Oxidation of Cyclohexane by Molecular Oxygen Photoassisted by *meso*-Tetraarylporphyrin Iron(III)−Hydroxo Complexes

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The photochemical and photocatalytic properties of iron *meso*-tetraarylporphyrins bearing an OH^- axial ligand and different substituents in the β-positions of the porphyrin ring are reported. Irradiation ($\lambda = 365$ nm) in the absence of dioxygen leads to the reduction of Fe^{III} to Fe^{II} with the formation of $OH^{\bullet}$ radicals. Substituents at the pyrrole β-positions are found to markedly affect the photoreduction quantum yields. Under aerobic conditions, this photoreaction can induce the subsequent oxidation of cyclohexane to cyclohexanone and cyclohexanol by O_2 itself. The process occurs under mild conditions (22 °C; 760 Torr of O_2) and without the consumption of a reducing agent. The polarity of the solvent and the nature of the porphyrin ring have a remarkable effect on the selectivity of the photooxidation process, likely controlling the cleavage of O−O bonds of possible iron peroxoalkyl intermediates. In particular, in pure cyclohexane, oxidation occurs with the selective formation of cyclohexanone; in contrast, in dichloromethane/cyclohexane mixed solvent, the main oxidation product is cyclohexanol. Phenyl-*tert*-butylnitrone (pbn) has been found to quench the radical chain autoxidation of the substrate thus increasing the yield of cyclohexanol. This becomes the only oxidation product when iron 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin hydroxide ($Fe^{III}(TDCPP)(OH)$) is used as photocatalyst.

Introduction

There is great interest in the discovery of new catalysts to induce selective oxygenation reactions of unactivated C−H bonds in alkanes by molecular oxygen.[1] Iron porphyrin complexes have been found to be biomimetic catalysts for alkane hydroxylation by O_2 with consumption of a stoichiometric amount of a reducing agent, according to the monooxygenation equation (1).[2]

$$RH + O_2 + 2e^- + 2H^+ \rightarrow ROH + H_2O \qquad (1)$$
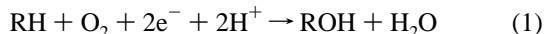
Moreover, iron porphyrins have been found to be able of catalyzing the oxidation of alkanes to alcohols and ketones at 80 °C under an oxygen pressure of 10 atm.[3] In that regard, to find catalytic systems able to perform alkane oxidation by O_2 under mild conditions and in the absence of a reducing agent appears of particular interest. In this framework, the redox reactivity of photoexcited iron porphyrins is receiving increasing attention.[4] In particular, several authors recently focused their interest on the development of new oxidation catalysts based on photoexcited metalloporphyrins.[5] These are commonly used in homogeneous phases, although "composite" systems, in which the metal complex is bound to the surface of semiconducting oxides, have also shown an interesting activity.[6]
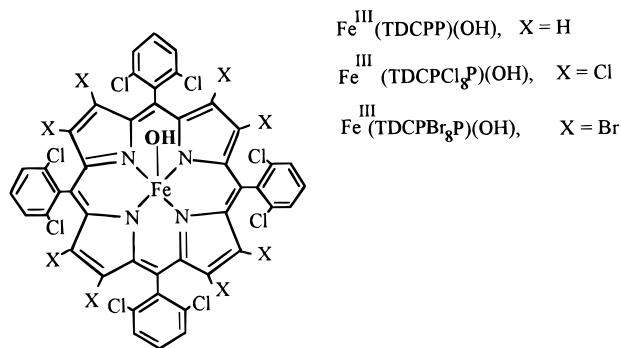
It was previously reported that the irradiation of Fe(III) porphyrins in the wavelength range 350−400 nm can result in an intramolecular electron transfer from the axial ligand to iron, leading to reduction of Fe^{III} to Fe^{II} according to eq 2 ($Fe^{III}P$ = iron porphyrin, L = axial ligand) with quantum yield values ranging from 10^{-5} to 10^{-2} .[4,7] The efficiency of the process

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(1) Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989.
(2) Recent reviews: (a) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450, Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum Press: New York and London, 1986. (b) Mansuy, D. *Pure Appl. Chem.* **1990,** *62,* 741. (c) Meunier, B. *Chem. Rev.* **1992,** *92,* 1411.
(3) Ellis, P. E.; Lyons, J. E. *Coord. Chem. Rev.* **1990,** *105,* 181.
(4) (a) Maldotti, A.; Amadelli, R.; Bartocci, C.; Carassiti, V.; Polo, E.; Varani, G. *Coord. Chem. Rev.* **1993,** *125,* 143. (b) Suslick, K. S.; Watson, R. A. *New J. Chem.* **1992,** *16,* 633.

