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## Redox properties of photoexcited (nBu<sub>4</sub>N)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/Fe<sup>III</sup> porphyrins composite systems

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### Abstract

The photochemical and photocatalytic properties of (nBu<sub>4</sub>N)<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>) was investigated in the presence of several Fe<sup>III</sup>-*meso*-tetrarylporphyrins. The photochemical excitation of the polyoxotungstate in the presence of 2-propanol or cyclohexane leads to its reduction and simultaneous oxidation of the organic substrate. The reduced polyoxotungstate is able, in turn, to transfer one electron to the Fe<sup>III</sup> porphyrin to give the ferrous complex. In the presence of anaerobic cyclohexane,  $\sigma$ -alkyl-Fe<sup>III</sup> complexes are obtained as a consequence of the reaction between cyclohexyl radicals and the iron porphyrin in its reduced form. Subsequent oxidative migration of the  $\sigma$ -bound cyclohexyl group from the iron to one of the pyrrole nitrogens leads to the formation of *N*-substituted porphyrin. The results obtained by laser flash photolysis experiments indicate that the electron transfer from the photoreduced polyoxotungstate to the Fe<sup>III</sup> porphyrin complexes is faster than to O<sub>2</sub>. Therefore, the photoexcited polyoxotungstate can operate as a source of electrons for the reduction of the Fe<sup>III</sup> porphyrin to the ferrous form, thus creating the site at which O<sub>2</sub> is reductively activated. Continuous irradiation of the composite systems under aerobic conditions leads to the oxidation of cyclohexane to cyclohexanol and cyclohexanone. In comparison with the Fe<sup>III</sup> porphyrins alone, the composite photocatalysts present higher yields of the oxidation products. In comparison with PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> alone, they produce higher amounts of the hydroxylated product.

**Keywords:** Polyoxotungstates; Photocatalysis; Iron porphyrins; Oxygen activation; Laser flash photolysis; Biomimetic oxidation

### 1. Introduction

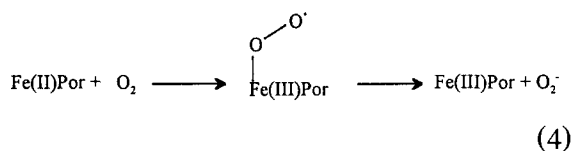
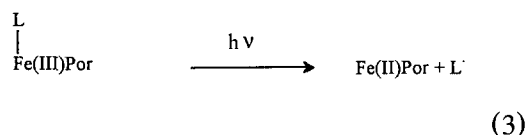
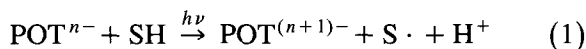
There is a considerable interest in the search of new systems able to catalyse the reductive activation of dioxygen for the oxygenation of inactivated C–H bonds under mild conditions [1]. In this contest, photocatalysts based on the use of either polyoxometallates or metal porphyrin complexes are intensively investigated.

In particular, it has been demonstrated that photochemically induced reduction of polyoxotungstates (POT<sup>*n*-</sup>) [2–6] and Fe<sup>III</sup> porphyrins (Fe<sup>III</sup>Por) [7–13] under aerobic conditions brings about the subsequent oxygenation of hydrocarbons.

The photoreduction of POT<sup>*n*-</sup> is accompanied by the oxidation of organic substrates (SH) according to Eq. (1) [2–6]. Subsequent reoxidation of the catalyst occurs through a mechanism which involves the oxidation of the photore-

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duced polyoxotungstate by  $O_2$  [14,16] (Eq. (2)). In the case of  $Fe^{III}Por$ , light induces an intramolecular electron transfer which leads to the oxidation of some axial ligand such as  $C_2H_5O^-$ ,  $OH^-$ ,  $N_3^-$ ,  $Cl^-$  and the formation of  $Fe^{II}$  [17–22] (Eq. (3)). The ferrous porphyrin can, in turn, coordinate  $O_2$  with regeneration of the  $Fe^{III}$  centre through the reductive activation of  $O_2$  (Eq. (4)), if  $Fe^{III}$  porphyrins bearing bulky substituents, able to prevent the formation of  $\mu$ -oxo-dimer porphyrin complexes [13,23,24], are used.



