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Photochemistry of Iron-porphyrin complexes. Biomimetics and catalysis.

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Abstract

An intramolecular electron transfer can occur in iron porphyrin complexes that are irradiated with light of suitable wavelength corresponding to axial ligand-to-metal charge transfer transitions. This process leads to the reduction of Fe(III) to Fe(II) and to the oxidation of the axial ligand to a radical species. The efficiency of the photoredox process is increased in the presence of species able of trapping the ferrous complex and/or the radical in competition with the back electron transfer process. Photoredox reactions of iron porphyrins and heme-proteins (cytochrome c) are examined in the framework of the fundamental role of electron transfer processes in biological systems. The products of the primary photoprocess can induce reactions leading to reduction or oxidation of various substrates with catalytic efficiency. This biomimetic aspect of the photoredox behavior of iron porphyrins is pointed out examining the results obtained in investigations concerning the iron-porphyrin based photoreduction of CCl_4 in homogeneous solution, and photooxygenation of alkanes in both homogeneous and heteterogeneous systems.

1. INTRODUCTION

The photochemistry of porphyrins and their metal complexes has long been an interesting subject for many research groups. For many years a large part of investigations aimed to clarifying the complex mechanism of the photosynthesis. For this reason most of investigations have concerned magnesium-porphyrins or other closed shell metal porphyrins (e.g., Sn and Zn porphyrins) and free bases. These compounds (*emitting* porphyrins), because of their long living excited states, can give rise to efficient energy transfer to ground state substrates, producing very reactive species (sensitization) which can initiate processes of wide interest in different fields which are difficult to realize by traditional chemical ways. [1] For example, energy transfer processes have found very important applications in

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tumor phototherapy in which the production of singlet oxygen by porphyrin sensitization plays a fundamental role.[2]

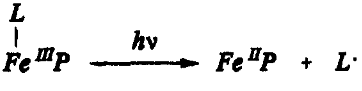
The photochemistry of open shell *non emitting* metal porphyrins, in particular iron and manganese porphyrins, has attracted the interest of a large number of authors[3,4] because of the biomimetic behavior of those compounds which have been found to efficiently catalyze thermal redox reactions on organic substrates mimicking the *in vivo* behavior of Cytochrome P-450. *Non emitting* porphyrins do not lead to sensitization reactions because of very short lifetime of their excited states. Nonetheless, these complexes show photochemical activity which is due to a light induced intramolecular electron transfer involving the metal and the axial ligands. This a way to induce redox processes in metal-porphyrin complexes which are known frequently to achieve their catalytic activity through reversible modification of the oxidation state of the metal centre.

Herein, we review the most recent results obtained in investigations on intramolecular photoredox reactions of iron porphyrins and their involvement in biomimetic photocatalysis.

2. PHOTOREDOX REACTIONS

2.1. Iron-porphyrin complexes

The first case of an intramolecular redox process involving an iron-porphyrin complex has been reported already in 1980 by Bartocci et al.[5]. In that investigation the authors observed that the irradiation in the near ultraviolet of de-aerated alkaline ethanol-water solutions of hemin (Fe(III)-protoporphyrin IX, Fe(III)P) gave rise to an electron transfer from the axial ethanolate ligand to Fe(III) leading to the reduction of Fe(III) to Fe(II) and the oxidation of ethanolate to ethoxyl radical. Several papers concerning similar investigations involving different iron porphyrins (FeP) and axial ligands (L) in different media were successively published.[6-13] The axial ligands involved in these investigations include alcohols, azide , halides, pyridine and imidazole. In every case the result was the reduction of iron and the oxidation, with consequent detachment, of the axial ligand (eq. 1).



$$\overset{L}{\underset{|}{}}\!Fe^{III}P \xrightarrow{h\nu} Fe^{II}P + L^{\cdot} \qquad (1)$$

This mechanism is supported by laser-flash photolysis experiments, by the observation of the esr spectrum of the paramagnetic leaving radicals, by the Raman signal of the porphyrin ring.

The observed photoreaction quantum yields range from 1×10^{-5} to 1×10^{-2} and depend on: *i)* the nature of the porphyrin ring; *ii)* the charge separation occurring in competition with the radiationless deactivation of the excited state; *iii)* the possibility for the $L^{\cdot}$ radical to escape from the first coordination sphere of the metal before cage re-oxidation; *iv)* the ability of $L^{\cdot}$ to reduce additional Fe(III)P.

