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Photoredox and Photocatalytic Characteristics of Various Iron *meso*-Tetraarylporphyrins

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The photoredox behavior of various iron *meso*-tetraarylporphyrins in ethanol-containing solvents is examined. The reduction of Fe(III) to Fe(II) is observed in every case under irradiation with light of 350–450 nm. The electron-drawing or -repelling power of the meso-aryl substituents are found to have a scarce influence on the energy and the reactivity of the excited states responsible for the photoreduction process. On the other hand, the photoreduction quantum yield is appreciably influenced by the composition of the solvent in proximity to the iron porphyrin molecules. The iron porphyrins examined are observed to catalyze the photoreduction of CCl$_4$ by ethanol. The compounds containing bulky meso-aryl substituents are very resistant to degradation, so that they appear the best suited for catalytic purposes. A mechanism is proposed in which the primary process consists of an electron transfer from the axially ligated ethanolate to iron, giving an iron(II) porphyrin species and an ethoxy radical. These species are able to react with CCl$_4$, initiating a catalytic cycle leading to the formation of Cl$^-$, CH$_3$CHO, and CHCl$_3$.

Introduction

The redox properties of metalloporphyrins have attracted the interest of many authors, mainly in view of the use of these compounds as catalysts for several chemical reactions involving organic molecules.[1-4] In particular, many studies have been devoted to the use of iron porphyrins as catalysts for monooxygenation reactions[2-4] as well as for reduction of haloalkanes.[1] Besides their importance in chemical catalysis, these processes, mimicking the behavior in vivo of cytochrome P-450, allow one to better understand the detailed mechanism of this ubiquitous enzyme in biological systems. One of the obstacles met in the studies of catalysis by iron porphyrins is the susceptibility of these compounds to degradation. In recent years, good results have been obtained with a number of iron porphyrins having the meso positions protected by various substituents.[4,5-9]

Light is able to induce redox reactions in iron porphyrins. In particular, it has been demonstrated that the irradiation in the axial ligand to metal charge-transfer (LMCT) band results in an intramolecular electron transfer from the axial ligand to iron, leading to reduction of Fe(III) to Fe(II) and, at the same time, to the formation of a free-radical species from the axial ligand.[10-16] It has been reported that both Fe(II) and the free radical can induce catalytic reactions on organic substrates as, for instance, the oxidation of alkenes in the presence of oxygen[15,17] and the reduction of CCl$_4$.[18,19] The instability of the porphyrin ring, as observed in chemical catalysis, is a serious obstacle that limits the use of iron porphyrins in photocatalysis. For this, we have taken into consideration for photocatalytic purposes iron porphyrins with substituents in the meso positions which were expected to protect the porphyrin ring against the attack by radical species. In a preliminary investigation we have obtained good results using iron *meso*-tetrakis(2,6-dichlorophenyl)porphyrin as a catalyst for the photoreduction of CCl$_4$ in ethanol.[19] In the present paper we compare the photochemical behaviors of a series of iron *meso*-tetraarylporphyrins. Their efficiency in undergoing an intramolecular photoredox transfer, their resistance to photodegradation, and their photocatalytic activity are related to the characteristics of the meso-phenyl substituents (e.g., steric hindrance, polarity, and electronegativity) in order to obtain information on the mechanism by which iron porphyrins carry on their photocatalytic activity.

Experimental Section

Apparatus. UV–vis spectra were recorded on a Kontron Model Uvikon 860 spectrophotometer, and X-band 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. Columns packed with Carbowax 20 M 5% on Chromosorb W-AW or 10% UCW 982 on Chromosorb W-AW were used for analysis of acetaldehyde or chloroform and acetaldehyde diethyl acetal, respectively. Potentiometric titrations were performed with an Amel Model 337 pH meter. Irradiation equipment was as previously reported.[19]

Materials. Phenyl-*tert*-butylnitrone (pbn) and 5,5-dimethylpyrroline *N*-oxide (dmpo) were commercial products (Aldrich) and were used as received. Iron 5,10,15,20-tetraphenylporphyrin chloride (Fe(TPP)(Cl)) was bought from Porphyrin Products Inc. Iron 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin chloride (Fe(TPFPP)(Cl)), iron 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin chloride (Fe(TDCPP)(Cl)), iron 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin chloride (Fe(TMP)(Cl)), and iron tetrakis(6-methylphenyl)porphyrin chloride (Fe(TTP)(Cl)) were prepared and purified as previously reported.[20] Ethanol and carbon tetrachloride were spectroscopic grade solvents and were dried and purified by standard methods. All the other chemicals were commercial products and were used without further purification.