Both  $Fe^{III}Por$  and  $POT^{n-}$  have advantages and disadvantages in oxidation photocatalysis. In comparison with the iron(III) porphyrins, with the same substrate,  $POT^{n-}$  are characterized by higher photooxidation quantum yields. On the other hand, only few systematic studies of the reductive activation of  $O_2$  by these compounds have been reported [15,16], 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, as they exhibit quantum yields at least one order of magnitude lower than those typical for  $POT^{n-}$ . 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 compos-

ite systems, that are potentially able to combine the high photochemical efficiency of polyoxotungstates and the biomimetic activity of metal porphyrins. In particular, we have recently investigated the photocatalytic properties of  $(nBu_4N)_4W_{10}O_{32}$  ( $W_{10}O_{32}^{4-}$ ) in the presence of iron porphyrin complexes in the oxygenation of cyclohexane [25].

It has often been stated that polyoxometalates can be considered models of transition metal oxides and can mimic the interactions between molecular compounds and solid surfaces of interest in heterogeneous catalysis [2,26–28]. Therefore, the  $POT^{n-}/Fe^{III}Por$  composite systems may provide homogeneous phase models, whose study is accessible with a large variety of experimental techniques, for clarifying the photocatalytic behaviour of the previously investigated heterogeneous photocatalysts in which the porphyrin complex was anchored on the surface of semiconducting oxides [10,12].

In the present paper, we examine the photochemical and photocatalytic properties of integrated systems consisting of mixtures of  $(nBu_4N)_3PW_{12}O_{40}$  ( $PW_{12}O_{40}^{3-}$ ) and several iron porphyrin complexes whose structures are depicted in Fig. 1. In particular, we report the results of experiments on the kinetics of electron transfer between the photoreduced polyoxotungstate and  $Fe^{III}$  porphyrins obtained by laser flash photolysis. Some data on their efficiency in the photoinduced oxygenation of cyclohexane by  $O_2$  are also reported. The investigations

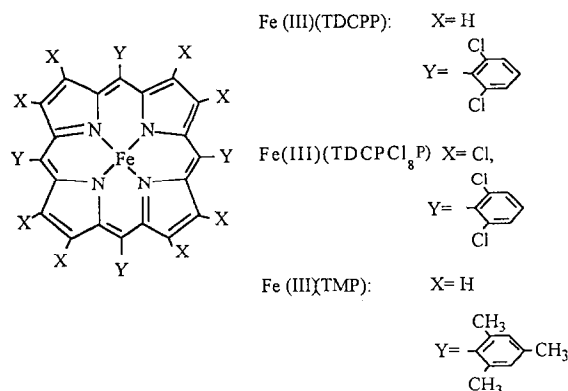


Fig. 1. Structure of the substituted iron porphyrins investigated.

discussed here are not only relevant to oxidation catalysis but can provide a contribution to the modelling of polyoxometallate–protein interactions, a research topic whose interest is increasing because of the applications of polyoxometallates as antiviral drugs [29–31].

## 2. Experimental

### 2.1. Materials

The complexes iron(III)-*meso*-tetrakis(dichlorophenyl)-porphyrin chloride ( $\text{Fe}^{\text{III}}$ (TDCPP)), iron(III)-*meso*-tetrakis(dichlorophenyl)octa- $\beta$ -chloroporphyrin chloride ( $\text{Fe}^{\text{III}}$ (TDCPCl<sub>8</sub>P)) and iron(III)-*meso*-tetrakis(trimethylphenyl)-porphyrin chloride ( $\text{Fe}^{\text{III}}$ (TMP)) were prepared and purified as previously reported [32].  $(\text{nBu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$  was prepared according to literature data [33]. All the solvents were spectroscopic grade reagents and were used without further purification.

### 2.2. Apparatus

UV–vis. spectra were recorded with a Kontron Model Uvikon 940 spectrophotometer. 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.

Irradiations were carried out with a low pressure mercury lamp 254 nm thermostable cell holder ( $22 \pm 1^\circ\text{C}$ ). The light intensity was measured by the ferrioxalate actinometric method [34]. 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

For laser flash photolysis experiments,  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $5 \times 10^{-5}$  mol dm<sup>-3</sup>) and  $\text{Fe}^{\text{III}}\text{P}$  ( $2 \times 10^{-5}$  mol dm<sup>-3</sup>) were dissolved in  $\text{CH}_3\text{CN}/i\text{PrOH}$  (1:1) and irradiated in a 4 cm spectrophotometric cell. In the  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}/\text{CH}_3\text{CN}$  (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.