2.2. Cytochrome c

Cytochrome c, a hemoprotein from the mithocondrial respiratory chain, plays a fundamental but not completely clarified role in biological electron transport. Experimental evidence [14] indicates that the site governing the physiological functions of cytochrome c is the heme group where the iron centre can alternate between diamagnetic Fe(II) and low spin Fe(III). At neutral pH both the oxidized and the reduced form contain histidine-18 and methionine-80 as axial ligands.

A large part of investigations concerning cytochrome c are directed at clarifying its electron carrier properties by studying the kinetics and the mechanism of its redox reactions with biological as well as with chemical reagents. A redox process may cause, in the proteic structure of the hemoprotein, modification from which useful information on both the structure and the activity-structure relationship can be obtained. The induction of redox reactions by irradiation of cytochrome c with light of selected wavelength proved to be a very useful way to perform appropriate chemical changes in the protein [15] and, at the same time, to study the mechanism of electron transfer processes involving cytochrome c in the mithocondrial respiratory chain. [16]

The photoredox processes involving the metal centre in cytochrome c have been studied in our laboratory. [17,18] The results obtained indicate that the photochemistry of cytochrome c is quite similar to that of iron-porphyrin complexes. Indeed, under irradiation, Fe(III) cytochrome c undergoes reduction to the ferrous form, presumably as a consequence of an intramolecular electron transfer from an axial ligand (histidine-18 or methionine-80) to Fe(III) (eq. 2).

$$Met_{80}\text{-}S\text{-}Fe^{III} \xrightarrow{h\nu} Met_{80}\text{-}S^{+}\text{-}Fe^{II} \tag{2}$$

The photoreduced species gives rise, upon re-oxidation, to a Fe(III) cytochrome complex without any proteic activity. This product displays an electronic absorption spectrum different from that of the native protein in the long wavelength field where the 695-nm band is missing. Since this band is the fingerprint of the coordination of the methionine-80 to iron, its absence in the spectrum has been taken as an indication of the breaking of the iron-methionine bond.

The esr spectrum carried out at 90 K shows that the iron hexacoordination is maintained in the photomodified cytochrome after the irradiation and the g values are very close to those obtained for Fe(III)-porphyrin complexes with imidazole and a phenoxyl group as axial ligands. [19] On this basis, it appears reasonable that tyrosine-67, being in a favorable position, is the sixth ligand of iron in the photomodified protein. This hypothesis is confirmed by the negative shift of 250 mV in the $E_{1/2}$ of the cytochrome observed after the photomodification.

The photoreduction quantum yield was observed to depend on pH reaching its maximum value at pH 6. At this pH the most of the protein is present as the native state(B) with methionine-80 and histidine-18 axially bound to iron, confirming that state B is the only photoreactive species. Although a direct correlation between the photoredox behavior of the heme-protein and its biological activity is not quite correct, the above results are indicative of the important role of methionine-80 in the redox processes of cytochrome c.

Successive experiments showed that the presence of the biological reductant NADH (the reduced form of nicotinamide adenine dinucleotide) significantly affects the photoreduction mechanism.[20] It has been observed, in fact, that in the presence of the nucleotide *i)* the quantum yield increases about 5 times, *ii)* after re-oxidation the native protein is enterely recovered without any appreciable modification, *iii)* experimental evidence of the formation of NAD^+ was obtained. An explanation of these results is given by a mechanism which can be summarized as in eqs. 3-5.

$$Met_{80}\text{-}S^{+}\text{-}Fe^{II} + NADH \longrightarrow Met_{80}\text{-}S\text{-}Fe^{II} + NAD^{\cdot} + H^{+} \quad (3)$$

$$NAD^{\cdot} + Met_{80}\text{-}S\text{-}Fe^{III} \longrightarrow NAD^{+} + Met_{80}\text{-}S\text{-}Fe^{II} \quad (4)$$

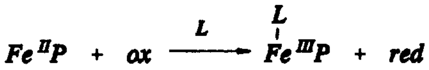
$$Met_{80}\text{-}S\text{-}Fe^{II} + ox \longrightarrow Met_{80}\text{-}S\text{-}Fe^{III} + red \quad (5)$$

The oxidation of NADH (eq. 3) is achieved by an electron transfer from the nucleotide to the methionyl radical cation formed in the primary photoredox process (eq. 2). The electron transfer occurs before the methionyl cation can diffuse away from the first coordination sphere of iron allowing the complete restorement of the methionine-80-Fe(II) bond. As a consequence, since the only modification underwent by cytochrome c is the reduction of Fe(III) to Fe(II), the native protein could be recovered by a simple oxidation process (eq. 5).

