Photocatalytic oxidation of cyclohexane by (nBu₄N) ₄W₁₀O₃₂/Fe(III)porphyrins integrated systems

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Abstract

The oxidation of cyclohexane by photoexcited $(nBu_4N)_4W_{10}O_{32}$ has been investigated in the presence of iron *meso*-tetraarylporphyrins bearing different substituents in the β-pyrrole positions and/or in the *meso*-aryl groups. Irradiation at 325 nm leads to the reduction of the polyoxotungstate with the simultaneous oxidation of cyclohexane to cyclohexyl radicals which can be detected by the ESR spin trapping technique. In oxygen-free solutions, the photoreduced polyoxotungstate is able to transfer one electron to the Fe(III)porphyrin to give the ferrous complex. The subsequent reaction between this species and cyclohexyl radicals leads to the formation of σ-alkyl-Fe(III)porphyrin complexes, as demonstrated by UV-VIS and NMR spectroscopy. In the presence of oxygen, the photoreduced polyoxotungstate has the role of initiating the activation of O_2 through its reduction to O_2^- and H_2O_2. As a consequence, cyclohexane is converted to cyclohexanone and cyclohexanol in a cyclic way. The Fe(III)porphyrin complex strongly affects the product distribution probably through its hydrogen peroxide and alkyl-hydroperoxide-dependent oxidation. In comparison with $(nBu_4N)_4W_{10}O_{32}$ alone, a higher selectivity is obtained with the formation of cyclohexanol as a major product.

Keywords: Photocatalysis; Oxidation catalyst; Biomimetic oxidation; Oxygen activation; Iron-porphyrins; Polyoxotungstate

1. Introduction

Both the use of metal porphyrin complexes and polyoxotungstates in the catalytic oxidation of alkanes (RH) are very active areas of chemical research. Metal porphyrins have been found to be efficient biomimetic catalysts for alkane monooxygenation in the presence of either various oxygen atom donors (i.e., iodosylbenzene, peracids, alkylhydroperoxides, hydrogen peroxide) or O_2 itself in the presence of a reducing agent according to Eq. (1) [1–3].

$$RH + O_2 + 2e^- + 2H^+ \rightarrow ROH + H_2O. \qquad (1)$$
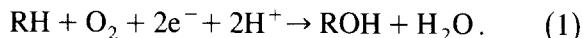
It has been demonstrated that light can be used as a clean redox agent to induce the catalytic oxygenation of hydrocarbons by O_2 in the presence of catalytic amounts of various metal porphyrin complexes including

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iron(III)porphyrins (Fe(III)P) [4–10]. A common feature of the investigated systems is that the oxygenation of the organic substrate occurs as a consequence of O_2 reductive activation by the metal center according to the reactions reported in Scheme 1a. Light causes an intramolecular electron transfer which leads to the formation of Fe(II)P with simultaneous oxidation of axial ligands (L) such as OH^-, Cl^-, N_3^-, $C_2H_5O^-$ to radical species which can undergo subsequent reactions [11–16]. The Fe(II) species can, in turn, coordinate O_2 which is reduced to superoxide anion (O_2^-) [10,17,18] regenerating the Fe(III)P center.

There are close relationships in the photocatalytic behaviour of Fe(III)porphyrins and polyoxotungstates (POT^{n-}). Indeed, in the latter case too, a photocatalytic activity has been demonstrated in the oxidation of a variety of organic compounds including saturated hydrocarbons as shown in Scheme 1b [19–23]. These photocatalysts undergo reduction in the near UV region with the concomitant oxidation of the organic substrate. We have recently obtained direct evidence of the formation of alkyl radicals by ESR experiments [24]. The key step in the photocatalytic cycle under aerobic conditions is the reoxidation of the catalyst through a mechanism which likely involves the one electron oxidation of the photoreduced polyoxotungstate by O_2 [24–26], probably after the formation of an adduct between $POT^{(n+1)-}$ and O_2 [27].

Both Fe(III)P and POT^{n-} have advantages and disadvantages in oxidation catalysis. POT^{n-}s are very efficient from the photochemical point of view, often presenting quantum yield values higher than 0.1. On the other hand, only few systematic studies of the reductive activation of O_2 by these compounds have been reported [26,27], with radical chain autoxidation often playing a dominant role in the overall substrate oxidation process. Iron(III)porphyrins are less active from the photochemical point of view, presenting quantum yields at least one order of magnitude lower than those typical of

POT^{n-}s. Nevertheless, the oxygen activation mechanism leading to highly selective biomimetic catalysis by these complexes has been extensively investigated.

On this basis, we have begun the study of composite systems potentially able of combining the high photochemical efficiency of polyoxotungstates and the biomimetic activity of metal porphyrins. Besides their potentialities in oxidation catalysis, it has been outlined that these investigations can give some contributions to the modelling of polyooxometalate–protein interactions, a research topic whose interest is increasing because of the applications of polyoxometalates as antiviral drugs [28–30].