For the continuous irradiation experiments,  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>) and  $\text{Fe}^{\text{III}}\text{Por}$  ( $2 \times 10^{-5}$  mol dm<sup>-3</sup>) were dissolved in  $\text{CH}_3\text{CN}/i\text{PrOH}$  (1:1) or  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}/\text{CH}_3\text{CN}$  (6:3:1) and irradiated at 254 nm in a 1-cm spectrophotometric cell. When necessary, the solutions were degassed to less than  $1 \times 10^{-5}$  torr by means five vacuum-line freeze–thaw–pump cycles. Blank irradiation experiments in the absence of both the polyoxotungstate and the iron(III)porphyrin or with the latter alone did not bring about any oxidation of cyclohexane.

## 3. Results and discussion

### 3.1. Photoredox properties

$\text{PW}_{12}\text{O}_{40}^{3-}$  ( $2 \times 10^{-4}$  mol dm<sup>-3</sup>) was irradiated at 254 nm in deaerated  $\text{CH}_3\text{CN}/i\text{PrOH}$  (1:1) mixed solvent containing one of the investigated  $\text{Fe}^{\text{III}}$  porphyrin ( $2 \times 10^{-5}$  mol dm<sup>-3</sup>). Fig. 2 reports the UV–vis. spectral variations observed in the case of the  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TMP) system. Very similar results were obtained with all the other  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ Por investigated systems. The red shift of the Soret band is a clear indication that  $\text{Fe}^{\text{III}}$  undergoes reduction to the ferrous state [7]. The original spectrum of the ferric porphyrin was recovered after oxygenation of the solution.

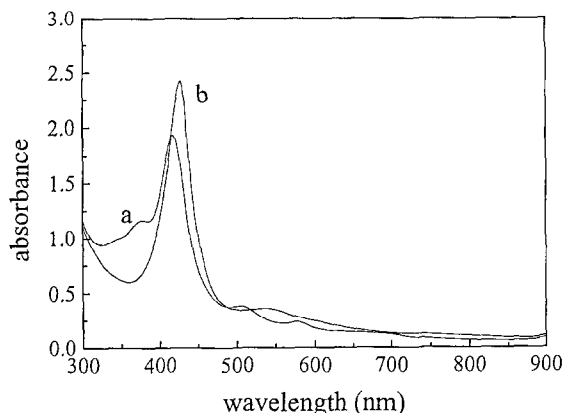
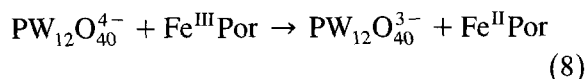
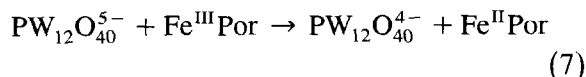
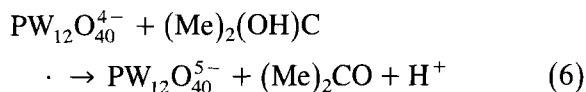
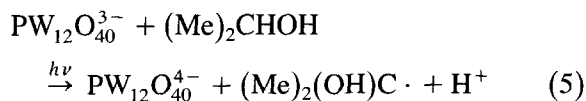


Fig. 2. Uv-vis. spectral changes observed during irradiation at 254 nm of  $\text{CH}_3\text{CN}/i\text{PrOH}$  (1:1) deaerated solutions containing  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) and  $\text{Fe}^{\text{III}}(\text{TMP})$  ( $2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ). (a) Before irradiation, (b) after 10 min irradiation.

Polyoxotungstate can be considered as the photochemical active moiety of the  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}\text{Por}$  integrated systems, since under our conditions, it absorbs more than 90% of incident light. It has been stated earlier that photoexcitation of  $\text{PW}_{12}\text{O}_{40}^{3-}$  in the presence of  $i\text{PrOH}$  induces the one electron reduction of the polyoxotungstate with the simultaneous oxidation of the alcohol to  $(\text{Me})_2(\text{OH})\text{C}\cdot$  radical according to Eq. (5). As shown in Eq. (6), the monoreduced polyoxotungstate can, in turn, accept a second electron from  $(\text{Me})_2(\text{OH})\text{C}\cdot$  radicals [35–37]. The work by Fox et al. [36] and our own [28] show that the oxidizable substrate is coordinated to the polyoxotungstate prior to electron transfer. In principle, the organic radical which is formed should be able to transfer a second electron to the polyoxotungstate before it diffuses away (Eq. (6)). This is the basis of the well known phenomenon of ‘current doubling’ taking place at semiconductor surfaces. On the basis of reported electrochemical data [16,33,38,39], both photogenerated  $\text{PW}_{12}\text{O}_{40}^{4-}$  and  $\text{PW}_{12}\text{O}_{40}^{5-}$  are able to transfer an electron to the ferric porphyrin according to Eqs. (7) and

(8), thus explaining the observed spectral changes.