(5) (a) Maldotti, A.; Bartocci, C.; Amadelli, R.; Carassiti, V. *J. Chem. Soc. Dalton Trans. 2* **1989,** 1197. (b) Hendrickson, D. N.; Kinnaird, M. G.; Suslick, K. S. *J. Am. Chem. Soc.* **1987,** *109,* 1243. (c) Weber, L.; Haufe, G.; Rehorek, D.; Hennig, H.; *J. Chem. Soc., Chem. Commun.* **1991,** 502. (d) Maldotti, A.; Bartocci, C.; Amadelli, R.; Polo, E.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1991,** 1487. (e) Weber, L.; Imiolezyk, I.; Haufe, G.; Rehorek, D.; Hennig, H. *J. Chem. Soc. Chem. Commun.* **1992,** 301. (f) Polo, E.; Amadelli, R.; Carassiti, V.; Maldotti, A. *Inorg. Chim. Acta* **1992,** *192,* 1. (g) Maldotti, A.; Bartocci, C.; Amadelli, R.; Varani, G.; Polo, E.; Carassiti, V. In *Chemistry and Properties of Biomolecular Systems, Topics in Molecular Organization and Engineering Series;* Rizzarelli, E., Theophanides, T., Eds.; Kluwer: Dordrecht, 1991; p 103. (h) Weber, L.; Hommel, R.; Behling, J.; Haufe, G.; Hennig, H. *J. Am. Chem. Soc.* **1994,** *116,* 2400.
(6) (a) Amadelli, R.; Bregola, M.; Polo, E.; Carassiti, V.; Maldotti, A. *J. Chem. Soc., Chem. Commun.* **1992,** 1355. (b) Polo, E.; Amadelli, R.; Carassiti, V.; Maldotti, A. In *Heterogeneous Catalysis and Fine Chemicals III;* Cuisnet, M., et al., Eds.; Elsevier: Amsterdam, 1993.
(7) (a) Bartocci, C.; Scandola, F.; Ferri, A.; Carassiti, V. *J. Am. Chem. Soc.* **1980,** *102,* 7067. (b) Bartocci, C.; Maldotti, A.; Traverso, O.; Bignozzi, C. A.; Carassiti, V. *Polyhedron* **1983,** *2,* 97. (c) Richman, R. M.; Peterson, M. V. *J. Am. Chem. Soc.* **1982,** *104,* 5795. (d) Ozaki, Y.; Iriyama, K.; Ogoshi, H.; Kitagawa, T. *J. Am. Chem. Soc.* **1987,** *109,* 5583. (e) Hoshino, M.; Ueda, K.; Takahashi, M.; Yamaji, M.; Hama, Y. *J. Chem. Soc., Faraday Trans.* **1992,** *88,* 405. (f) Tohara, A.; Sato, M. *Chem. Lett.* **1989,** 153.

$Fe^{III}(TDCPP)(OH)$, X = H

$Fe^{III}(TDCPCl_8P)(OH)$, X = Cl

$Fe^{III}(TDCPBr_8P)(OH)$, X = Br

Figure 1. Structures of the substituted iron porphyrins investigated.

depends on the nature of both the porphyrin and axial ligand as well as on the nature of the solvent which can favor a back electron transfer process by an efficient cage effect. Species able to trap the $Fe^{II}P$ intermediate or the $L^•$ radical can also favor the photoredox process competing with solvent cage effects. It has been demonstrated that O_2 can play this role by effectively reacting with the Fe^{II} porphyrin intermediate (eqs 3 and 4) and favoring the separation of the products of the primary
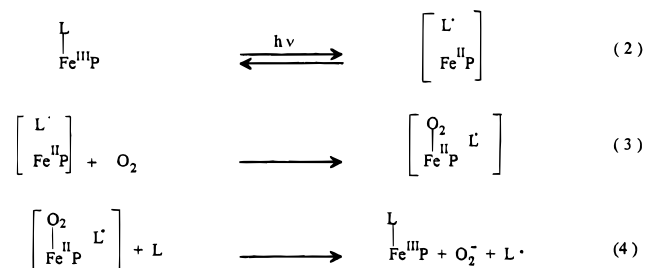
electron transfer.[8] A peculiar aspect of the overall process (eqs 2–4) is that the reductive activation of O_2 is obtained in a catalytic manner with the photoassistance of the iron porphyrin.

In this study we examine the ability of the iron porphyrin complexes reported in Figure 1 to act as photocatalysts in the reductive activation of O_2 and the subsequent oxygenation of cyclohexane. The instability of the porphyrin ring is a serious obstacle limiting the use of iron porphyrins as catalysts. For this reason, we have taken into consideration *meso*-tetraaryl iron porphyrins bearing halogen substituents in the pyrrole β-positions and/or in the *meso*-aryl groups. In fact, besides their electron-withdrawing effects, these substituents are known to provide a steric protection of the porphyrin ring against free radical attack and so to decrease the oxidative degradation of the complex during both thermal[9] and photochemical[10] catalytic processes. The photooxidation experiments were performed both in pure cyclohexane and in more polar cyclohexane/dichloromethane mixed solvent. The results obtained show that it is possible to orientate the selectivity of cyclohexane oxidation toward either cyclohexanone or cyclohexanol as a function of the nature of the solvent and the presence of radical scavengers.

Experimental Section

Materials. Phenyl-*tert*-butylnitrone (pbn) and 5,5′-dimethylpyrroline *N*-oxide (dmpo) were commercial products (Aldrich) and were used as received. The complexes iron(III) *meso*-tetrakis(dichlorophenyl)-porphyrin hydroxide ($Fe^{III}(TDCPP)(OH)$), iron(III) *meso*-tetrakis-(dichlorophenyl)octa-β-chloroporphyrin hydroxide ($Fe^{III}(TDCPCl_8P)$-

(OH)), and iron(III) *meso*-tetrakis(dichlorophenyl)octa-β-bromoporphyrin hydroxide ($Fe^{III}(TDCPBr_8P)(OH)$) (Figure 1) were prepared and purified as previously reported.[11] Cyclohexane and dichloromethane were spectroscopic grade solvents and were dried and purified by standard methods. All other chemicals were commercial products and were used without further purification.

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. 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.

Irradiation was carried out with a medium-pressure Hanau Q 400 mercury lamp. The required monochromatic light was obtained with Corning filters. These filters can selectively isolate the 365-nm line of the medium-pressure mercury lamp. The light intensity was measured by a ferrioxalate actinometric method.[12]

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 (355 nm, 5 ns half-width, 150 mJ). Transient decays were stored and read on a LeCroy 9360 fast digitizing oscilloscope.