In the present paper we examine the photocatalytic properties of integrated systems consisting of mixtures of $(nBu_4N)_4W_{10}O_{32}$ $(W_{10}O_{32}^{4-})$ and an iron porphyrin complex, their reactivity under anaerobic conditions, their effi-
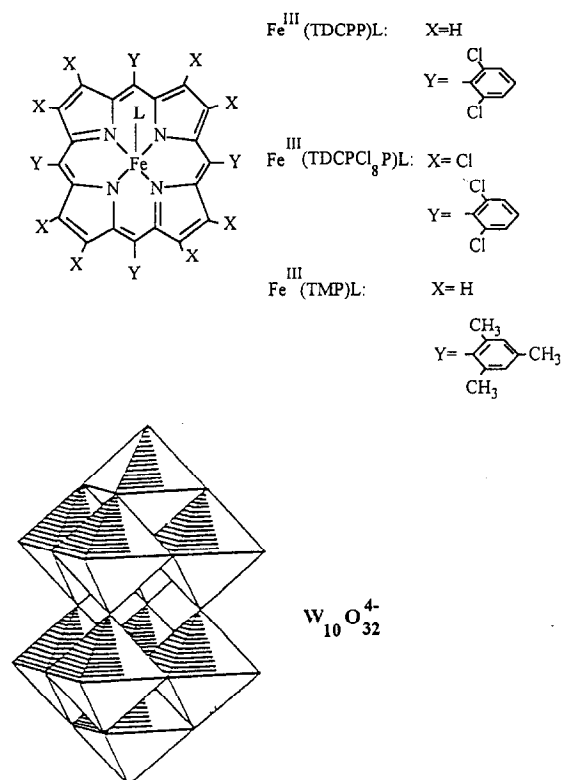

Fig. 1. Structures of the substituted Fe(III)porphyrins and of $W_{10}O_{32}^{4-}$.

ciency in the oxygenation of cyclohexane by O_2, their selectivity under controlled aerobic conditions, and their resistance to photodegradation. The structure of $W_{10}O_{32}^{4-}$ is depicted in Fig. 1 together with those of the iron porphyrin complexes employed in this work. We used *meso*-tetraaryl iron porphyrins bearing bulky substituents in the β-pyrrole positions and/or in the *ortho* positions of the *meso*-aryl groups. These substituents are known to provide a steric protection of the porphyrin ring against oxidative degradation of the complex during both thermal [31,32] and photochemical catalytic processes [10,16]. Moreover, they prevent the formation of μ-oxo dimer porphyrin complexes [33] which can deactivate the photocatalysts.

2. Experimental

2.1. Materials

The complexes Fe(III)-*meso*-(tetrakis(2,6-dichlorophenyl)porphyrin Fe(III)(TDCPP), Fe(III)-*meso*-(tetrakis(2,6-dichlorophenyl)-octa-β-chloroporphyrin Fe(III)(TDCPCl$_8$P) and Fe(III)-*meso*-(tetrakis(2,4,6-trimethylphenyl)-

Scheme 1. Photocatalytic behaviour of Fe(III)P and POT^{n-} in the presence of O_2.

porphyrin Fe(III)(TMP) were prepared and purified as previously reported [34]. $W_{10}O_{32}^{4-}$ was prepared according to literature data [35,36]. All the solvents were spectroscopic grade reagents and were used without further purification. Phenyl-*tert*-butylnitrone (pbn) was a commercial product (Aldrich) and was used as received.

2.2. Apparatus

UV-vis spectra were recorded with a Kontron Model Uvikon 940 spectrophotometer and X-band Electron spin resonance (ESR) spectra with a Bruker 220 SE spectrometer that was calibrated by using α,α'-diphenylpicrylhydrazyl. ^{1}H-NMR experiments were performed with a Varian Gemini 300 MHz, chemical shift in ppm (positive values downfield from TMS). A mixture of $CD_2Cl_2/C_6D_{12}/CD_3CN$ (6:3:1) was used as solvent.

Gas chromatography (GC) analyses were carried out with a DANI 8521 gas chromatograph, equipped with a flame ionization detector, using columns packed with Carbowax 20 M 5% on Chromosorb W-AW. The reaction products were determined by comparison of their retention times with those of authentic samples, using iodobenzene as internal standard.

Irradiations were carried out with a 250 W xenon source equipped with an f/3.4 grating monochromator (Applied Photophysics) with thermostatable cell holder (22 ± 1°C). The light intensity was measured by the ferrioxalate actinometric method [37]. Laser flash photolysis experiments were carried out using an Applied Photophysics detection system, coupled with a Continuum Surelite II-10 Neodimium YAG Laser, equipped with a frequency multiplier (266 nm, 5 ns half-width, 150 mJ). Transient decays were stored and read on a LeCroy 9360 fast digitizing oscilloscope.