Procedures. The iron porphyrins were dissolved in the appropriate solvent and the solutions degassed to less than 1×10^{-5} Torr by means five vacuum-line freeze–thaw–pump cycles. The irradiation was carried out at 22 ± 1 °C and the photoreaction monitored by UV–vis spectros-

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(1) Brault, D. *Environmen. Health Perspect.* **1985**, *64*, 53.
(2) Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578.
(3) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450, structure, mechanism and biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum Press: New York, London, 1986.
(4) Mansuy, D. *Pure Appl. Chem.* **1987**, *59*, 759.
(5) Traylor, P. S.; Dolphin, D.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1984**, 279.
(6) Mashiko, T.; Dolphin, D.; Nakano, T.; Traylor, T. G. *J. Am. Chem. Soc.* **1985**, *107*, 3735.
(7) Traylor, T. G.; Marsters, J. C.; Nakano, T.; Dunlop, B. E. *J. Am. Chem. Soc.* **1985**, *107*, 5537.
(8) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.
(9) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512.
(10) Bartocci, C.; Scandola, F.; Ferri, A.; Carassiti, V. *J. Am. Chem. Soc.* **1980**, *102*, 7067.
(11) Bizet, C.; Morliere, P.; Brault, D.; Delgado, O.; Bazin, M.; Santus, R. *Photochem. Photobiol.* **1981**, *34*, 315.
(12) Bartocci, C.; Maldotti, A.; Traverso, O.; Bignozzi, C. A.; Carassiti, V. *Polyhedron* **1982**, *2*, 97.
(13) Richman, R. M.; Peterson, M. W. *J. Am. Chem. Soc.* **1985**, *104*, 5795.
(14) Bartocci, C.; Maldotti, A.; Carassiti, V.; Traverso, O.; Ferri, A. *Inorg. Chim. Acta* **1985**, *107*, 5.
(15) Hendrickson, D. N.; Kinnairs, M. G.; Suslick, K. S. *J. Am. Chem. Soc.* **1987**, *109*, 5583.
(16) Ozaki, Y.; Iniyama, K.; Ogashi, M.; Kitagawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 1243.
(17) Peterson, M. W.; Rivers, D. S.; Richman, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 2907.
(18) Maldotti, A.; Bartocci, C.; Amadelli, R.; Carassiti, V. *J. Chem. Soc., Dalton Trans.* **1989**, 1197.
(19) Bartocci, C.; Maldotti, A.; Varani, G.; Carassiti, V.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1989**, 964.
(20) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fart, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462 and references cited therein.

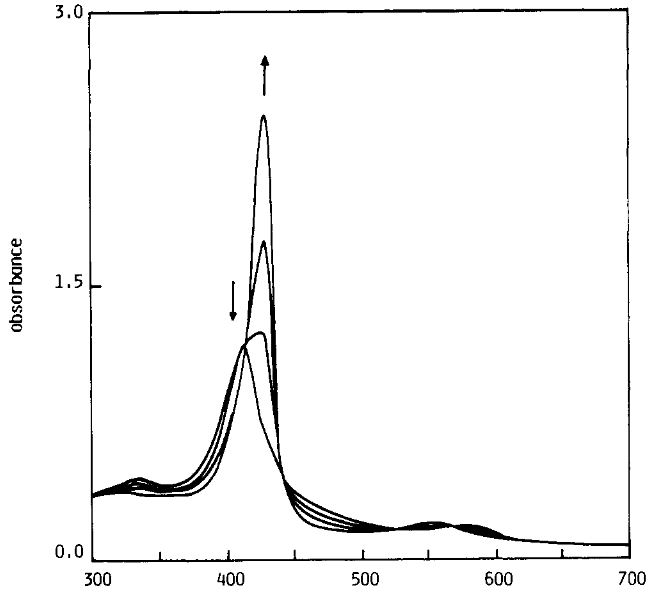


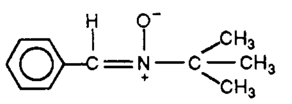
Figure 1. Spectral variations obtained under irradiation of a deaerated solution of iron(III) *meso*-tetrakis(2,2-dichlorophenyl)porphyrin (Fe(TDCPP)) at λ > 350 nm (Fe(TDCCP) concentration 1×10^{-5} mol dm^{-3}).

copy. The light intensity was measured by a ferrioxalate actinometric method.[21] The amount of Cl$^-$ formed was measured by potentiometric titration with $AgNO_3$. Other reaction products were determined by GC by comparison of their retention times with authentic samples using C_6H_5I as internal standard. Irradiation in the ESR cavity was carried out at room temperature with light of λ > 350 nm to avoid photolysis of the trap. 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.