Procedures. Photoreduction of Iron Porphyrins. The iron porphyrins $Fe^{III}(TDCPP)(OH)$, $Fe^{III}(TDCPCl_8P)(OH)$, and Fe^{III}-$(TDCPBr_8P)(OH)$ (3×10^{-5} mol dm^{-3}) were dissolved in the mixed solvent dichloromethane/cyclohexane (3:2) and the solutions degassed to less than 1×10^{-5} Torr by means of five vacuum-line freeze–thaw–pump cycles. The irradiation was carried out at 365 nm in a 1-cm spectrophotometric cell at 22 ± 1 °C and the photoreaction monitored by UV–vis spectroscopy. Extinction coefficients of the reduced forms of all the iron porphyrins used were determined by reducing the oxidized species with zinc amalgam or sodium dithionite in carefully deaerated solution. The photoreduction quantum yields were determined as previously reported.[10]

ESR Spin Trapping. The iron porphyrins (2×10^{-4} mol dm^{-3}) dissolved in the appropriate solvent were irradiated in the presence of the spin trap dmpo or pbn (5×10^{-3} mol dm^{-3}). Irradiations were carried out inside the ESR cavity using a flat quartz cell, at room temperature. When necessary, deaerated samples were obtained by bubbling pure nitrogen into the solution for some minutes. No signal of significant intensity was observed when blank experiments were run in the dark.

Cyclohexane Photooxidation. The iron porphyrins (3×10^{-5} mol dm^{-3}) were dissolved in the appropriate solvent and irradiated under an O_2 pressure of 760 Torr, at 22 ± 1 °C. The maintenance of OH$^-$ bound to the porphyrin was ensured by vigorously stirring for several minutes the solutions with aqueous $Bu_4N^+OH^-\cdot 30H_2O$ at regular time intervals. The reaction products were determined by GC analysis by comparison of their retention times with those of authentic samples, using C_6H_5I as internal standard. No oxidation products were observed when blank experiments were run in the dark. The product concentrations in time were also followed in the dark, after a few minutes of irradiation. The result was that no increase of concentration was observed.

Results

Photochemical Behavior in Dioxygen-Free Solution. Fe^{III}-$(TDCPP)(OH)$, $Fe^{III}(TDCPCl_8P)(OH)$ and $Fe^{III}(TDCPBr_8P)(OH)$ (3×10^{-5} mol dm^{-3}) were irradiated at $\lambda = 365$ nm in oxygen-free dichloromethane/cyclohexane (3:2) mixed solvent. UV–vis spectral variations indicate that the photochemical excitation leads to the reduction of Fe^{III} to Fe^{II}, as shown in Figure 2 for $Fe^{III}(TDCPP)(OH)$. The absorbance in the Soret region was observed to change linearly, indicating that the photoreduction process followed zero-order kinetics. This allowed us to

(8) Maldotti, A.; Bartocci, C.; Chiorboli, C.; Ferri, A.; Carassiti, V. *J. Chem. Soc., Chem. Commun.* **1985**, 881.

(9) (a) Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279. (b) Traylor, T. G.; Tshuchiya, S. *Inorg. Chem.* **1987**, *26*, 1338.

(10) Bartocci, C.; Maldotti, A.; Varani, G.; Battioni, P.; Carassiti, V.; Mansuy, D. *Inorg. Chem.* **1991**, *30*, 1255.

(11) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, J. F.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462 and references cited therein.

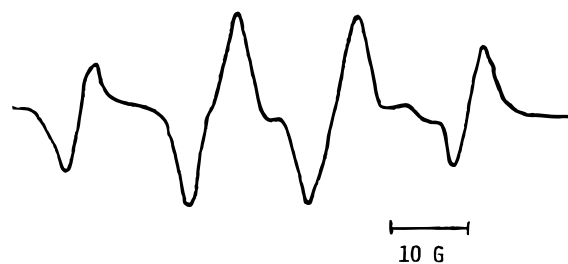(12) Murov, S. L. *Handbook of Photochemistry*; M. Dekker: New York, 1973; p 119.
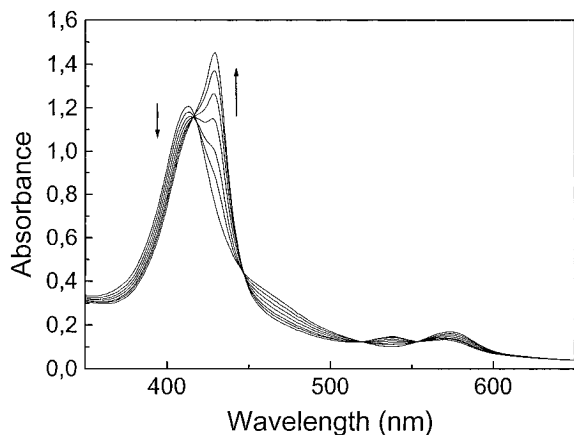
Figure 2. Spectral changes observed during the irradiation at 365 nm of deaerated dichloromethane/cyclohexane (3:2) solution containing $Fe^{III}(TDCPP)(OH)$ (3×10^{-5} mol dm^{-3}). Time interval between spectral scans: 3 min.
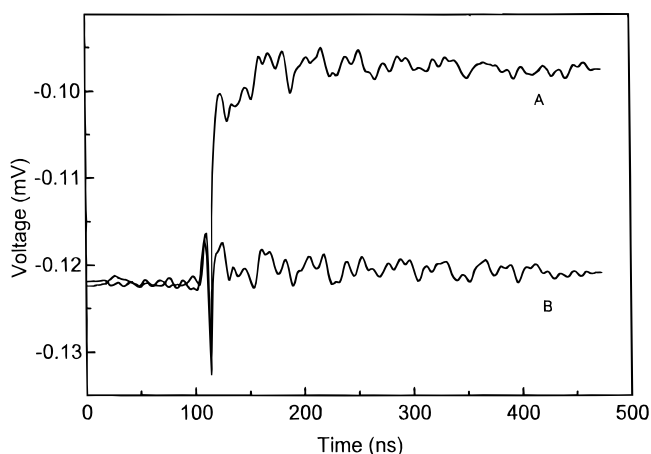
Figure 3. Laser flash photolysis of dichloromethane/cyclohexane (3:2) solutions containing $Fe^{III}(TDCPP)(OH)$ (3×10^{-5} mol dm^{-3}): (A) deaerated solution; (B) aerated solution. Analysis wavelength: 435 nm.

