concentration of Fe(TDCPP)Cl: 2×10^{-5} mol × dm^{-3}. – [e] 180 minutes after light interruption. – [f] The photocatalyst has been used for four consecutive cycles, leading to similar values within the experimental error.

A confirmation that the overall oxidation process is initiated by a hydrogen abstraction process from the cycloalkene comes from some additional experiments in which the decatungstate was irradiated in the presence of styrene which, under our photocatalytic conditions, is not oxidised at all.

Since we observe that the oxidation of both cyclohexene and cyclooctene does not continue when irradiation is interrupted, we can conclude that the photoreduced decatungstate plays a key role in the oxidation mechanism. In particular, it could participate in the formation of RO· and ROO· according to Equations 5–7.

As a final note on the use of the heterogeneous photocatalyst **2**, we should point out that it presents the important characteristic of not suffering irreversible modification, except a negligible release of the polyoxotungstate into solution (less than 2%). Moreover, it could be reused several times without any significant loss of photocatalytic activity. These features make **2** a very promising system in heterogeneous catalysis, where the advantages deriving from a higher ease of employment and recycling of the photocatalyst are often priority objectives.

Photocatalyzed Oxygenations with $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{W}_{10}\mathrm{O}_{32}$ and $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{W}_{10}\mathrm{O}_{32}/\mathrm{SiO}_2$ in the Presence of Fe(TDCPP)Cl

Irradiation of **1** and **2** was also carried out in the presence of Fe(TDCPP)Cl (2×10^{-5} mol·dm^{-3}) as cocatalyst. Since the decatungstate absorbs more than 95% of the selected incident light, it can be considered the photochemically active moiety of both the integrated systems **1**/Fe(TDCPP)Cl and **2**/Fe(TDCPP)Cl. The presence of Fe(TDCPP)Cl induces the following main effects on the photocatalytic properties of **1** in the oxidation of cyclohexene (Table 1): (i) the efficiency in terms of total turnover increases; (ii) a lower amount of allylic hydroperoxide is obtained; (iii) the sum of the alcohol and the ketone represents 40% of the overall oxidised cycloalkene; (iv) the ketone to alcohol concentration ratio decreases (from 4.1 to 1.6). Table 1 also shows that the presence of the iron porphyrin has the additional effect of inducing a residual catalytic activity after irradiation is interrupted. This activity changes the product distribution by converting the allylic hydroperoxide mainly to cyclohex-2-en-1-ol, whose concentration increases to almost 100%.

Fe(TDCPP)Cl also affects the catalytic properties of **2** during irradiation as well as in the dark. In these cases, the effects are similar to those observed in the homogeneous phase, but appear less evident. This could be due to the fact that the iron porphyrin complex preferably remains in solution, thereby reducing its interactions with the supported photocatalyst and the reactive species photogenerated in the neighbours.

As far as the stability of the porphyrin complex is concerned, we do not observe any appreciable bleaching of its UV/Vis spectrum in the wavelength range from 350 to 700 nm thus indicating that it does not undergo any significant degradation during the irradiation. This fact represents an important improvement with respect to both the photocatalytic activity of the iron porphyrins alone[19] and the same composite system used in the photooxidation of cyclohexane.[6b]

The possibility that the photoreduced decatungstate can transfer one electron to the iron(III) porphyrin,[20] so creating a ferrous complex able to induce the reductive activation of O_2, can be ruled out, since the reoxidation of $W_{10}O_{32}{}^{5-}$ by O_2 is known to be the kinetically favoured process under aerobic conditions.[6b,6c] Therefore, we consider that the iron porphyrin in its oxidised form plays a dominant role in the overall oxidation mechanism. In particular, an iron-porphyrin-mediated decomposition of allylic hydroperoxides to give the corresponding alcohols according to Equations 10−13 can be proposed on the basis of intensive studies on halogenated iron porphyrins.[21] The great significance of this reaction pathway in the overall oxidation mechanism is demonstrated by the residual reactivity observed after irradiation. In fact, under these conditions, cyclohex-2-en-1-ol cannot undergo photoinduced oxidation by the decatungstate (Equation 8) and so has the possibility to reach concentrations higher than those of cyclohex-2-en-1-one.