Laser flash photolysis experiments with 266 nm excitation light allowed us to follow the

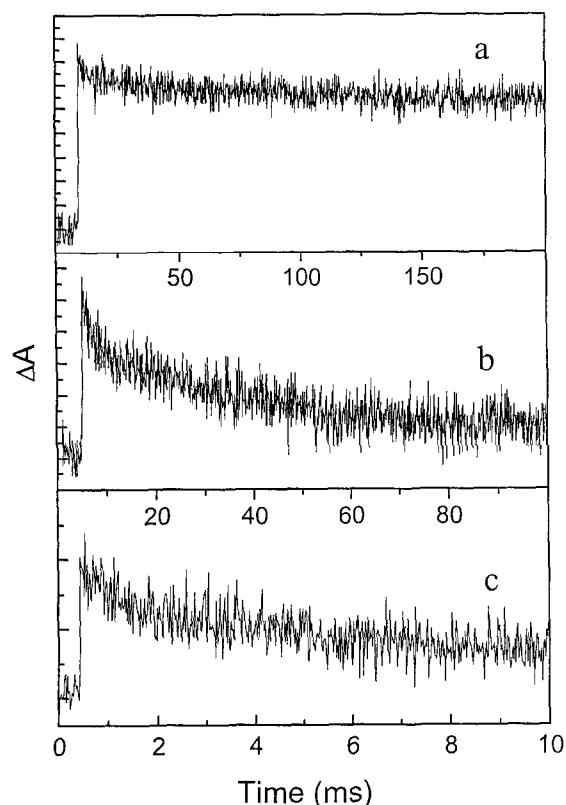


Fig. 3. Laser flash photolysis of  $\text{CH}_3\text{CN}/i\text{PrOH}$  (1:1) solutions containing  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ). (a) In the absence of both  $\text{O}_2$  and  $\text{Fe}^{\text{III}}(\text{TMP})$ , (b) oxygen free solutions containing and  $\text{Fe}^{\text{III}}(\text{TMP})$  ( $2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ), (c) in the presence of both  $\text{O}_2$  (760 Torr) and  $\text{Fe}^{\text{III}}(\text{TMP})$  ( $2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ).

primary  $\text{PW}_{12}\text{O}_{40}^{3-}$  photoreduction (Eq. (5)) and its subsequent reoxidation process (Eq. (8)). The one electron photoreduction of  $\text{PW}_{12}\text{O}_{40}^{3-}$  can be easily monitored by the characteristic absorption band appearing at 750 nm [36].

Fig. 3 shows the results obtained by following the absorbance variations at 750 nm after photoexcitation of  $\text{PW}_{12}\text{O}_{40}^{3-}$  in  $\text{CH}_3\text{CN}/i\text{PrOH}$  (1:1). Fig. 3a reports the results obtained by irradiation of dioxygen free solutions of  $\text{PW}_{12}\text{O}_{40}^{3-}$  in the absence of  $\text{Fe}^{\text{III}}$  porphyrin. The flash causes a very fast (less than 5 ns) absorbance increase due to the monoreduced species  $\text{PW}_{12}\text{O}_{40}^{4-}$ .

Fig. 3b reports, as an example, the results obtained when oxygen free solutions of  $\text{PW}_{12}\text{O}_{40}^{3-}$  were photoexcited in the presence of  $\text{Fe}^{\text{III}}$ (TMP) ( $2 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ). An analysis of the decay curve indicates that the reoxidation of photogenerated  $\text{PW}_{12}\text{O}_{40}^{4-}$  by the  $\text{Fe}^{\text{III}}$  porphyrin (Eq. (8)) follows pseudo first order kinetics with respect to the reduced polyoxotungstate (about  $5 \times 10^{-6}$  mol  $\text{dm}^{-3}$ ). An analogous behaviour is observed when the polyoxotungstate was irradiated in the presence of either  $\text{Fe}^{\text{III}}$ (TDCPP) or  $\text{Fe}^{\text{III}}$ (TDCPCl<sub>8</sub>P). From the mono-exponential decay curves it has been possible to obtain the pseudo-first-order rate constants for reaction (8) (Table 1). The lower values observed for  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TDCPCl<sub>8</sub>P) as compared with  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TDCPP) and

$\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TMP) seem to indicate that the electron transfer is controlled by steric effects.