calculate the photoreduction quantum yield defined as the ratio of the moles of iron(II) porphyrin per minute to the moles of photons absorbed per minute (see Experimental Section). The photoreduction quantum yield values (Φ_{red}) are as follows: Fe^{III}-(TDCPP)(OH), $(6.0 \pm 1.0) \times 10^{-3}$; $Fe^{III}(TDCPCl_8P)(OH)$, $(3.0 \pm 0.5) \times 10^{-3}$; $Fe^{III}(TDCPBr_8P)(OH)$, $(1.4 \pm 0.2) \times 10^{-3}$.

The results obtained by laser flash photolysis experiments conducted on solutions of $Fe^{III}(TDCPP)(OH)$ are reported in Figure 3. The flash gives rise to an instantaneous absorbance increase at 435 nm (Figure 3, trace A) indicating that the reduction of Fe^{III} to Fe^{II} occurs in a time lower than the laser pulse (about 5 ns). On the other hand, the laser flash photolysis experiments conducted in aerated solutions do not give rise to any absorbance change (Figure 3, trace B).[13] Evidence for the formation of OH• radicals was obtained by an ESR spin-trapping investigation. This technique is a powerful tool for detecting the formation of short-lived radicals[14] and has been fruitfully employed in photochemical studies on metal porphyrins.[10,15] It is based on the ability of some molecules such as nitrones to

(13) We could not obtain any data with this technique for either Fe^{III}-(TDCPCl$_8$P)(OH) or Fe^{III}(TDCPBr$_8$P)(OH) because of the too low absorbance difference between the reduced and oxidized forms in the entire wavelength range.
(14) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31.
(15) Maldotti, A.; Bartocci, C.; Amadelli, R.; Carassiti, V. *Inorg. Chim. Acta* **1983**, *74*, 275.
(16) Eberson, L. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 171.
(17) (a) Harbour, J. R.; Hair, M. L. *Can. J. Chem.* **1974**, *52*, 3549. (b) Perkins, M. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 1.
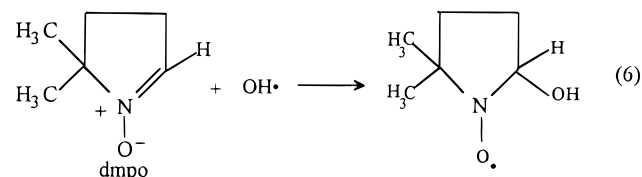
Figure 4. ESR spectrum obtained by irradiation of the iron porphyrins in the presence of dmpo in both cyclohexane and dichloromethane/cyclohexane (3:2).

trap radicals to give nitroxides (eq 5) stable enough to be studied

$$(5)$$
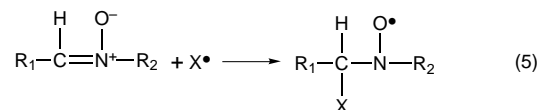
by ESR techniques. In some instances, the nature of the trapped radical (X•) can be identified by the parameters obtainable from the ESR spectrum. On the other hand, the spin-trapping technique presents some important limitations. First, the spectrum frequently consists of a triplet of doublets due to the nitrogen and β-H coupling, with only small differences among various spin adducts; second, some nitrones, as well as their paramagnetic adducts, can undergo photoinduced fragmentation reactions,[14,16] which can complicate the investigation of the radical processes. Dmpo is able to trap the OH• radical according to eq 6 to give a stable nitroxide exhibiting a typical

$$(6)$$

1:2:2:1 pattern of four lines, which can be interpreted as equivalent hyperfine splitting from both the β-hydrogen and the nitroxide nitrogen ($A_N = A_H = 14.8$ G).[17] This spectrum (Figure 4) is obtained upon irradiation of oxygen-free solutions of the iron porphyrins (2×10^{-4} mol dm^{-3}) in the presence of dmpo (5×10^{-3} mol dm^{-3}), indicating that the photochemical excitation of the investigated complexes leads to the formation of OH• radicals.

Photocatalytic Behavior in Oxygenated Cyclohexane Solutions. Photochemical excitation ($\lambda = 365$ nm) of Fe^{III}-(TDCPP)(OH), $Fe^{III}(TDCPCl_8P)(OH)$, and $Fe^{III}(TDCPBr_8P)$-(OH) (3×10^{-5} mol dm^{-3}) in cyclohexane, under an oxygen pressure of 760 Torr, led to the formation of cyclohexanone. The process follows a zero-order kinetics, allowing us to calculate the photooxidation quantum yield defined as the ratio of the moles of obtained oxidation products per minute to the moles of absorbed photons per minute (Table 1). During the photochemical experiments the only observed UV–vis spectral variation is a slow absorbance decrease in the whole wavelength range. This means that (i) the porphyrin catalyst undergoes a slow degradation, (ii) the Fe^{II} porphyrin is not accumulated in a detectable amount, and (iii) the axial coordination of OH$^-$ is retained.