2.3. Procedures

$W_{10}O_{32}^{4-}$ $(2 \times 10^{-4}$ mol dm$^{-3})$ and Fe(III)P $(3 \times 10^{-5}$ mol dm$^{-3})$ were dissolved in
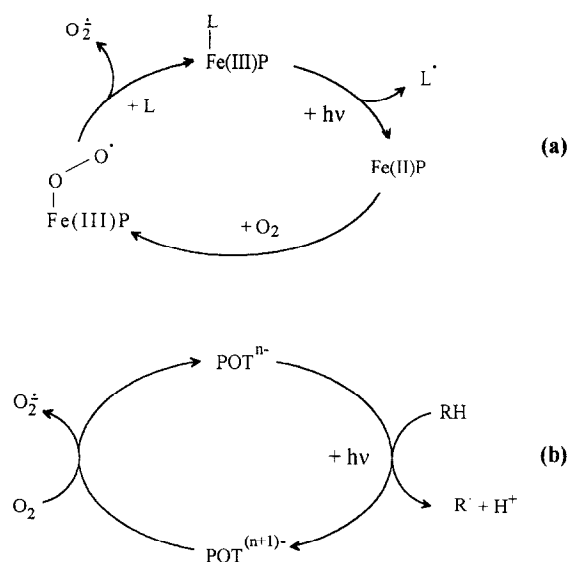
$CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) and irradiated at 325 nm in a 1-cm spectrophotometric cell. When necessary, the solutions were degassed to less than 1×10^{-5} torr by means five vacuum-line freeze-thaw-pump cycles or kept under controlled O_2 pressure. For Laser flash photolysis experiments, $W_{10}O_{32}^{4-}$ (5×10^{-5} mol dm^{-3}) and Fe(III)P (2×10^{-5} mol dm^{-3}) were dissolved in CH_3CN/Pr^iOH (1:1) and irradiated in a 4 cm spectrophotometric cell. In the $CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) mixed solvent, it was impossible to follow the optical variations of the polyoxotungstate on a long time scale due to light diffusion phenomena, probably arising from the optical inhomogeneity of the medium.

In the ESR-spin trapping investigation, $W_{10}O_{32}^{4-}$ (1×10^{-3} mol dm^{-3}) and Fe(III)P (1×10^{-4} mol dm^{-3}) in $CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) were irradiated in the presence of pbn (5×10^{-3} mol dm^{-3}). Irradiations were carried out inside the ESR cavity using a flat quartz cell, at room temperature, utilising a cut off filter able to stop light of wavelength lower than 280 nm. No signal of significant intensity was observed in blank experiments with solutions containing both $W_{10}O_{32}^{4-}$ and Fe(III)P in the absence of cyclohexane. Moreover, no signal was observed when blank experiments were run in the dark.

3. Results and discussion

3.1. Photoredox properties in oxygen-free solutions

Continuous irradiations have been carried out at 325 nm on $CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) solutions containing $W_{10}O_{32}^{4-}$ (2×10^{-4} mol dm^{-3}) and Fe(III)P (3×10^{-5} mol dm^{-3}). Since the polyoxotungstate absorbs more than 95% incident light in these conditions, it can be considered as the photochemical active moiety of the integrated systems $W_{10}O_{32}^{4-}$/Fe(III)P.
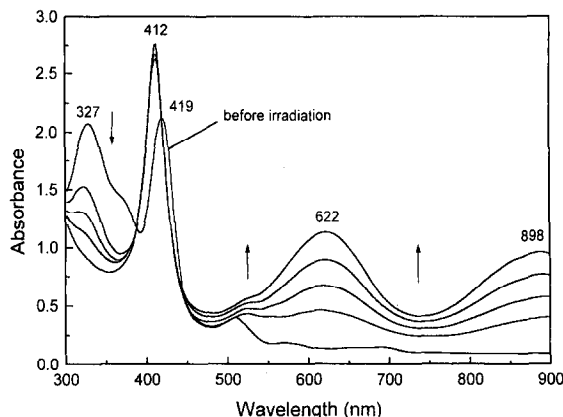

Fig. 2. UV-vis spectral changes observed during irradiation at 325 nm of $CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) deaerated solutions containing $W_{10}O_{32}^{4-}$ (2×10^{-4} mol dm^{-3}) and Fe(III)(TMP) (3×10^{-5} mol dm^{-3}); time interval between spectral scans: 10 min.

Irradiation of oxygen-free solutions of these systems causes the reduction of polyoxotungstate, as revealed by the formation of blue species. Details of the spectral behaviour of irradiated $W_{10}O_{32}^{4-}$ have been already published [38–40]. Typical UV-vis spectral variations are reported in Fig. 2 in the case of the $W_{10}O_{32}^{4-}$/Fe(III)(TMP) system. Before irradiation, the spectrum is the result of the superimposition of $W_{10}O_{32}^{4-}$ ($\lambda_{max} = 327$ nm) and Fe(III)(TMP) ($\lambda_{max} = 419, 510$ nm) spectra. The photoreduction of $W_{10}O_{32}^{4-}$ is demonstrated by the loss of the 327 nm band and the growth of two bands at 622 and 898 nm, respectively. On the other hand, in the spectral behaviour of the iron porphyrin we note that the Soret band undergoes an intensity increase and a blue shift to 412 nm. The original spectrum of the ferric porphyrin was regenerated after oxygenation of the solution.

We speculate that this spectral behaviour is due to the formation of a Fe(III)-σ-alkyl complex which is known both to decompose in the presence of O_2 leading to the starting Fe(III)porphyrin, and to exhibit a blue-shifted Soret band by comparison with Fe(III)P [41,42]. In fact, on the basis of the reported redox

potentials [38] [43], the photogenerated $W_{10}O_{32}^{5-}$ system is able to transfer one electron to the ferric porphyrin according to Eq. (2). The sub-