### 3.2. Photocatalytic reductive activation of $\text{O}_2$

The above results indicate that photoexcited  $\text{PW}_{12}\text{O}_{40}^{3-}$  can operate as a source of electrons for the reduction of the  $\text{Fe}^{\text{III}}$  porphyrin to the ferrous form, thus creating the site at which  $\text{O}_2$  is reductively activated (Eq. (4)).

The decay curve of  $\text{PW}_{12}\text{O}_{40}^{4-}$  in the presence of both  $\text{Fe}^{\text{III}}$ (TMP) and  $\text{O}_2$  reported in Fig. 3 (curve c) indicates that the electron transfer rate from  $\text{PW}_{12}\text{O}_{40}^{4-}$  to  $\text{Fe}^{\text{III}}$ (TMP) is faster than that found under anaerobic conditions (curve b). This result can be explained taking into account that the very fast reaction of the ferrous porphyrin with  $\text{O}_2$  (Eq. (4)) strongly competes with the cage reoxidation (Eq. (7)), reverse reaction), favouring the separation of the products of the primary electron transfer [7]. An inspection of the rate constant values reported in Table 1 shows that analogous results were obtained with the other  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ Por systems examined here.

The ability of  $\text{PW}_{12}\text{O}_{40}^{4-}$  to reduce  $\text{O}_2$  is well documented [14,16] (Eq. (2)). Kinetic data from laser flash photolysis experiments have been published earlier [40–44]. In particular, it has been demonstrated that the rate constant of the electron transfer from the photoreduced polyox-

Table 1  
Rate constants <sup>a</sup> for the reoxidation process of the photogenerated  $\text{PW}_{12}\text{O}_{40}^{4-}$  <sup>b</sup>

System	$k \times 10$ ( $\text{s}^{-1}$ )	
	Without $\text{O}_2$	With $\text{O}_2$ (760 Torr)
$\text{PW}_{12}\text{O}_{40}^{3-}/h\nu$	No electron transfer process	0.13
$\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TMP) <sup>c</sup> / $h\nu$	4.6	33
$\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TDCPP) <sup>c</sup> / $h\nu$	4.0	4.6
$\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}$ (TDCPCl <sub>8</sub> P) <sup>c</sup> / $h\nu$	1.3	2.9

<sup>a</sup> By laser flash photolysis of  $i\text{PrOH}$  (1:1) containing  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $2 \times 10^{-4}$  mol  $\times$   $\text{dm}^{-3}$ ). The error on the value reported is about 30%.

<sup>b</sup> On the basis of absorbance decrease at 750 nm.

<sup>c</sup> ( $2 \times 10^{-5}$  mol  $\times$   $\text{dm}^{-3}$ ).

otungstate to  $O_2$  is strongly affected by the nature of the reaction environment, with  $H^+$  concentration playing a fundamental role. Under our experimental conditions, this process seems to be relatively slow since no bleaching of the solution is observed after the flash in 200 ms full scale. The rate constant values reported in Table 1 have been obtained by laser flash photolysis experiments on a longer time scale.

### 3.3. Photooxidation of cyclohexane in anaerobic conditions

The catalytic behaviour of the  $PW_{12}O_{40}^{3-}/Fe^{III}Por$  composite systems has been preliminarily tested by studying the oxidation of cyclohexane. The spectral variations shown in Fig. 4 were obtained when  $CH_2Cl_2/C_6H_{12}/CH_3CN$  (6:3:1) solutions containing both  $PW_{12}O_{40}^{3-}$  and  $Fe^{III}(TMP)$  were irradiated under anaerobic conditions.

After few minutes irradiation, the Soret band (419 nm) undergoes a blue shift to 412 nm and an increase in intensity (curve b). The original

spectrum of the oxidized porphyrin is observed again after oxygenation of the solution. On the basis of previous work, it seems reasonable to ascribe this spectral behaviour to the formation of a  $Fe^{III}-\sigma$ -cyclohexyl complex [45,46]. This complex should be formed as a consequence of the very fast reaction between the reduced porphyrin and cyclohexyl radicals (Eqs. (9) and (10)), following the primary photoprocess. The same product has been recently obtained upon irradiation of the isopolyanion  $W_{10}O_{32}^{4-}$  in the presence of  $Fe^{III}$  porphyrins [25].