Results

Irradiation of iron(III) *meso*-tetraarylporphyrins (Fe^{III}(P)) at 365 nm in carefully deaerated solutions containing ethanol as a coordinating solvent led to the absorption spectral variations reported in Figure 1. The most obvious change appears to be the red shift and the intensity increase of the Soret band. The original spectrum was restored when the irradiated solutions were aerated. Identical behavior was observed when Fe^{III}(P) was reduced by reducing agents (see Experimental Section). These results clearly indicate that the irradiation results in a reduction of Fe^{III}(P) to Fe^{II}(P). The absorbance in the Soret region was observed to change linearly for the first 10 min of irradiation, indicating that the photoreduction process followed zero-order kinetics. This allowed us to calculate the photoreduction quantum yields (Φ_{red})[22] for all the iron porphyrins examined. The results (Table I) show that the quantum yields are independent of the nature of the meso-aryl substituents. On the other hand, they appreciably depend on the solvent composition and the presence of acrylamide, which is known to be a good radical scavenger.[23,24]

Evidence for the formation of a free-radical species was obtained by irradiating iron porphyrin solutions containing phenyl-*tert*-butylnitrone (pbn) (**1**) or 5,5-dimethylpyrroline *N*-oxide (dmpo) (**2**) as a spin trap[25] in the cavity of an ESR spectrometer.



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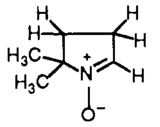

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Table I. Quantum Yields of Fe^{II}(P) Formation ($10^2\Phi_{red}$) by Irradiation of Fe^{III}(P) in Different Solvents[a]

	solvent		
Fe^{III}(P)[b]	ethanol	ethanol–cyclohexane (60/40)	ethanol–cyclohexane (20/80)
Fe(TPP)	1.8 ± 0.2	1.3 ± 0.2	0.8 ± 0.1
Fe(TPFPP)	1.6 ± 0.2	1.6 ± 0.2	1.8 ± 0.2
Fe(TMP)	1.9 ± 0.2	1.3 ± 0.2	0.8 ± 0.1
Fe(TDCPP)	1.8 ± 0.2	1.8 ± 0.2	1.8 ± 0.2
Fe(TTP)	1.9 ± 0.2	1.3 ± 0.2	0.9 ± 0.1
Fe(TDCPP)[c]	0.8 ± 0.1		

[a] Irradiation wavelength 365 nm; Fe^{III}(P) concentration 1×10^{-5} mol dm^{-3}. [b] TPP = *meso*-tetraphenylporphyrin; TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrin; TMP = *meso*-tetramesitylporphyrin; TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin; TTP = *meso*-tetra-*p*-tolylporphyrin. [c] In the presence of 1 mol dm^{-3} acrylamide.