sequent very fast reaction between the reduced porphyrin and the cyclohexyl radicals obtained as a consequence of the primary photoprocess
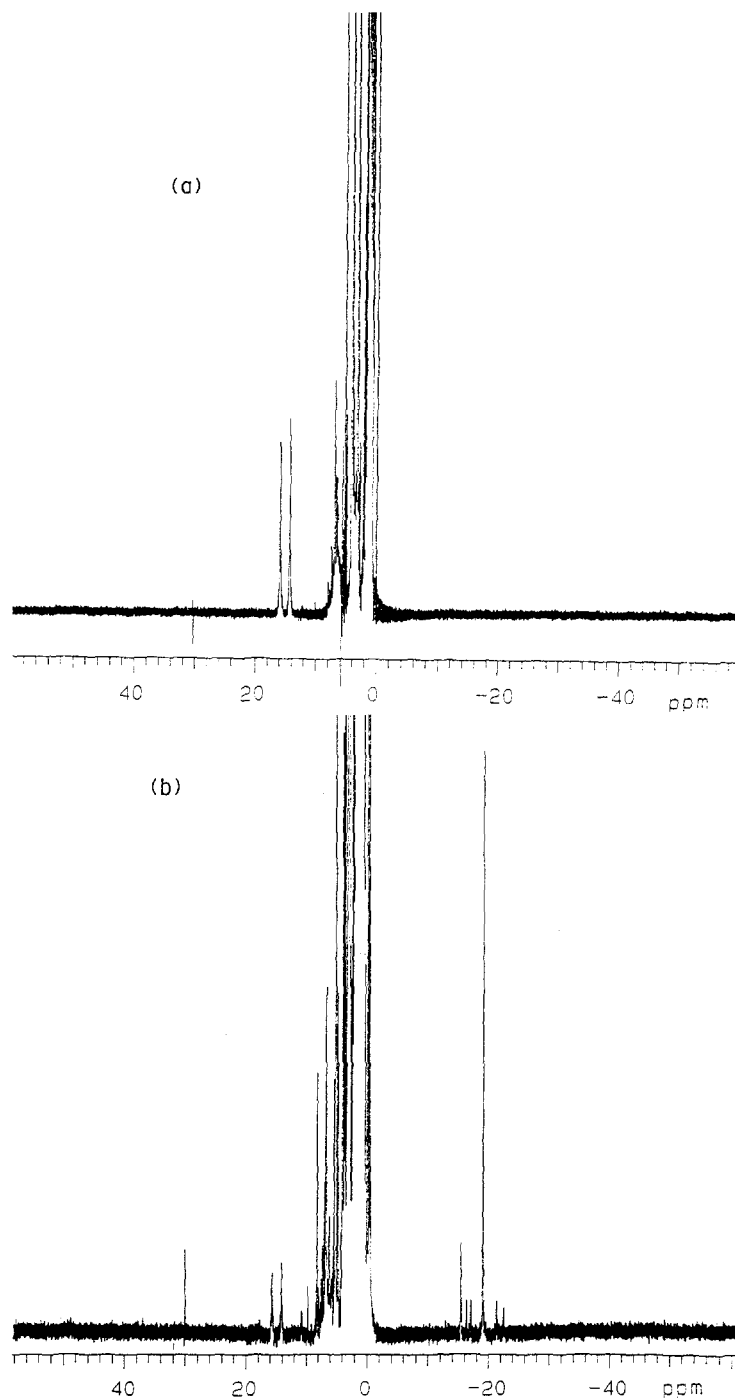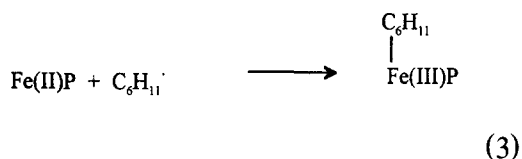

Fig. 3. ^{1}H-NMR spectral changes observed during irradiation at 325 nm of $CD_2Cl_2/C_6D_{12}/CD_3CN$ (6:3:1) deaerated solutions containing $W_{10}O_{32}^{4-}$ (4 × 10^{-3} mol dm^{-3}) and Fe(III)(TMP) (1.75 × 10^{-3} mol dm^{-3}). (a) before irradiation, (b) after 60 min irradiation.

(see Scheme 1b) should lead to the formation of an Fe(III)-σ-alkyl complex (Eq. (3)) [44].

$$W_{10}O_{32}^{5-} + Fe(III)P \rightarrow W_{10}O_{32}^{4-} + Fe(II)P. \quad (2)$$

$$Fe(II)P + C_6H_{11}\cdot \longrightarrow \underset{\underset{Fe(III)P}{|}}{\overset{C_6H_{11}}{}} $$

$$(3)$$

In order to confirm the ability of $W_{10}O_{32}^{5-}$ to transfer one electron to Fe(III)P to give Fe(II)P according to Eq. (2), we have added the iron(III) porphyrin to a deaerated solution of the polyoxotungstate previously irradiated for a length of time sufficient to produce its reduced form. The observed red shift to 425 nm of the Soret band is consistent with reduction of Fe(III) to Fe(II)P [16]. A very similar behaviour is shown by all the other integrated systems investigated.

The formation of a Fe(III)-σ-alkyl complex, as described by Eq. (3), is supported by ^{1}H-NMR evidence. The spectrum of the solution containing Fe(III)TMP and $W_{10}O_{32}^{4-}$ (Fig. 3a) shows two characteristic broad singlets at $+15.9$ and $+14.3$ ppm and no peak highfield from TMS. After irradiation of the oxygen-free solution, those peaks are unchanged in shift, and two new peaks at -15 and -19 ppm are observed (Fig. 3b) that can be assigned to the pyrrole protons of a Fe(III)-σ-alkyl low spin complex, as reported by D. Lexa et al. [41]. They attribute the presence of two new peaks to a loss of symmetry in the plane of the ring; this can be reasonably the situation in our case too, because of the metal alkylation on one side of the porphyrin plane. When oxygen is added to the solution, the highfield peaks disappear, and the spectrum of the ferric high spin porphyrin is observed again.