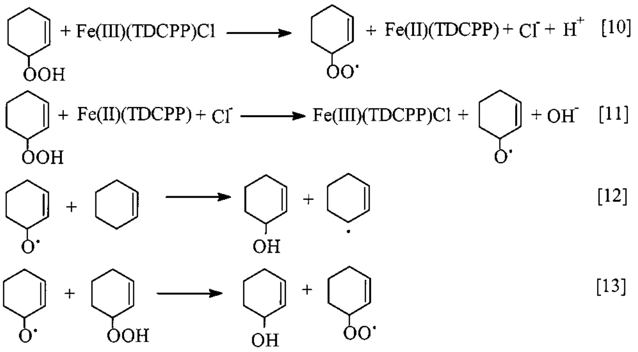


Table 2 shows that the iron porphyrin also affects the chemoselectivity of the oxidation of cyclooctene, significantly increasing the epoxide/hydroperoxide concentration ratio. Its main effect is likely to be that it favours the decomposition of the allylic hydroperoxide to give ROO• and RO• radicals following reactions similar to those shown in Equations 10 and 11 for cyclohexene. In agreement with previous evidence, these species are able to epoxidize cyclooctene by addition to the double bond.[5]

On the basis of the bleaching of the iron porphyrin during the photoinduced cyclooctene oxidation we conclude that about 300 equivalents of allylic hydroperoxide and cyclooctene epoxide were formed per equivalent of consumed iron porphyrin.

Conclusion

Photoexcitation of $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{W}_{10}\mathrm{O}_{32}$ is a suitable means of performing the catalytic oxidation of cycloalkenes by O_2 at room temperature and pressure. This process can be carried out in homogeneous solution as well as by using the decatungstate in a dispersed form after its heterogenisation on silica. Cyclohexene and cyclooctene are mainly oxidized to allylic hydroperoxides as a consequence of allylic hydrogen abstraction both in homogeneous solution and in the heterogeneous system. In the case of cyclooctene, the heterogenization of the decatungstate on the solid support affects the epoxide/hydroperoxide concentration ratio. The EPR spin trapping investigation has revealed for the first time the formation of cyclohexenyl radicals during the photocatalytic process.

The Fe(TDCPP)Cl complex can increase the efficiency of the photocatalytic process and affects its chemoselectivity. In particular, the iron porphyrin can catalyse the decomposition of allylic hydroperoxides giving, exclusively, the allylic alcohol from cyclohexene. On the contrary, this process induces the formation of epoxide from cyclooctene.

The possibility of obtaining allylic hydroperoxides in the presence of metalloporphyrins with molecular oxygen and light as reagents can open new perspectives for the development of new, clean processes of interest in oxidative syntheses.

Experimental Section

General: IR: Nicolet 510P FTIR instrument in KBr, fitted with a Spectra-Tech collector diffuse reflectance accessory (range from 4000 to 200 cm^{-1}). − EPR: X-band Bruker 220 SE, calibrated with α-α′-diphenylpicrylhydrazyl. − UV/Vis: Kontron Uvikon 940. − GC: Dani 8521, equipped with a FID detector and a packed column (Carbowax, 20 M, 5% on Chromosorb W-AW). − Irradiation: medium-pressure Hanau Q-400 mercury lamp.

Compound **1** and Fe(TDCPP)Cl were synthesised following literature procedures.[22] CH_3CN was a commercial spectroscopic grade solvent (Carlo Erba), used as received. Cycloalkenes were purchased from Fluka and employed after distillation. Phenyl *tert*-butyl nitrone was purchased from Aldrich and employed without any further purification.