The peculiar aspect of the photochemistry of the cytochrome c-NADH system is that an electronic transition involving the sixth coordination site of the central iron leads to the production of the activated species (met-80)-S^+ capable of behaving as an electron acceptor via the methionyl cation. The reaction sequence forms the intermediate species $NAD^{\cdot}$ and NAD^+ which are potentially reactive toward certain substrates.

3. PHOTOCATALYSIS BY IRON PORPHYRINS

The primary photoredox process schematized in eq. 1 may be followed by the re-oxidation of the ferrous porphyrin complex (eq. 6) so realizing a photoassisted cycle in which both the intermediates Fe(II)P and the free radical L˙ can induce catalytic processes.[3,4]



$$Fe^{II}P + ox \xrightarrow{L} \overset{L}{Fe^{III}P} + red \tag{6}$$

We report below on the photocatalytic properties of a series of iron meso-tetraaryl porphyrin complexes in the reductive conversion of CCl_4 and in oxygenation of hydrocarbons in both homogeneous and heterogeneous environment.

3.1. Homogeneous systems

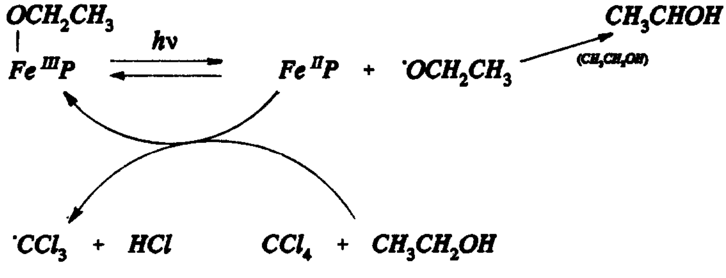
3.1.1. Reduction of CCl_4

Iron-porphyrin complexes were found to photocatalyze the reduction of CCl_4 by ethanol according to equation 7.[21]

$$CCl_4 + C_2H_5OH \longrightarrow HCl + CHCl_3 + CH_3CHO \tag{7}$$

The proposed reaction mechanism is reported in Scheme 1:

Scheme 1.



$$^{\cdot}CCl_3 + CH_3CH_2OH \longrightarrow CHCl_3 + CH_3CHOH$$

$$CH_3CHOH + CCl_4 \longrightarrow CH_3CHO + HCl + {}^{\cdot}CCl_3$$

The two products of the primary photoreduction, Fe(II)P and the ethoxyl radical react with CCl_4 and ethanol producing $^{\cdot}CCl_3$ and hydroxyethyl radicals which, in turn, initiate, in the absence of oxygen, a chain process leading to the formation of $CHCl_3$, CH_3CHO and HCl (eq. 7).

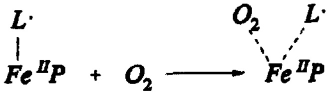
Iron meso-tetradichloro-phenyl porphyrin (Fe(TDCPP)) and iron meso-tetramesityl porphyrin (Fe(TMP)) were found to be good catalysts exhibiting catalyst turnovers greater than 130.000. Both the complexes proved to be very resistant against the irreversible modifications frequently observed under irradiation of iron-porphyrins without meso substituents, e.g., Fe(TPP).[21] This suggests that the hindrance of ortho phenyl substituents plays the important function of protecting the meso positions of the porphyrin ring against the attack by the free radicals formed during irradiation.

The toxicity of CCl_4 and other halogenated alkanes in living organisms is in large part caused by free radicals produced in the metabolism of those compounds by cytochrome P-450.[22] For this reason, the results obtained on the kinetics and the mechanism of the photoinduced reduction of CCl_4 by iron porphyrins appear to be of interest to derive a model for the toxicity of haloalkanes.

3.1.2. Oxygenation of hydrocarbon by O_2

In some cases the photoreduction of metal porphyrins (eq. 1) is accompanied by the formation of reactive species capable of oxidizing organic substrates. For example, the irradiation of Fe(III)P with a halide as an axial ligand is reported to lead to the formation of halogen atoms which can initiate radical chain autooxidation of hydrocarbons.[23] Fe(III)P μ-oxo dimers are also reported to be photoactive.[9] The irradiation of these species, in fact, produces a disproportionation reaction giving Fe(II)P and the hypervalent species Fe(IV)P=O which can abstract hydrogen atoms from hydrocarbons. A very interesting example of selective, porphyrin based, photocatalytic system has been recently reported by Weber et al.[24] who observed that supramolecular catalysts consisting of iron and manganese cyclodextrin-linked porphyrin complexes, photocatalyze the enantioselective oxygenation of a racemic mixture od (S)-α- and (R)-β-pinene with O_2.