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 complex. The obtained values are 80 for $Fe^{III}(TDCPCl_8P)(OH)$ and $Fe^{III}(TDCPBr_8P)$-(OH) and 60 for $Fe^{III}(TDCPP)(OH)$, indicating that the presence

Table 1. Photocatalytic Properties[a] of Iron Porphyrins[b] in Pure C$_6$H$_{12}$

iron porphyrin	reaction medium	$10^3\Phi_{ox}$[d]
Fe(TDCPP)(OH)	C$_6$H$_{12}$	1.6 ± 0.2[11]
Fe(TDCPP)(OH)	C$_6$H$_{12}$ + pbn[c]	1.4 ± 0.2
Fe(TDCPCl$_8$P)(OH)	C$_6$H$_{12}$	1.2 ± 0.2
Fe(TDCPCl$_8$P)(OH)	C$_6$H$_{12}$ + pbn[c]	1.1 ± 0.2
Fe(TDCPBr$_8$P)(OH)	C$_6$H$_{12}$	1.0 ± 0.2
Fe(TDCPBr$_8$P)(OH)	C$_6$H$_{12}$ + pbn[c]	0.8 ± 0.2

[a] Irradiations were carried out at 22 ± 1 °C, in the presence of 760 Torr of oxygen. Excitation wavelengths: 365 nm. [b] Initial concentration: 3×10^{-5} mol dm^{-3}. [c] pbn concentration: 1×10^{-4} mol dm^{-3}. [d] Moles of formed cyclohexanone per minute/moles of absorbed photons per minute.

of halogen atoms at the pyrrole β-positions increases the stability of the porphyrin.

In order to obtain more insight into the contribution of possible radical reactions to the photooxidation process, we have carried out experiments in the presence of radical scavengers. In particular, we have investigated the effects of the two nitrones dmpo and pbn (1×10^{-4} mol dm^{-3}). The scavengers were chosen on the basis of the conclusions of a previous investigation[10] where we observed that the two spin traps used, dmpo and pbn, exhibit different behaviors with iron porphyrins

pbn
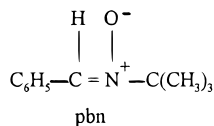
containing bulky ring substituents. In particular, we have reported that dmpo is able to trap the radical species formed in the primary photoreaction, when they are still interacting with the metal center. In contrast, the more bulky pbn can only trap free radicals diffusing away from the first coordination sphere of iron.
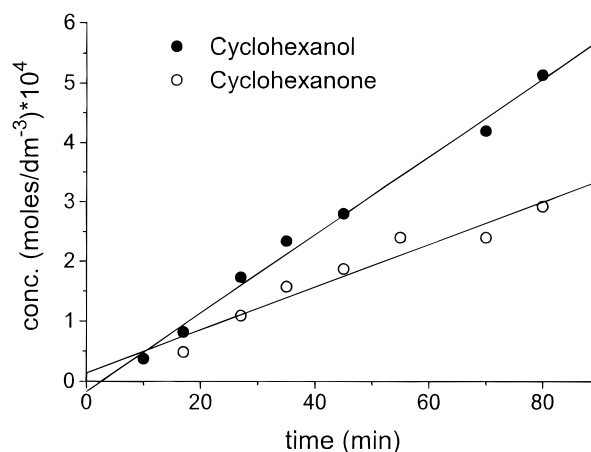
Irradiation of oxygenated cyclohexane solutions of the iron porphyrins in the presence of dmpo leads to the appearance of the 1:2:2:1 quartet typical of the dmpo−OH paramagnetic adduct (Figure 4), indicating the trapping of OH• radicals. At the same time, no appreciable evidence of photocatalytic oxidation of cyclohexane is obtained.

When irradiation is carried out in the presence of pbn, no evidence of radical trapping is obtained and the only observable ESR signal is a weak triplet of three equally intense lines (Figure 5A) due to the photodecomposition of pbn with the possible formation of [(CH$_3$)$_3$C]$_2$NO• nitroxide.[16] In fact, although under our experimental conditions more than 90% of the incident light is absorbed by the metal porphyrin, direct photochemistry of pbn cannot be ruled out entirely. As far as the effect of pbn on the efficiency of the photocatalytic oxidation processes is concerned, the data reported in Table 1 indicate that it does not significantly affect the photooxidation yields from the qualitative as well as quantitative point of view.

Photocatalytic Behavior in Oxygenated Dichloromethane/ Cyclohexane Solutions. The irradiation of the iron porphyrins (3×10^{-5} mol dm^{-3}) in dichloromethane/cyclohexane (3:2) mixed solvent results in the formation of both cyclohexanone and cyclohexanol, as shown in Figure 6 in the case of Fe^{III}-(TDCPP)(OH). This Figure shows that the formation of both cyclohexanol and cyclohexanone follows zero-order kinetics, indicating that consecutive reactions can be ruled out. In Table 2 the product distribution and the photochemical efficiency for all the iron porphyrins investigated are summarized. The ratio of the moles of cyclohexane oxidation products to those of consumed porphyrin is 80 for Fe^{III}(TDCPP)(OH) and 110 for Fe^{III}(TDCPCl$_8$P)(OH) and Fe^{III}(TDCPBr$_8$P)(OH).
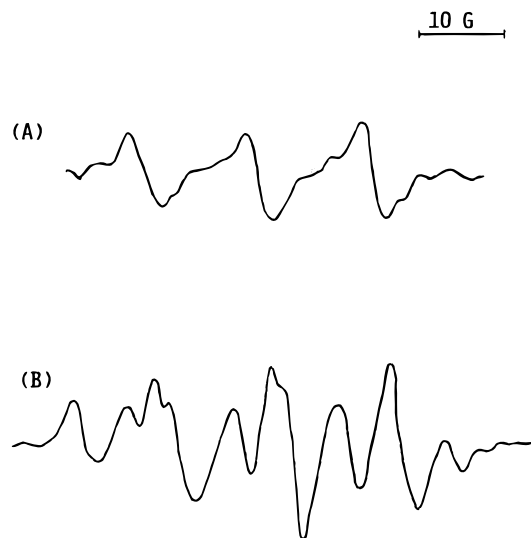
Figure 5. ESR spectra obtained by irradiation of the iron porphyrins in the presence of pbn: (A) in pure cyclohexane; (B) in dichloromethane/cyclohexane (3:2).