Procedures: Heterogenisation of **1** on silica, leading to **2**,[4] was performed by dissolving 0.1 g of the decatungstate in CH_3CN and adding 1 g of colloidal silica (0.012 μm, Strem Chemicals). Subsequently, the suspension was continuously shaken at room temperature for two hours. The excess CH_3CN was evaporated at 80 °C, and the sample was then dried at 100 °C for 24 hours. UV/Vis spectra indicated that after this treatment the powder photocatalysts were stable and did not release the decatungstate in CH_3CN. IR spectra of the solid sample **2** have shown the characteristic bands for tetraalkylammonium cations [$\tilde{\nu}$ = 2963 and 2875 cm^{-1} (-CH_3 and -CH_2), 1481 (C−H of CH_3, C−H of CH_2), 1383 (C−H of CH_3)] and for $W_{10}O_{32}{}^{4-}$ [$\tilde{\nu}$ = 958, 890, 802 cm^{-1}].[23]

EPR spin-trapping experiments were carried out by irradiating ($\lambda >$ 320 nm), directly in the EPR cavity, an aerated solution of **1** (1×10^{-3} mol·dm^{-3}) in CH_3CN and cycloalkene (6:1) containing phenyl *tert*-butyl nitrone (5×10^{-3} mol·dm^{-3}). A flat quartz cell was used as the reaction vessel. Signals of significant intensity were not observed in the absence of the polyoxoanion, or cycloalkene or light. Analogous experiments were carried out with **2** (20 g·dm^{-3}) dispersed in the same mixed solvent.

Continuous irradiations were performed with a Hg medium pressure lamp, selecting a wavelength range from 300 to 370 nm with a chemical-optical filter made from a Corning glass filter and a cuvette with a path length of 1 cm containing a $NiSO_4$ solution (0.8 g·cm^{-3}). The amounts of irradiated photocatalysts have been chosen in order to have the maximum absorption of incident light in any case. A 3 mL solution of **1** (2×10^{-4} mol·dm^{-3}, 0.6 μmol of decatungstate) in CH_3CN and cycloalkene (6:1) mixed solvent was irradiated for 120 minutes under an O_2 pressure of 760 Torr at 22 ± 1 °C. The same procedure has been followed for **2** (20 g·dm^{-3}, 1.93 μmol of decatungstate). Catalyst **2** was kept in suspension by magnetic stirring. The UV/Vis spectrum of the CH_3CN/cycloalkene mixture after the photocatalytic experiment with **2** indicated that between 1% or 2% of decatungstate had been lost from the silica-supported catalyst. When needed, Fe(TDCPP)Cl (2×10^{-5} mol·dm^{-3}) was added before irradiation.

The reaction products were determined by GC analysis comparing their retention times with those of authentic samples, and with iodobenzene as internal standard. No oxidation products were observed when blank experiments were run in the dark.

The determination of hydroperoxides was performed by a spectrophotometric standard method reported in the literature.[24] The concentrations of the allylic oxidation products obtained from cyclohexene could not be determined by GC analysis of the irradiated sample because the allylic hydroperoxide is thermally unstable and is expected to decompose inside the chromatographic column to give a mixture of cyclohex-2en-1ol and cyclohex-2-en-1-one.[14c] On the other hand, it was possible to perform the GC analysis of the ketone in the irradiated sample, after a complete reduction of the allylic hydroperoxide to the corresponding alcohol by an excess of iodide; control experiments showed that the ketone is not reduced to the corresponding alcohol by iodide. The difference between the alcohol concentration obtained in this last experiment and that of the allylic hydroperoxide obtained by the spectrophotometric method represents the amount of alcohol formed during the photocatalytic experiment. On this basis, we could also calculate the amounts of alcohol and ketone formed inside the chromatographic column: the allylic hydroperoxide was decomposed by 45% to give a mixture of the corresponding alcohol and ketone in the concentration ratio 1:2.

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