In the above examples the primary photochemical process leads to direct formation of reactive species able of initiating the auto-oxidation of hydrocarbons. In other cases, the oxidation of the substrate is achieved by molecular oxygen activated by coordinating to Fe(II) in the ferrous porphyrin (eqs. 8-9).



$$\overset{L\cdot}{Fe^{II}P} + O_2 \longrightarrow \overset{O_2\quad L\cdot}{Fe^{II}P}$$

(8)

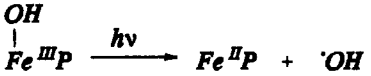
$$\overset{O_2\quad L\cdot}{Fe^{II}} \longrightarrow Fe^{III}P + O_2^- + L\cdot$$

(9)

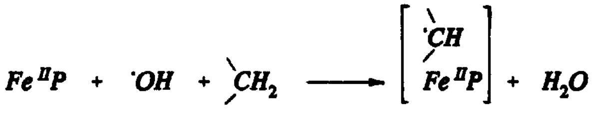
The ability of O_2 of trapping Fe(II)P increasing the efficiency of the L-to-Fe(III) electron transfer (eq. 1) is, in fact, well known.[25]

In this regard we have recently shown for the first time that cyclohexane is efficiently photooxidized by oxygen in mild conditions (22°C, 200 torr of O_2) in the presence of catalytic amounts of Fe(TDCPP) containing OH^- as an axial ligand.[26] In this system cyclohexane is selectively oxidized to cyclohexanone with a quantum yield of 1.7×10^{-3}. The iron porphyrin complex is slowly destroyed during the irradiation, but 80 moles of product are obtained per mole of consumed catalyst.

The proposed mechanism (eqs. 10-13) suggests that the ·OH radical, formed by photocleavage of the Fe-OH bond (eq. 10), abstracts an H atom from cyclohexane, leading to the formation of a cyclohexyl radical pair (eq. 11).

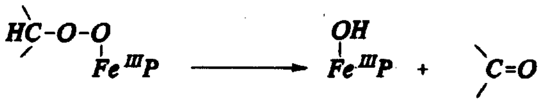


$$\mathrm{(OH)Fe^{III}P} \xrightarrow{h\nu} \mathrm{Fe^{II}P} + {}^{\cdot}\mathrm{OH} \qquad (10)$$



$$\mathrm{Fe^{II}P} + {}^{\cdot}\mathrm{OH} + \mathrm{{>}CH_2} \longrightarrow \left[\begin{array}{c}\mathrm{{>}{}^{\cdot}CH} \\ \mathrm{Fe^{II}P}\end{array}\right] + \mathrm{H_2O} \qquad (11)$$

$$\left[\begin{array}{c}\mathrm{{>}{}^{\cdot}CH} \\ \mathrm{Fe^{II}P}\end{array}\right] + \mathrm{O_2} \longrightarrow \mathrm{{>}HC\text{-}O\text{-}O\text{-}Fe^{III}P} \qquad (12)$$



$$\mathrm{{>}HC\text{-}O\text{-}O\text{-}Fe^{III}P} \longrightarrow \mathrm{(OH)Fe^{III}P} + \mathrm{{>}C{=}O} \qquad (13)$$

This, reacting with O_2, generates a Fe(III)-peroxyalkyl complex (eq. 12) which is known to decompose with formation of cyclohexanone regenerating the original reactant (OH)Fe(III)(TDCPP).[27] The described photoassisted oxidation of ciclohexane into cyclohexanone does not need any consumption of reagent in contrast with most of the previously described iron porphyrin based thermal systems and its mechanism better corresponds to a dioxygenase rather than to a monooxygenase reaction.

3.2. Heterogeneous systems

The interest in the study of metal porphyrins in heterogeneous and microheterogeneous has greatly increased in the last years,[28,29] due to a number of advantages offered by the isolation on a solid support: easy recovery of the catalysts, enhancement of their reactivity, inhibition of degradative intermolecular self-reactions and mimicking the proteic environment of the hemoprotein.