3.2. Reductive activation of O_2

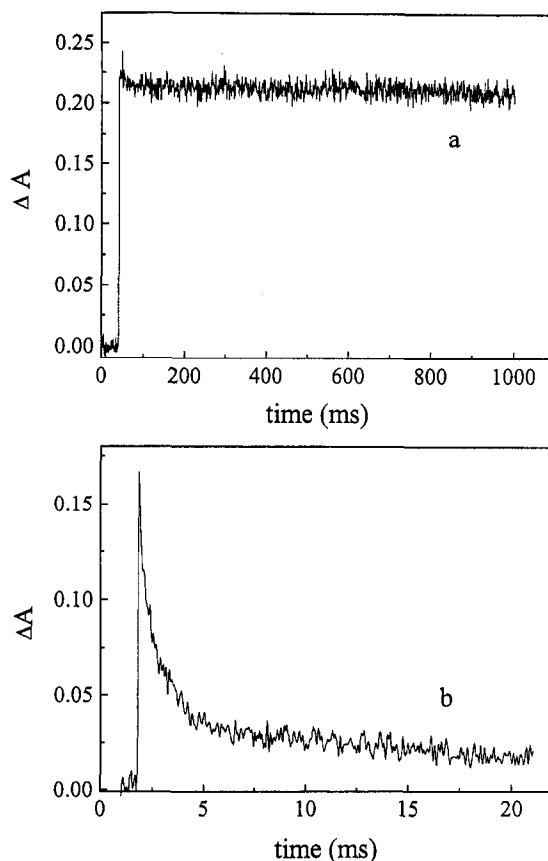When the photochemical excitation of the $W_{10}O_{32}^{4-}$/Fe(III)P systems is carried out in the

Fig. 4. Laser flash photolysis of CH_3CN/iPrOH (1:1) solutions containing $W_{10}O_{32}^{4-}$ (5×10^{-5} mol dm^{-3}) and Fe(III)(TDCPP) (2×10^{-5} mol dm^{-3}); excitation wavelength: 266 nm; analysis wavelength: 800 nm; (a) in oxygen-free solutions, (b) in the presence of 760 torr of O_2.

presence of O_2, its reaction with the photoreduced polyoxotungstate competes with reaction 2. Kinetic factors are of fundamental importance in determining which reoxidation pathway prevails. For this reason, we have carried out some Laser flash photolysis experiments.

Fig. 4 reports, as an example, the results obtained for the $W_{10}O_{32}^{4-}$/Fe(III)(TDCPP) system in CH_3CN/iPrOH (1:1) solutions. In the absence of dioxygen (Fig. 4a), the flash gives rise to a very fast (less than 5 ns) absorbance increase at 780 nm due to the formation of $W_{10}O_{32}^{5-}$ as a consequence of the photoreduction of $W_{10}O_{32}^{4-}$ by iPrOH [36]. Taking $\epsilon = 1.0 \times 10^4$ [38] at this wavelength, we can estimate a concentration of photogenerated

$W_{10}O_{32}^{5-}$ of 5×10^{-6} mol dm^{-3}. After that, no bleaching of the solution is observed in the following second, indicating that no electron transfer from $W_{10}O_{32}^{5-}$ to Fe(III)(TDCPP) occurs within this time.

Fig. 4b shows typical results obtained when $W_{10}O_{32}^{4-}$ is photoexcited in the presence of 760 torr of O_2. An analysis of the decay curve indicates that the reoxidation of photogenerated $W_{10}O_{32}^{5-}$ by O_2 (about 10^{-2} mol dm^{-3}) follows pseudo-first-order kinetics with respect to the polyoxotungstate. From the mono-exponential decay curve observed at 800 nm, a pseudo-first-order constant of $(1.5 \pm 0.3) \times 10^2$ s^{-1} was obtained. Experimentally, we observe that the presence of the Fe(III)porphyrin does not accelerate the reoxidation of the polytungstate by oxygen.

In conclusion, laser flash photolysis experiments clearly indicate that the reoxidation of the photogenerated $W_{10}O_{32}^{5-}$ by O_2 precedes that by Fe(III)P. This means that the first step of O_2 activation by the $W_{10}O_{32}^{4-}$/Fe(III)P system is its reduction by the photoreduced polyoxotungstate without the involvement of the porphyrin complex in its ferrous form.

3.3. Photocatalytic properties

Continuous irradiation at $\lambda = 325$ nm of $CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) solutions of the integrated systems $W_{10}O_{32}^{4-}$/Fe(III)P under an oxygen pressure of 760 torr leads to the oxidation of cyclohexane with formation of both cyclohexanol and cyclohexanone. While complete mineralization of some organic substrates by photoexcited POT^{n-} has been reported in aqueous solution [44], we have checked that oxidative degradation of cyclohexane with the formation of CO_2 and H_2O does not occur in this system.