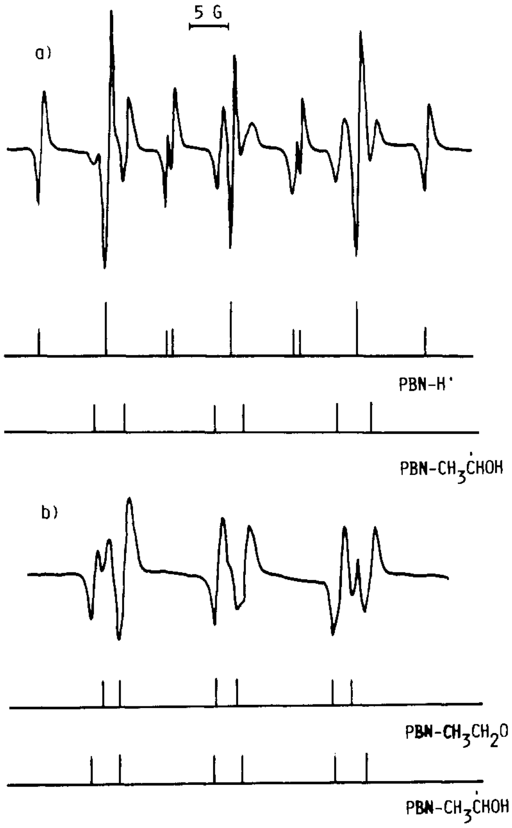

Figure 2. ESR spectra with stick-diagram reconstructions obtained after 3-min irradiations of 2×10^{-4} mol dm^{-3} Fe(TPP) (a) and Fe(TDCPP) (b) in the presence of 3×10^{-2} mol dm^{-3} pbn. Hyperfine coupling constants (gauss) for pbn-radical adducts: $CH_3\dot{C}HOH$, a_N = 15.5, a_H = 3.7; H, a_N = 16.5, a_H = 9.1; $CH_3CH_2O^\bullet$, a_N = 15.5, a_H = 2.4.

The spectra obtained are typical for adducts of the spin traps with hydrogen or with $CH_3\dot{C}HOH$ or $CH_3CH_2O^\bullet$ radicals.[26,27] In Figure 2 typical ESR spectra of pbn adducts are reported: spectrum a was obtained in photochemical experiments conducted with Fe(TPP). It is quite similar to that obtained for Fe(TTP) and presents two superimposed signals that can be assigned to adducts of pbn with $CH_3\dot{C}HOH$ radicals and hydrogen atoms. Spectrum b, obtained with Fe(TDCPP), consists of signals typical of $CH_3CH_2O^\bullet$ and $CH_3\dot{C}HOH$ radical adducts. Similar spectra were obtained with Fe(TMP) and Fe(TPFPP). The ESR spectra obtained with dmpo exhibit, besides typical signals indicating the trapping of hydrogen atoms (a_N = 16.5, a_H = 22.0), other su-

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(21) Murov, S. L. In *Handbook of Photochemistry*; M. Dekker: New York, 1973; p 119.

(22) Φ_{red} = moles of Fe(II) porphyrin per minute per mole of photons absorbed per minute.

(23) Natarajan, L. V.; Santappa, M. *J. Polym. Sci.* **1968**, *6*, 3245.

(24) The formation of polyacrylamide during the irradiation gave experimental evidence of the efficient radical trapping by acrylamide.

(25) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31.

(26) Maldotti, A.; Bartocci, C.; Amadelli, R.; Carassiti, V. *Inorg. Chim. Acta* **1983**, *74*, 275.

(27) Ledwith, A.; Russel, P. J.; Sutcliffe, L. M. *Proc. R. Soc. London, A* **1973**, *332*, 151.

Table II. Efficiency of $Fe^{III}(P)$ Complexes as Catalysts for the Photoreduction of CCl_4 by Ethanol[a]

$Fe^{III}(P)$[b]	$10^2\Phi_{Cl}$[c]	% $Fe^{III}(P)$ consumed	irradn time, h
Fe(TDCPP)	2.7 ± 0.2	<2	20
Fe(TDCPP)[d]	1.1 ± 0.1	<2	20
Fe(TMP)	3.3 ± 0.2	<2	20
Fe(TPFPP)		>99	<2
Fe(TPP)		>99	<2
Fe(TTP)		>99	<2

[a] $Fe^{III}(P)$ concentration 2×10^{-5} mol dm^{-3}; CCl_4 concentration 1 mol dm^{-3}; photons absorbed at $\lambda > 350$ nm $\approx 2.6 \times 10^{-3}$ mol dm^{-3} min^{-1}. [b] See note *b* in Table I. [c] (mol of product/min)/(mol of photons absorbed/min). [d] In the presence of 3×10^{-2} mol dm^{-3} pbn.