Figure 6. Kinetics of formation of cyclohexanol and cyclohexanone upon irradiation of dichloromethane/cyclohexane (3:2) oxygenated solutions containing Fe^{III}(TDCPP)(OH) (3×10^{-5} mol dm^{-3}).

UV−vis spectral variations observed during the irradiation provide evidence that: (i) the Fe^{II} porphyrins are not accumulated in detectable amounts, (ii) the tetrapyrrolic ring undergoes slow degradation with the formation of uncolored small fragments, and (iii) the axial ligand OH$^-$ of Fe^{III} is lost. The starting iron porphyrin complex is restored due to the presence of Bu$_4$N$^+$OH$^-$·30H$_2$O (see Experimental Section). In the absence of the hydroxide, the photocatalytic process is totally blocked.

Addition of dmpo (1×10^{-4} mol dm^{-3}) in dichloromethane/ cyclohexane mixed solvent has the same effect as in pure cyclohexane: ESR evidence for the formation of the dmpo−OH adduct is obtained and no appreciable photocatalytic oxidation of cyclohexane is observed. On the contrary, the results reported in Table 2 show that pbn has a strong effect on the efficiency of the photooxidation process. In particular, the cyclohexanol/ cyclohexanone ratio is significantly higher in the presence of the spin trap. The ESR spectrum (Figure 5B), moreover, is the result of the superimposition of signals of different unidentified spin adducts which are not observed if pbn is irradiated alone.

Discussion

Fe^{III}-Fe^{II} Photoreduction. The photoredox behavior of various Fe(III) *meso*-tetraarylporphyrins bearing alkoxo axial ligands has been discussed in a previous paper.[10] It has been

Table 2. Photocatalytic Properties[a] of Iron Porphyrins[b] in C_6H_{12}/CH_2Cl_2 Mixed Solvent

iron porphyrin	reaction medium	products	$10^3\Phi_{ox}$[d]	product distribn, %
Fe(TDCPP)(OH)	C_6H_{12}/CH_2Cl_2	cyclohexanone	4.1 ± 0.4	39
		cyclohexanol		61
Fe(TDCPP)(OH)	C_6H_{12}/CH_2Cl_2 + pbn[c]	cyclohexanone	1.0 ± 0.2	0
		cyclohexanol		100
Fe(TDCPCl$_8$P)(OH)	C_6H_{12}/CH_2Cl_2	cyclohexanone	5.0 ± 0.4	50
		cyclohexanol		50
Fe(TDCPCl$_8$P)(OH)	C_6H_{12}/CH_2Cl_2 + pbn[c]	cyclohexanone	2.7 ± 0.2	33
		cyclohexanol		67
Fe(TDCPBr$_8$P)(OH)	C_6H_{12}/CH_2Cl_2	cyclohexanone	2.2 ± 0.2	48
		cyclohexanol		52
Fe(TDCPBr$_8$P)(OH)	C_6H_{12}/CH_2Cl_2 + pbn[c]	cyclohexanone	1.0 ± 0.2	20
		cyclohexanol		80

[a] Irradiations were carried out at 22 ± 1 °C, in the presence of 760 Torr of oxygen. Excitation wavelength: 365 nm. [b] Initial concentration: 3×10^{-5} mol dm^{-3}. [c] pbn concentration: 1×10^{-4} mol dm^{-3}. [d] Moles of photooxidized cyclohexane per minute/moles of absorbed photons per minute.

demonstrated that the photoexcitation of these complexes induces an electron transfer from the axial ligand to the metal center. The quantum yield values for the subsequent reduction of Fe^{III} to Fe^{II} are very similar for all the porphyrins studied, indicating that the energy and redox reactivity of the excited states involved do not appreciably depend on the electron-withdrawing or -repelling property of the *meso*-aryl substituents. The iron *meso*-tetraarylporphyrin complexes investigated in the present work bear an OH$^-$ axial ligand and different substituents in the pyrrole β-positions of the porphyrin ring. Laser flash photolysis experiments indicate that the primary photochemical step consists of a very fast (less than 5 ns) cleavage of the iron–OH bond (Figure 3). Detection of the corresponding Fe^{II} porphyrin (Figure 2) and OH$^\bullet$ radicals (Figure 4) during this reaction has been realized. The formation of OH$^\bullet$ radicals as a consequence of photoinduced dissociation of Fe^{III}–OH bonds has been already proposed by Groves and Swanson in an investigation of Fe^{III} hydrate.[18] In that work, the authors provided evidence for subsequent hydroxylation of cyclohexanol.

The presence of β-halogen substituents on the porphyrin ring results in a decrease of the photoreduction quantum yield in the order Fe^{III}(TDCPP)(OH) > Fe^{III}(TDCPCl$_8$P)(OH) > Fe^{III}-(TDCPBr$_8$P)(OH). The experimental observation that Fe^{III}-(TDCPCl$_8$P)(OH) and Fe^{III}(TDCPBr$_8$P)(OH) are less photoreducible than Fe^{III}(TDCPP)(OH) is apparently in contrast with the redox potential of these complexes which are known to be strongly stabilized in their ferrous form by electron-withdrawing halogen substituents at the pyrrole β-positions.[19] Actually, generally speaking, photochemically generated excited states can present energies and redox reactivities different from those of the ground state. Moreover, for the photochemical system discussed here, Φ_{red} depends (i) on the efficiency of the charge separation between the primary photoproducts Fe^{II} and OH$^\bullet$ radicals occurring in competition with the radiationless deactivation of the excited state and (ii) on the tendency of OH$^\bullet$ radicals to diffuse away from the first coordination sphere of the metal. On these bases, halogen substituents at the pyrrole β-positions able both to affect the strength of Fe^{III}–OH bonds and to cause a significant distortion of the porphyrin ring[20] are expected to influence Φ_{red} in an unpredictable way.