The formation of both cyclohexanol and cyclohexanone follows zero-order kinetics, allowing us to calculate the reaction quantum yields shown in Table 1 which also reports some our recent data of an investigation on the photocatalytic properties of $W_{10}O_{32}^{4-}$ in the absence of Fe(III)P [24]. Within the experimental error, the photooxidation quantum yields are almost independent of the presence of the iron porphyrin complex which, on the contrary, strongly affects the product distribution. In particular, photochemical excitation of the integrated system $W_{10}O_{32}^{4-}$/Fe(III)(TDCPCl$_8$P) results in the formation of cyclohexanol as the major product (cyclohexanol to cyclohexanone concentration ratio: 1.85). Conversely, photoexcitation of $W_{10}O_{32}^{4-}$ alone gives mainly cyclohexanone (cyclohexanol to cyclohexanone concentration ratio: 0.5). The kinetics of products formation did not change if irradiation is carried out in the presence of cyclohexanol or cyclohexanone which rules out consecutive reactions. This statement is also confirmed by the observation that both product concentrations increase linearly with time.

Table 1
Photocatalytic properties [a] of $W_{10}O_{32}^{4-}$/Fe(III)P integrated systems [b] in $CH_2Cl_2/C_6H_{12}/CH_3CN$ (6:3:1) mixed solvent, in the presence of 760 torr of O_2

Photocatalyst	Φ_{ox} [c]	Product ratios(%)		Cycle number [d]
		Cyclohexanol	Cyclohexanone	
$W_{10}O_{32}^{4-}$ [e]	0.35 ± 0.05	35	65	–
$W_{10}O_{32}^{4-}$ Fe(III) (TMP)	0.30 ± 0.05	50	50	200
$W_{10}O_{32}^{4-}$ Fe(III) (TDCPP)	0.30 ± 0.05	50	50	1200
$W_{10}O_{32}^{4-}$ Fe(III) (TDCPCl$_8$P)	0.4 ± 0.05	65	35	1000

[a] Irradiations were carried out at 22 ± 1°C, at 325 nm.
[b] Initial concentration $W_{10}O_{32}^{4-}$: 2×10^{-4} mol dm^{-3}, initial concentration Fe(III)P: 3×10^{-5} mol dm^{-3}.
[c] Moles of oxidized cyclohexane/moles of absorbed photons.
[d] Moles of oxidized cyclohexane/mole of consumed iron porphyrin.
[e] Ref. [24].

During the photochemical experiments (about 90 min), the only observed spectral variation is a slow bleaching of the spectrum in the wavelength range from 350 to 700 nm, indicating that only the porphyrin moiety of the integrated photocatalysts undergoes a slow degradation. Moreover, neither the polyoxotungstate nor the iron porphyrin complex are accumulated in their reduced forms. On the basis of the absorbance decrease, it has been possible to evaluate the ratio between the moles of photooxidized cyclohexane and the moles of degraded porphyrin complex. The obtained values reported in the last column of Table 1 indicate that the halogenated iron porphyrins are more stable than Fe(III)TMP. It is noteworthy that the ratio between the moles of photooxidized cyclohexane and the moles of degraded Fe(III)(TDCPP) and Fe(III)(TDCPCl$_8$P) are significantly higher (two orders of magnitude) than those observed when the same porphyrins are used as photocatalysts for cyclohexane oxidation in the absence of W$_{10}$O$_{32}^{4-}$ [10].

In order to verify the effects of the dioxygen concentration on the yields of cyclohexane oxi-

dation products, we have irradiated W$_{10}$O$_{32}^{4-}$ in the presence of the relatively stable Fe(III)(TDCPP) or Fe(III)(TDCPCl$_8$P), under dioxygen controlled conditions. The overall photooxidation quantum yields do not change significantly. On the other hand, the results reported in Table 2 show that the cyclohexanol to cyclohexanone ratio increases by decreasing dioxygen concentration. This trend is similar to that previously described for W$_{10}$O$_{32}^{4-}$ alone [24], also reported for comparison in the table. It is noteworthy that, in this case, the alcohol to ketone ratios are lower than those obtained in the presence of iron porphyrins for all dioxygen pressures.

3.4. Mechanism of cyclohexane oxidation

The primary possible intermediates derived from cyclohexane oxidation by photoexcited W$_{10}$O$_{32}^{4-}$ are shown in Scheme 1b. We have recently observed [24] that, besides C$_6$H$_{11}^{\cdot}$ radicals, this photocatalytic system leads to the formation of OH$^{\cdot}$ radicals as intermediates. The formation of both radical intermediates and the final products cyclohexanol and cyclohexanone may be explained by Eqs. (6)–(12). The reactions formulated have been chosen on the basis of literature data previously reported for the oxidation of hydrocarbons both on polyoxotungstates [24,27] and semiconducting oxides [44,45].
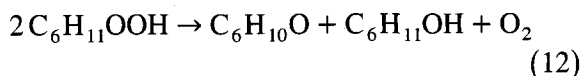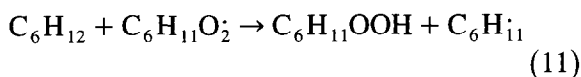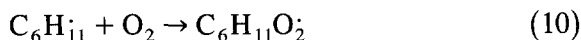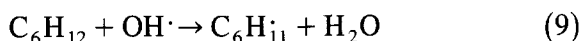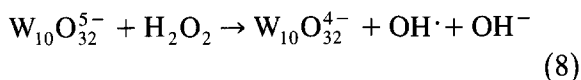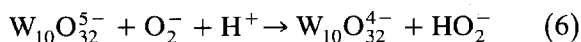
Table 2
Photocatalytic properties [a] of W$_{10}$O$_{32}^{4-}$/Fe(III)P integrated systems [b] in CH$_2$Cl$_2$/C$_6$H$_{12}$/CH$_3$CN (6:3:1) mixed solvent, at different O$_2$ pressure