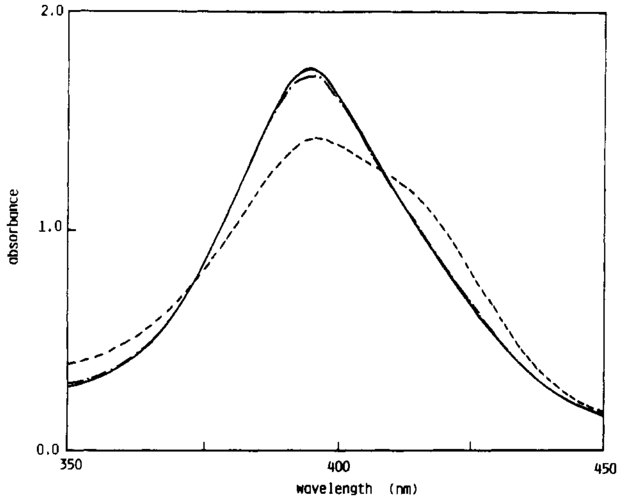
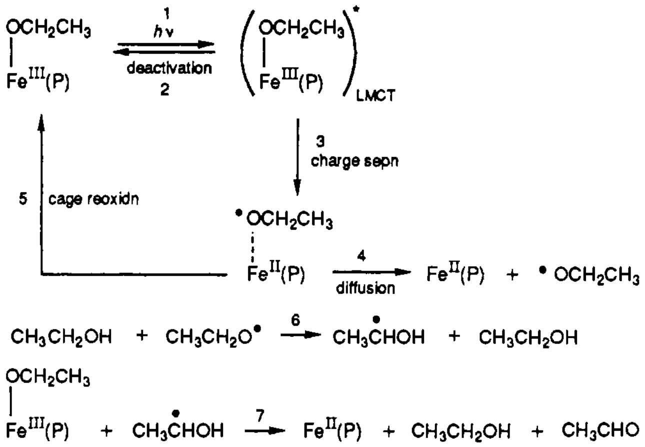


Figure 3. Spectral variations obtained upon irradiation of a 2×10^{-5} mol dm^{-3} deaerated ethanol solution of Fe(TPP) containing 1 mol dm^{-3} CCl_4 at $\lambda > 350$ nm: —, initial spectrum; - - -, spectrum after 20-min irradiation; –·–, spectrum after 20-min irradiation in the presence of 3×10^{-2} mol dm^{-3} pbn.

perimposed signals of difficult analysis, but presumably attributable to $CH_3\dot{C}HOH$ adducts.

In a recent communication[19] we reported that Fe(TDCPP) could efficiently catalyze the photoreduction of CCl_4 by ethanol to Cl^- and $CHCl_3$, since it resists destruction or deactivation. We have irradiated deaerated ethanol solutions of the above mentioned iron porphyrins at 350–450 nm in the presence of CCl_4 (1 mol dm^{-3}) in order to test their ability in catalyzing the photoreduction of haloalkane derivatives as compared with that of Fe(TDCPP). The obtained results (Table II) show that, while all the compounds examined can potentially catalyze the photoreduction of CCl_4 by ethanol, Fe(TPP), Fe(TTP), and Fe(TPFPP) have their catalytic efficiency greatly impaired by rapid irreversible photodegradation and inactivation, as previously observed for iron octaethylporphyrin (Fe(OEP)).[18] The degradation process was observed to become negligible in the presence of pbn, which in this case operates as a radical scavenger[28] (Figure 3). The analysis of the reaction products (see Procedures) was carried out after 20 h of irradiation only for Fe(TDCPP) and Fe(TMP), which were observed to undergo negligible degradation under irradiation.[29] The results were as follows (mol dm^{-3}): Cl^- $(8.3 \pm 0.2) \times 10^{-2}$; $CHCl_3$, $(8.0 \pm 0.2) \times 10^{-2}$; CH_3CHO, $(6.6 \pm 0.2) \times 10^{-3}$; acetaldehyde diethyl acetal, $(7.4 \pm 0.2) \times 10^{-2}$. The catalytic efficiency of the system was quantitatively expressed by the turnover, which has been calculated as moles of product per mole of consumed catalyst. After 20 h of irradiation a value of about 70 000 was found for Fe(TDCPP) and Fe(TMP).

Scheme I



The analysis of the reaction products was also carried out in solutions irradiated for several hours and then taken in the dark for the same time. The results showed that, while the products were formed with the same stoichiometric ratio as that obtained immediately after irradiation, their concentration was about 20% higher. This is an indication that free-radical species induced thermal chain reactions which were occurring also after the irradiation was stopped.

Identical photochemical experiments conducted in aerated solutions led to qualitatively similar results. The Φ_{Cl} values, determined after short irradiation periods, do not present appreciable differences with respect to those obtained in the absence of dioxygen. Complex spectral variations, indicative of irreversible reactions occurring at the porphyrin ring, were, however, observed when the irradiation was carried on for long periods. This behavior did not allow a precise calculation of Φ_{Cl}, which appeared, however, lowered with respect to those obtained in deoxygenated solution.