Catalytic Photooxidation of Neat Cyclohexane by O$_2$. We recently reported[5d] preliminary results showing that cyclohexane can be selectively oxidized by O$_2$ to cyclohexanone in the
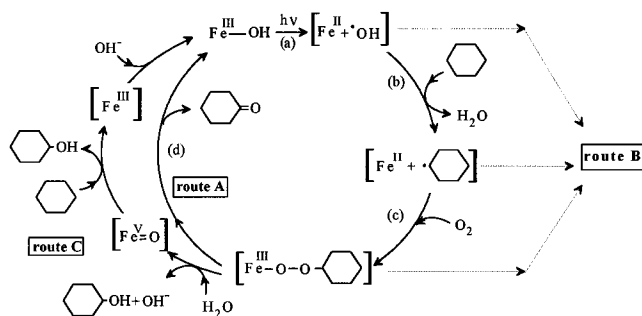
Figure 7. Possible mechanism of photocatalytic oxidation of cyclohexane.

presence of catalytic amounts of photoexcited Fe^{III}(TDCPP)-(OH) under mild conditions (22 °C; 200 Torr of O$_2$). The mechanism that was proposed to take into account this selective formation of cyclohexanone with only traces of cyclohexanol (steps a–d in Figure 7) involves $^\bullet$OH radicals formed upon photocleavage of the Fe^{III}–OH bond (step a). The $^\bullet$OH radical can easily abstract a hydrogen atom from cyclohexane, leading to the formation of an Fe^{II}–cyclohexyl radical pair (step b). The very fast reaction of O$_2$ with Fe^{II} in the presence of an alkyl radical leads to the formation an Fe^{III}–peroxoalkyl complex (step c) which, in nonpolar solvents, is known to undergo an intramolecular decomposition, leading rapidly and selectively to the corresponding ketone as well as the starting Fe^{III}(TDCPP)(OH) complex[21] (step d). The fact that, in an oxygenated solvent, the Fe^{II} reoxidation occurs during the laser pulse (see Figure 3) suggests that dioxygen reacts in less than 5 ns with the coordinatively unsaturated Fe^{II} porphyrin intermediate (eq 3). Since Fe^{III}(TDCPP)(OH) is unable to form a μ-oxo dimer complex for steric reasons,[22] it can initiate a new photochemical cycle.

The photochemical excitation of Fe^{III}(TDCPCl$_8$P)(OH) and Fe^{III}(TDCPBr$_8$P)(OH) in neat cyclohexane results in the formation of cyclohexanone as the only reaction product (Table 1), indicating that the mechanism shown in Figure 7 (steps a–d) is also operative for these perhalogenated iron porphyrins.

The results obtained by using the two radical scavengers, dmpo and pbn, are in complete agreement with this mechanism. Thus, dmpo, which was previously shown to be able to reach the radical species formed in the primary photoreaction of iron porphyrins bearing bulky *meso*-aryl substituents,[10] completely suppressed cyclohexanone formation from photoirradiation of

(18) Groves, J. T.; Swanson, W. W. *Tetrahedron Lett.* **1975**, 1953.
(19) Kadish, K. M. *Electrochemical and Spectroelectrochemical Studies of Biological Redox Components;* Advances in Chemistry Series 201; American Chemical Society: Washington, DC, 1982.
(20) Mandon, D.; Fischer, J.; Weiss, R.; Jayaray, K.; Austin, R. N.; Gold, A.; White, P. S.; Brigaud, O.; Battioni, P.; Mansuy, D. *Inorg. Chem.* **1992**, *31,* 2044.

(21) (a) Arasasingham, R. D.; Balch, A. L.; Cornman, C. R.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1989**, *111*, 4357. (b) Arasasingham, R. D.; Balch, A. L.; Hart, R. L.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1990**, *112*, 7566.
(22) Cheng, R. L.; Latos-Grazynsky, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412.

the three iron porphyrins used in this study (see above). In contrast, the more bulky pbn, which can only trap free radicals diffusing away from the [Fe^{II}---R·] cage,[10] had almost no effect on cyclohexanone formation (Table 1). In fact, the results obtained with iron porphyrins irradiated in neat cylohexane seem to favor active intermediates [Fe^{II} •OH], [Fe^{II} R·], and [Fe^{III}–OOR] where the radical species are all in close proximity to the iron, either situated in the cage or bound to the iron. This would explain the selective formation of cyclohexanone, the expected product from decomposition of the Fe^{III}–OOR intermediate[21] in such a nonpolar environment.

Catalytic Photooxidation of Cyclohexane by O_2 in More Polar Solvents. The use of a more polar solvent (CH_2Cl_2/C_6H_{12}) leads to a more complex mixture of cyclohexanone and cyclohexanol, the ratio of which is highly dependent on the presence of pbn and on the nature of the iron porphyrin (Table 2). Accordingly, one should expect that, in a more polar medium, intermediate cyclohexyl or cyclohexyloxy radicals would diffuse out from the cage more easily, and the Fe^{III}–OOR intermediate would have a different fate. Here again, the use of pbn, which is supposed to only trap free radicals in the bulk, was very useful, as it led to a drastic decrease of cyclohexanol and cyclohexanone formation, indicating that these products were in great part derived from autoxidation reactions involving free cyclohexyl and cyclohexyloxy radicals. Figure 5B confirms that pbn traps several free radicals during photoirradiation of Fe(TDCPP)(OH) in CH_2Cl_2/C_6H_{12}.