A peculiar behaviour of the  $PW_{12}O_{40}^{3-}/Fe^{III}(TMP)$  system is the occurrence of further spectral variations, following those described above, indicating the disappearance of the  $Fe^{III}-\sigma$ -cyclohexyl complex and the formation of a new species characterized by a red shifted Soret band and three less intense bands between 500 and 700 nm (curve c). Finally, curve d is obtained after irradiation is stopped and oxygen is admitted. The species giving rise to spectra c and d may be respectively attributed to  $Fe^{II}$  and  $Fe^{III}-N$ -cyclohexyl porphyrin complexes, by

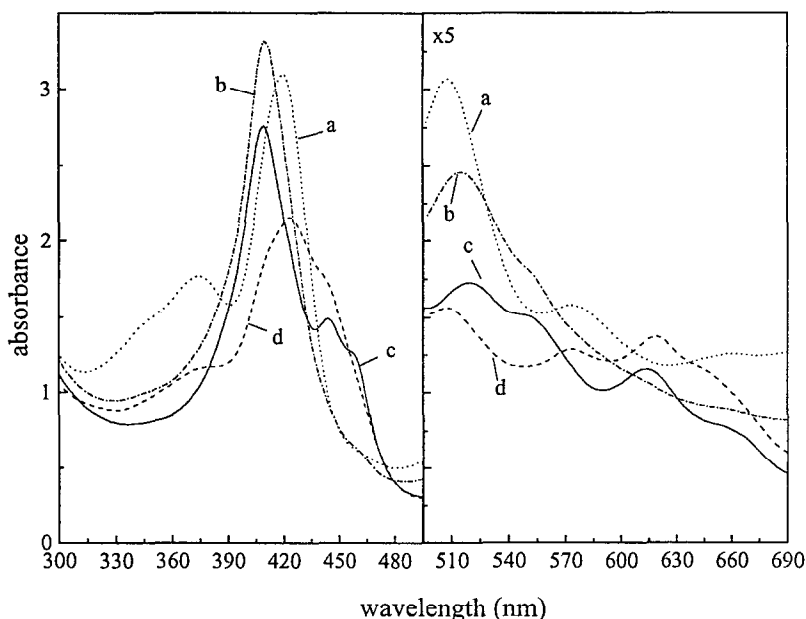
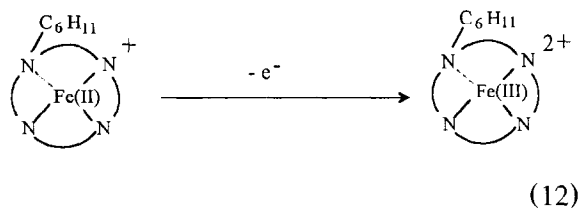
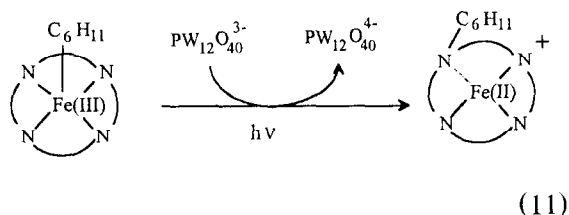
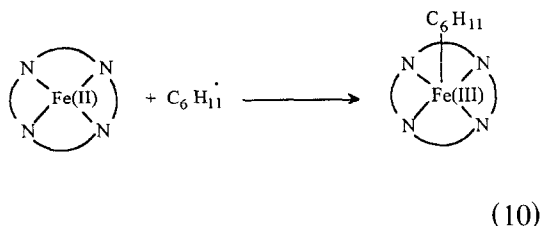
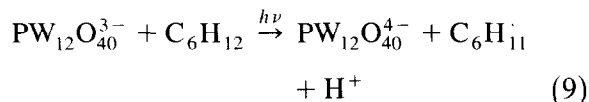


Fig. 4. Uv-vis. spectral changes observed upon irradiation at 254 nm of  $CH_2Cl_2/C_6H_{12}/CH_3CN$  (6:3:1) solutions containing  $PW_{12}O_{40}^{3-}$  ( $2 \times 10^{-4}$  mol  $dm^{-3}$ ) and  $Fe^{III}(TMP)$  ( $2 \times 10^{-5}$  mol  $dm^{-3}$ ). (a) Before irradiation, (b) after 15 min irradiation in the absence of  $O_2$ , (c) after 75 min irradiation in the absence of  $O_2$ , (d) 90 min after irradiation is stopped and  $O_2$  is admitted.

comparison with the data reported by Balch et al. [47]. *N*-substituted porphyrins have been extensively investigated because of their involvement as intermediates in the ‘suicidal degradation’ of hemoproteins [48].