System	O$_2$ pressure (torr)	[Cyclohexanol]/ [cyclohexanone]
W$_{10}$O$_{32}^{4-}$ [c]	20	6.2
	40	1.5
	60	0.64
	100	0.59
W$_{10}$O$_{32}^{4-}$ Fe(III) (TDCPP)	20	6.4
	30	2.7
	60	1.3
	100	1.2
W$_{10}$O$_{32}^{4-}$ Fe(III) (TDCPCl$_8$P)	20	7.4
	30	3.5
	60	2.1
	100	1.6

[a] Irradiations were carried out at $22 \pm 1°C$, at 325 nm.
[b] Initial concentration W$_{10}$O$_{32}^{4-}$: 2×10^{-4} mol dm^{-3}, initial concentration Fe(III)P: 3×10^{-5} mol dm^{-3}.
[c] Ref. [24].

$$W_{10}O_{32}^{5-} + O_2^- + H^+ \rightarrow W_{10}O_{32}^{4-} + HO_2^- \qquad (6)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \qquad (7)$$

$$W_{10}O_{32}^{5-} + H_2O_2 \rightarrow W_{10}O_{32}^{4-} + OH^{\cdot} + OH^- \qquad (8)$$

$$C_6H_{12} + OH^{\cdot} \rightarrow C_6H_{11}^{\cdot} + H_2O \qquad (9)$$

$$C_6H_{11}^{\cdot} + O_2 \rightarrow C_6H_{11}O_2^{\cdot} \qquad (10)$$

$$C_6H_{12} + C_6H_{11}O_2^{\cdot} \rightarrow C_6H_{11}OOH + C_6H_{11}^{\cdot} \qquad (11)$$

$$2 C_6H_{11}OOH \rightarrow C_6H_{10}O + C_6H_{11}OH + O_2 \qquad (12)$$

OH· radicals may originate from the one electron reduction of H_2O_2 (Eq. (8)) which has been proposed to be a possible intermediate in O_2 reduction by $W_{10}O_{32}^{5-}$ (Eq. (6) and Eq. (7)) [27]. In the bulk of the solutions both C_6H_{11} and OH· radicals can be involved in the well known radical chain autooxidation of cyclohexane and give both cyclohexanol and cyclohexanone through the formation of $C_6H_{11}OOH$ alkyl-hydroperoxide compounds (Eqs. (9)–(12)). The formation of cyclohexanone may also be expected from the polyoxotungstate mediated decomposition of $C_6H_{11}OOH$ according to Eq. (13).

$$W_{(VI)} \overset{O}{\underset{O-O}{\diagup}} \quad \overset{H}{\underset{C}{\diagup}} \longrightarrow W_{(VI)} \overset{OH}{\underset{O}{\diagup}} + O=\diagup \quad (13)$$
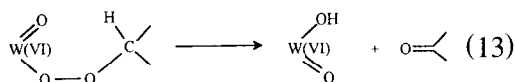
In the $W_{10}O_{32}^{4-}$/Fe(III)P systems, the latter can contribute to the hydroxylation of cyclohexane according to reported mechanisms. In particular, the iron(III)porphyrin can rapidly decompose the photogenerated alkyl-hydroperoxides according to Eq. (14) [46]. Eqs. (15)–(17) schematise the mechanism for the subsequent formation of cyclohexanol. An alternative mechanism can be proposed on the basis of intensive studies on hydrogen peroxide and alkyl-hydroperoxide-dependent oxidations of iron(III)porphyrins. Polar environments and the availability of protons seem to favour an heterolytic cleavage of their O–O bond with formation of a high-valent iron-oxo complex (formally equivalent to an Fe(V)=O intermediate) according to Eq. (18) and Eq. (19) [47–51].

$C_6H_{11}OOH + Fe(III)TDCPCl_8P$

$\rightarrow C_6H_{11}OO· + Fe(II)TDCPCl_8P + H^+$

$$(14)$$

$C_6H_{11}OOH + Fe(II)TDCPCl_8P$

$\rightarrow Fe(III)TDCPCl_8P + C_6H_{11}O· + OH^-$

$$(15)$$

$C_6H_{11}O· + C_6H_{12} \rightarrow C_6H_{11}OH + C_6H_{11}$ $\quad (16)$
$C_6H_{11}O· + C_6H_{11}OOH$