Interestingly enough, irradiation of Fe(TDCPP)(OH) in the presence of pbn leads to the exclusive formation of cyclohexanol, a situation completely opposite to that found for the same experiment performed in neat cyclohexane with the exclusive formation of cyclohexanone. This selective formation of cyclohexanol could be due to another species derived from Fe^{III}–OOR in a polar medium. The influence of the reaction environment on the mode of cleavage of iron–alkylperoxo complexes has been studied with many iron porphyrin biomimetic systems.[23] Polar environments and the availability of protons seem to favor a heterolytic cleavage of their O–O bonds with the formation of high-valent iron–oxo complexes (formally equivalent to Fe^V=O^+ species) according to eq 7. These species are equivalent to the iron–oxo intermediates of the catalytic cycles of catalase, peroxidase, and cytochrome P450. In the latter hemeprotein and model systems, such Fe^V=O^+ intermediates appear responsible for monooxygenations of substrates.

$$(P)Fe^{III}-O-O-CH + H^+ \longrightarrow CH-OH + (P)Fe^V=O^+ \quad (7)$$
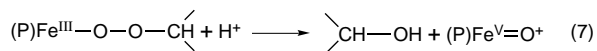
On the basis of the above discussion, one may explain the aforementioned results by considering the different possible fates of the species formed after photoirradiation, i.e. [Fe^{II} OH•],

[Fe^{II} R•], and [Fe^{III}–OOR] intermediates in Figure 7. In neat cyclohexane, radicals do not tend to escape from the cage and the Fe^{III}–O–O–cyclohexyl complex only undergoes an intramolecular decomposition with hydrogen transfer from cyclohexyl group to the Fe–O oxygen atom, formation of cyclohexanone, and regeneration of starting porphyrin Fe^{III}–OH (route A in Figure 7). When solvent polarity increases upon introduction of CH_2Cl_2 as a co-solvent and $Bu_4N^+OH^-$·$30H_2O$ to provide the OH^- iron ligand, escape of free radicals from the cage is strongly favored, as well as heterolytic cleavage of the O–O bond of Fe^{III}–OOR according to eq 7. Thus, two supplementary routes of oxidation of cyclohexane may occur: (i) a free-radical-dependent autoxidation of cyclohexane leading to cyclohexanol and cyclohexanone (route B in Figure 7); (ii) a selective monooxygenation of cyclohexane by an Fe^V=O^+ species leading exclusively to cyclohexanol (route C in Figure 7). On the basis of a recent work,[24] free radical cyclohexane autoxidation (route B) in the presence of the polyhalogenated porphyrins Fe(TDCPCl$_8$P)(OH) and Fe(TDCPBr$_8$P)(OH) includes also a radical-chain process in which the radicals are generated by oxidation and reduction of alkyl hydroperoxides.

Only route B, which is dependent on free radicals such as R•, RO•, and ROO•, is inhibited by pbn, whereas route C is not. The exclusive formation of cyclohexanol upon irradiation of Fe(TDCPP)(OH) in the presence of pbn strongly suggests that route C is only responsible for oxidation product formation under these conditions. In the absence of pbn, free radicals derived from cyclohexane lead to supplementary formation of cyclohexanol and cyclohexanone (route B). Upon irradiation of Fe(TDCPCl$_8$P)(OH) in the presence of pbn, a mixture of cyclohexanol and cyclohexanone (67:33) is formed (Table 2). This suggests that monooxygenation of cyclohexane according to route C remains predominant and that cyclohexanone formation by route A also occurs. In the absence of pbn, a greater amount of oxidation products is formed because of additional involvement of route B. The greater ability of Fe(TDCPP)(OOR) compared to Fe(TDCPCl$_8$P)(OOR) to evolve by route C than by route A could be related to the lower number of electron-withdrawing substituents that tend to disfavor the formation of a high-valent intermediate in the former complex. Irradiation of Fe(TDCPBr$_8$P)(OH) in CH_2Cl_2/C_6H_{12} leads to results very similar to those obtained with Fe(TDCPCl$_8$P)(OH) although with markedly lower quantum yields. Thus, it seems that the three routes A, B, and C also simultaneously occur in the case of Fe(TDCPBr$_8$P)(OH).

The aforementioned results are interesting, as they show that it is possible to oxidize alkanes by O_2 without the consumption of a reducing agent by using photoirradiated iron porphyrins. Moreover, even though further experiments are required to completely understand the detailed mechanisms of alkane oxidation in such systems, it is noteworthy that proper conditions were found for the highly selective oxidation either to cyclohexanone (neat cyclohexane) or to cyclohexanol (CH_2Cl_2/C_6H_{12} in the presence of pbn).

(23) (a) Traylor, T. G.; Popovitz-Biro, R. *J. Am. Chem. Soc.* **1988**, *110*, 239. (b) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1990**, *112*, 178. (c) Panicucci, R.; Bruice, T. C. *J. Am. Chem. Soc.* **1990**, *112,* 6063. (d) Gopinath, E.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113,* 4653. (e) Traylor, T. G.; Tsuchiya, S.; Byun, Y. S.; Kim, C. *J. Am. Chem. Soc.* **1993**, *115*, 2775. (f) Balch, A. L.; Olmstead, M. M.; Safari, N.; St. Claire, T. N. *J. Am. Chem. Soc.* **1994**, *33,* 2815. (g) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988***, 110,* 8443. (h) Yamaguchi, K.; Watanabe, Y.; Morishima, I. *J. Am. Chem. Soc.* **1993**, *115,* 5058.
(24) Grinstaff, M. W.; Hill, M. G.; Labinger, J. A.; Gray, H. B. *Science* **1994**, *264,* 1311.