The Fe<sup>II</sup>-*N*-substituted porphyrin would be produced by an oxidative migration of the  $\sigma$ -bound cyclohexyl group from the iron atom to one of the pyrrole nitrogen atoms; this oxidation can likely be induced by the photoexcited polyoxotungstate (Eq. (11)) [47]. Eventually, the Fe<sup>II</sup>-*N*-substituted porphyrin is oxidized to the ferric form (Eq. 12). The conversion of the Fe<sup>II</sup> to Fe<sup>III</sup> form is reversible, as confirmed by the addition of metallic zinc to a solution of the latter.



The systems  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}(\text{TDCPP})$  and  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}(\text{TDCPCl}_8\text{P})$  show a behaviour that is very similar to that described for  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}(\text{TMP})$ . It must be noted, however, that their iron *N*-alkyl derivatives are considerably more stable in their reduced form. This is understandable in view of the well known stabilizing effect of chlorine substituents on the reduced form of iron porphyrin complexes. The fact that photoexcitation of  $\text{W}_{10}\text{O}_{32}^{4-}$  did not give rise to the formation of Fe<sup>III</sup>-*N*-substituted porphyrins can be ascribed to the lower oxidizing properties of  $\text{W}_{10}\text{O}_{32}^{4-}$  with respect to  $\text{PW}_{12}\text{O}_{40}^{3-}$  [41].

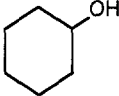
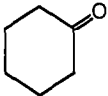
#### 4. Photocatalytic behaviour in the presence of O<sub>2</sub>

Continuous irradiation of  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}/\text{CH}_3\text{CN}$  (6:3:1) solutions of the composite catalysts  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}\text{Por}$  in the presence of 760 torr of dioxygen leads to the formation of both cyclohexanol and cyclohexanone. The product ratios are shown in Table 2 which also reports the results obtained when  $\text{PW}_{12}\text{O}_{40}^{3-}$  is irradiated alone. According to previous work [3,14], the photoexcitation of  $\text{PW}_{12}\text{O}_{40}^{3-}$  gives cyclohexanol and cyclohexanone, with a ratio of the alcohol to the ketone slightly less than one. The iron porphyrin complex affects this product distribution; in particular, the irradiation of the integrated system  $\text{PW}_{12}\text{O}_{40}^{3-}/\text{Fe}^{\text{III}}(\text{TDCPCl}_8\text{P})$  leads to the formation of cyclohexanol as the major product with a cyclohexanol to cyclohexanone concentration ratio of 1.63.

The photooxidation quantum yield, calculated as the ratio between mol of oxidised cyclohexane and mol of absorbed photons was  $(3.5 \pm 0.5) \times 10^{-2}$  independent of the presence and the nature of the iron porphyrin complex. It is noteworthy that this value is significantly higher (about ten times) than those observed when the same porphyrins are used as photocatalysts for cyclohexane oxidation in the absence of  $\text{PW}_{12}\text{O}_{40}^{3-}$  [13].

Table 2

Photocatalytic properties <sup>a</sup> of PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>/Fe<sup>III</sup>Por integrated systems <sup>b</sup> in CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>12</sub>/CH<sub>3</sub>CN (6:3:1) mixed solvent, in the presence of 760 Torr of O<sub>2</sub>

Photocatalyst	Product ratios/%		Cycle <sup>c</sup> number
			
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	49	51	–
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup> /Fe <sup>III</sup> (TMP)	57	43	330
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup> /Fe <sup>III</sup> (TDCPP)	56	44	3380
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup> /Fe <sup>III</sup> (TDCPCl <sub>8</sub> P)	62	38	330

<sup>a</sup> Irradiations were carried out at 22 ± 1°C, at 325 nm.