According to their photochemical behavior the supports can be divided in two classes:

1) Photochemically inert solids in which the only photoreactive species is the porhyrin complex as in homogeneous systems,

2) Photochemically active solids where the matrix is directly involved into the photocatalytic processes producing a matrix-metal synergistic effect (hybrid catalytic systems).

In a work concerning the first type of supports[30], Fe(TPP)Cl or Fe(TDCPP)Cl were caged inside a 2% or 4% cross-linked polystirene utilizing solvent-dependent swelling. The irradiation at λ= 365 nm of a suspension of the trapped porphyrin in cyclohexene resulted in the formation of allylic oxidation products with an efficiency close to that obtained in similar experiments carried out in homogeneous solution[24] and with the advantage of an easy recovery of the catalysts at the end of the experiment by simple filtration.

The most interesting aspect of these new organized systems is the possibility to control the access of the reactant molecules by taking advantage of the *tunable* size of the polymer pores in order to obtain selectivity degrees higher than those obtained with the same catalysts chemically linked to polymers, where reactions occur mainly at the polymer surface.

The photocatalytic properties of a hybrid system in which the iron porphyrin is covalently linked to the surface of the photoreactive semiconductor TiO_2, have also been studied in our laboratory. [31] For this purpose, the solid surface of the semiconductor was previously modified with triethoxyaminopropyl-silane (TiO_2-sil) and then allowed to react with Fe(III) meso-tetraphenylporphyne tetrasulphonated (TiO_2-sil-Fe(III)(TPPS)). The estimated surface coverage by the porphyrin was ~30%. The structure of this type of catalyst is illustrated in Figure 1.

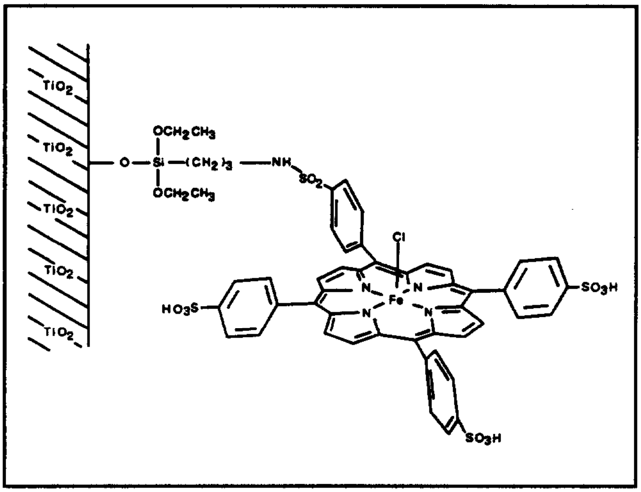


Figure 1 Structure of TiO_2-sil-Fe(III)(TPPS) catalyst.

Probably, the most important function of the support in this system is to work as an efficient source of charge when excited with light. It is well known that irradiation of semiconductors with light of energy higher than the band gap results in the transition of electrons into the conduction band and the creation of holes in the valence band. The electrons can then react with an oxidizing species while holes with a reducing one.[32]

The results obtained when suspensions of the powder catalyst (pristine or derivatized TiO_2) in oxygen saturated cyclohexane were irradiated at λ>350 nm are reported in Table 1.

Table 1. Photocatalytic oxidation of cyclohexane on $TiO_2$and surface modified TiO_2

Catalyst	Products	Quantum Yield[a]	Porphyrin Turnover[b]
TiO_2	Cyclohexanone	0.09	
	Cyclohexanol	c	
	CO_2	0.024	
TiO_2-sil	Cyclohexanone	c	
	Cyclohexanol	c	
	CO_2	c	
TiO_2-sil-Fe^{III}TPPS	Cyclohexanone	0.03	50
	Cyclohexanol	0.01	14
	CO_2	c	

a: moles of product/moles of absorbed photons; b: moles of product/moles of consumed porphyrin; c: below our revelation capability;

It is to be noted that, *i)* in agreement with the literature[31] TiO_2 is itself an active catalyst in the oxidation of cyclohexane yielding essentially cyclohexanone and CO_2; *ii)* the silanization drastically deactivates the semiconductor; *iii)* a novel interesting reactivity is observed when also the iron porphyrin is linked to the surface in that we obtain cyclohexanol in addition to cyclohexanone; *iv)* the quantum yields of hydrocarbon oxidation are much higher than those obtained when the same iron porphyrins are used as photocatalysts in homogeneous phase experiments.[26] Since the surface modification with silane produces a marked loss of activity of TiO_2 (point *i*), the porphyrin must be the responsible for the observed reactivity of the hybrid system.