$\rightarrow C_6H_{11}OH + C_6H_{11}OO·$ $\quad (17)$

$$Fe(III)P^- + C_6H_{11}OOH \text{ (or } H_2O_2) \rightleftarrows \overset{O-O\ C_6H_{11}}{\underset{Fe(III)P}{|}} + H^+$$

$$(18)$$

$$\overset{O-OC_6H_{11}}{\underset{Fe(III)P}{|}} + H^+ \longrightarrow \overset{O}{\underset{Fe(V)P}{\parallel}} + C_6H_{11}OH \quad (19)$$
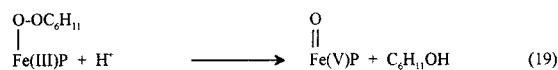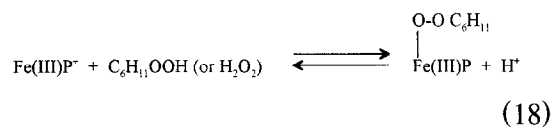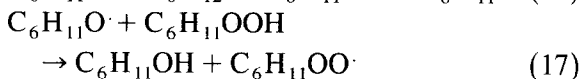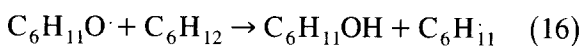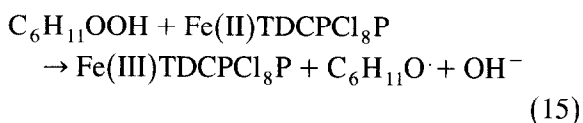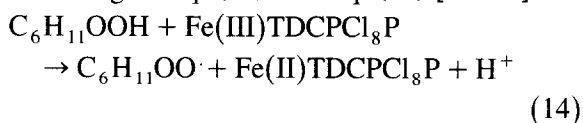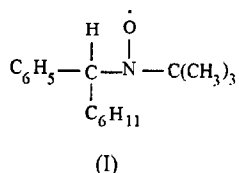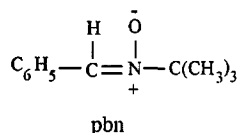
The possible involvement of radical species in the overall redox process has been tested by carrying on experiments in the presence of pbn which is known to trap radicals to give more stable nitroxides [52]. In many cases the nature of the trapped radical can be identified by the parameters deduced from the ESR spectrum. Irradiation of oxygenated cyclohexane/dichloromethane solutions of the integrated systems $W_{10}O_{32}^{4-}$/Fe(III)P in the spectrometer cavity gives rise to a spectrum consisting of a triplet of doublets whose hyperfine splitting constants $a_N = 14.5$ G, $a_H = 2.1$ G are consistent with the trapping of a cyclohexyl radical to give the paramagnetic adduct (I) [53]. This result totally agrees with the photoactivity of $W_{10}O_{32}^{4-}$ schematised in Scheme 1b. On the contrary, as already mentioned, previous experiments with $W_{10}O_{32}^{4-}$ alone provided evidence for the formation of both the adducts of pbn with C_6H_{11} and OH· radicals [24], in agreement with a mechanism which favours a Fenton-type reduction of H_2O_2 in this system. We were unable to establish the pbn effect on oxidation quantum yields and products distribution because at the photoexcitation wavelength employed (325 nm) its absorption of light is significant, and this may result in its decomposition during the irradiation period.

The influence of O_2 concentration on cyclohexane product distribution may probably be explained by considering that, in the presence of small amounts of O_2, the reaction between bulk phase radical intermediates and O_2 (Eq. (10)) are inhibited. Thus, the concentration of

$C_6H_{11}OOH$ decreases and, consequently, the probability of disproponation reactions is sensibly reduced. The observed enhancement in the formation of the alcohol may be explained by a reaction mechanism of the type described by Eqs. (14)–(16) where $C_6H_{11}OOH$ is reduced by the porphyrin or polyoxotungstate in their reduced forms.

Laser flash photolysis experiments carried out at low oxygen pressure (20 torr) give results

$$C_6H_5-\overset{\overset{H}{|}}{C}=\overset{\overset{O}{|}}{\underset{+}{N}}-C(CH_3)_3$$

pbn

$$C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{C_6H_{11}}{|}}{C}}-\overset{\overset{O}{|}}{N}-C(CH_3)_3$$

(I)

very similar to those reported in Fig. 4b with 760 torr of oxygen, indicating that also at the lowest oxygen concentration employed in photocatalytic experiments, the reoxidation of $W_{10}O_{32}^{5-}$ by O_2 precedes the reaction with the iron(III)porphyrin. Therefore, at low oxygen pressure too, the main role of the iron porphyrin in the integrated system is to react with H_2O_2, HO_2^- and $C_6H_{11}OOH$.

4. Conclusion

For the first time the oxidation of cyclohexane by photoexcited $W_{10}O_{32}^{4-}$ has been investigated in the presence of iron porphyrin complexes. In the absence of oxygen, σ-alkyl-Fe(III) complexes are obtained as a consequence of the reaction between cyclohexyl radical and the iron porphyrin in its reduced form. In the presence of dioxygen, the photoexcited polyoxotungstate has the role of initiating the activation of O_2

through its reduction to O_2^- and H_2O_2. The subsequent cleavage of O–O bonds occurs with the involvement of the iron porphyrin.

As far as the photocatalytic properties are concerned, the investigated systems are integrated photocatalysts consisting of two moieties which are able to function separately in the photochemically induced oxygenation of alkanes. In comparison with $W_{10}O_{32}^{4-}$ alone, a higher selectivity is obtained, with the formation of cyclohexanol as a major product. In comparison with iron porphyrins alone, higher yields in the oxidation products and higher stability of the porphyrins themselves are observed.

Acknowledgements

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