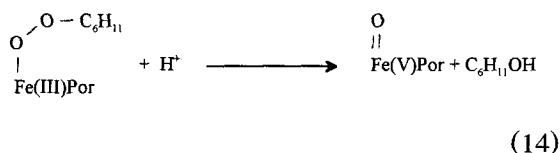
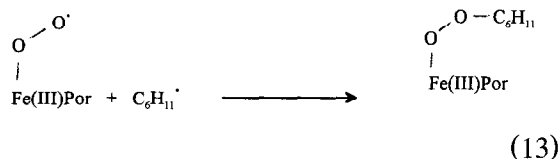
<sup>b</sup> Initial concentration PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>: 2 × 10<sup>-4</sup> mol dm<sup>-3</sup>, initial concentration Fe<sup>III</sup>Por: 2 × 10<sup>-5</sup> mol dm<sup>-3</sup>.

<sup>c</sup> Mol of oxidised cyclohexane/mole of consumed iron porphyrin.

During the photochemical experiments (about 180 min), the only observed spectral variation is a bleaching of the spectrum in the wavelength range from 350 to 700 nm, indicating that only the porphyrin moiety of the integrated photocatalysts undergoes an oxidative 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 mol of photooxidized cyclohexane and mol of degraded porphyrin complexes. The obtained values are reported in the last column of Table 2.

Although the formulation of a mechanism for the oxygenation of cyclohexane by the PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>/Fe<sup>III</sup>Por systems is premature, it is likely that the very fast reaction of O<sub>2</sub> with Fe<sup>II</sup>porphyrin in the presence of cyclohexyl radicals leads to the formation of Fe<sup>III</sup>peroxoalkyl complexes (Eq. (13)), as proposed for photoexcited Fe<sup>III</sup>porphyrins in the absence of polyoxotungstate [9,13]. Polar environments and the availability of protons favour a heterolytic cleavage of the O–O bond of the iron–alkylperoxo complexes with the formation of high-valent iron–oxo complexes (formally equivalent to Fe<sup>V</sup>=O) according to Eq. (14). These species are equivalent to the iron–oxo intermediates of the catalytic cycle of the monooxygenating hemoprotein cytochrome

P450. The described reaction pathway leads exclusively to the hydroxylation of cyclohexane, thus explaining the higher amount of cyclohexanol formed in the presence of the Fe<sup>III</sup>porphyrin complexes. On the other hand, the same high valent hydroxylating species may be obtained as a consequence of the reactions between the porphyrin in its oxidised form and the peroxide products formed by the direct reduction of O<sub>2</sub> by the photoreduced polyoxotungstate, such as H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub><sup>-</sup> and C<sub>6</sub>H<sub>11</sub>OOH [25].



## 5. Conclusion

Photochemical excitation of PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> in the presence of 2-propanol or cyclohexane leads to its reduction and simultaneous oxidation of the



organic substrate to radical species. The reduced polyoxotungstate is able, in turn, to transfer an electron to Fe<sup>III</sup>-*meso*-tetraarylporphyrins. In the absence of dioxygen,  $\sigma$ -alkyl-Fe<sup>III</sup> complexes are obtained as a consequence of the reaction between cyclohexyl radicals and the iron porphyrin in its reduced form. Subsequent oxidative migration of the  $\sigma$ -bound cyclohexyl group from the iron to one of the pyrrole nitrogens leads to the formation of *N*-substituted porphyrins. Since these intermediates are known to be involved in the 'suicidal degradation' of hemoproteins, a deeper investigation into the photoinduced redox processes of the PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>/Fe<sup>III</sup>Por systems is of interest in view of the possible application of polyoxometallates in medicine. Moreover, the results obtained may be considered as a starting point toward new ways for the 'clean' preparation of *N*-substituted porphyrin.

The electron transfer from the photoreduced polyoxotungstate to the Fe<sup>III</sup>porphyrin complexes precedes that to O<sub>2</sub>. Therefore, the Fe<sup>III</sup>porphyrin seems to be the active site for the reductive activation of O<sub>2</sub> by the PW<sub>12</sub>O<sub>40</sub><sup>3-</sup>/Fe<sup>III</sup>Por photosystems. The systems described here are composite ones, consisting of photocatalysts able to operate separately in the photooxidation of hydrocarbons. In comparison with the Fe<sup>III</sup>porphyrins alone, higher yields of the oxidation products are observed. In comparison with PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> alone, there are an increase of the cyclohexanol/cyclohexanone ratio, and the creation of a better defined site for O<sub>2</sub> reduction (the porphyrin complex).

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