Experiments carried out at different excitation wavelengths showed that the product yields matched the absorption spectrum of TiO_2 indicating that the semiconductor itself is the photoactive species. On this basis it is reasonable to suppose that the experimentally detected Fe(II)(TPPS) is formed via an electron transfer from the conduction band of TiO_2 to Fe(III)(TPPS). The reduction of Fe(III) to Fe(II) can be the first step of the subsequent reductive activation of molecular oxygen. A plausible mechanism is schematized in Figure 2.

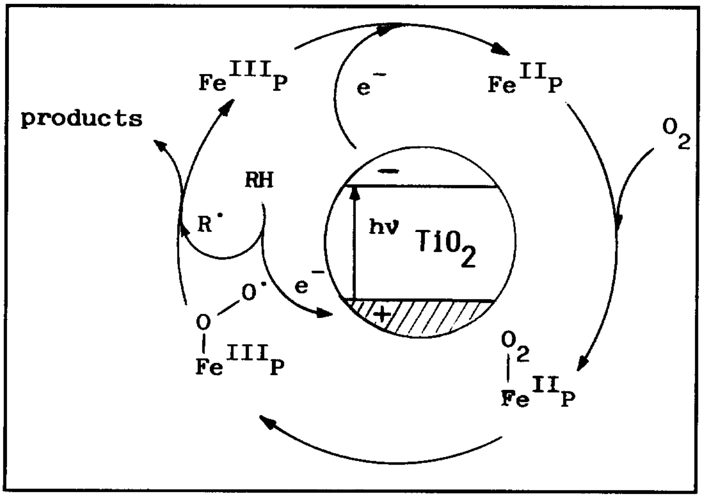
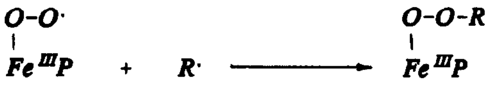


Figure 2. Mechanism of alkane photooxidation by TiO_2-Sil-Fe(TPPS) system.

The Fe(III) porphyrin is supposed to be reduced by an electron from the conduction band of the illuminated TiO_2. At the same time, a valence band hole is captured by the hydrocarbon RH giving an alkyl radical R·. One of the possible products of the reaction of the superoxo complex may be a peroxo complex as it has been proposed for the homogeneous phase oxidation of hydrocarbon photocatalyzed by iron porphyrins (eq. 14).



$$\underset{Fe^{III}P}{\overset{O-O^\cdot}{|}} + R^\cdot \longrightarrow \underset{Fe^{III}P}{\overset{O-O-R}{|}} \qquad (14)$$

The alkyl peroxo complex is the intermediate which can lead to the formation of the ketone and/or the alcohol.

The replacement of Fe(TPPS) on the surface of TiO_2 with a polyhalogenated iron porphyrin, e.g., iron (4-carboxymethyl-phenyl)-tris-(2,6-dichlorophenyl) porphyrin ($Fe(Cl_6TPP)$) resulted in an increase of the efficiency in the oxidation of cyclohexane. This has been tentatively ascribed to an increase of the hydrophobicity of the surface or, alternatively, to a higher intrinsic reactivity of the iron porphyrin. Peculiar results have been obtained with the TiO_2-sil-$Fe(Cl_6TPP)$

system in the photooxidation of methyl-cyclohexane. The results indicate that steric hindrance effects inducing regioselectivity in the functionalization of methyl cyclohexane are more important for unmodified TiO_2 than for the hybrid system. This is an evidence of less interaction of the substrate with the surface in the presence of the porphyrin complex, indicating that in this case the oxidation reaction occurs at same distance from the surface.

In conclusion, the important features of the hybrid systems can be summarized as follows:

1) In comparison with the solution systems, higher yields of the oxidation products are obtained, due to the increased efficiency of the photoreduction of Fe(III) to Fe(II) for the anchored complex.

2) In comparison with the unmodified TiO_2 one observes an increase in the hydroxilated species in the oxidation of the hydrocarbons and a different regioselectivity. The reduction of O_2 occurring at the porphyrin centres leads to the formation of Fe(III)-$O_2^{\cdot}$ which is possibly involved in reaction with radical intermediates of the oxidation process (eq. 14). In contrast, the reduction of O_2 on the unmodified TiO_2 is reported to lead to adsorbed peroxo species with an altogether different reactivity.[33]

4. ACKNOWLEDGEMENTS

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