Discussion

Intramolecular Photoredox Reactions. The photoreduction of $Fe^{III}(P)$ to $Fe^{II}(P)$ in solutions containing ethanol as a coordinating solvent has been previously reported.[10,11] The results obtained have shown that the primary photochemical act is an intramolecular electron transfer from an axially bound ethanolate (or ethanol)[30] ligand to iron (Scheme I). Under conditions where the excitation light is completely absorbed by the reactant, Φ_{red} essentially depends on (i) the efficiency of the charge separation (process 3) that occurs in competition with the radiationless deactivation of the excited state (process 2), (ii) the possibility for the $\dot{O}C_2H_5$ radical to diffuse away from the first coordination sphere of the metal (process 4) before it reoxidizes $Fe^{II}(P)$ to $Fe^{III}(P)$ (process 5), and (iii) the ability of the $CH_3\dot{C}HOH$ radical formed via reaction with ethanol (process 6) to reduce $Fe^{III}(P)$ to $Fe^{II}(P)$ (process 7).

The data reported in Table I indicate that the Φ_{red} values of all the porphyrins examined are very similar.[31] This implies that the LMCT excited state responsible for the photoreduction of Fe(III) to Fe(II) has energy and redox reactivity that are almost independent of the electron-drawing or -repelling power of the meso-aryl group substituents. The lower Φ_{red} value obtained in ethanol solutions containing acrylamide is caused by the scavenging of the $CH_3\dot{C}HOH$ radicals, which inhibits the secondary reduction of $Fe^{III}(P)$ (process 7).

The Φ_{red} values of Fe(TPFPP) and Fe(TDCPP) in 1/4 ethanol–cyclohexane mixed solvent are not appreciably different from those obtained in pure ethanol (Table I). This would suggest that, due to the formation of efficient hydrogen bonds between the halogen meso-phenyl substituents and ethanol, this is present in

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(28) pbn has been used instead of acrylamide because after prolonged irradiation, the formation of insoluble polyacrylamide interfered in the experimental determination of the reaction products.

(29) It has been observed that in 20 h of irradiation 3 mol dm^{-3} of photons was approximately absorbed while only 1×10^{-6} mol dm^{-3} of iron porphyrin was consumed.

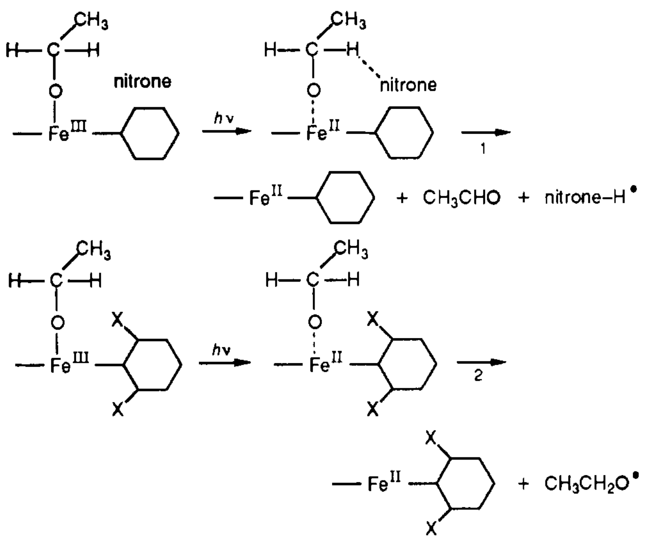
(30) Bartocci, C.; Scandola, F.; Ferri, A.; Carassiti, V. *Inorg. Chim. Acta* **1979**, *37*, L473.

(31) The lower value of Φ_{red} obtained in a previous work[26] was probably caused by a not carefully achieved deaeration.

much larger amount than cyclohexane in proximity to iron. As a consequence, the $CH_3CH_2O^{\bullet}$ radical, formed in process 4 (Scheme I), is rapidly trapped by ethanol, allowing the diffusion of $Fe^{II}(P)$ species into the solution bulk (process 6 in Scheme I). In the case of Fe(TPP), Fe(TTP), or Fe(TMP) the Φ_{red} values in pure ethanol are appreciably higher than those determined in ethanol–cyclohexane mixtures. The attribution of this difference to a change of the axial coordination of iron does not appear plausible because the addition of cyclohexane to ethanol solutions of $Fe^{III}(P)$ does not result in an appreciable variation in the electronic absorption spectra. Thus, the decrease of Φ_{red} in the mixed solvent could be accounted for in terms of a preferential solvation by cyclohexane with respect to ethanol of the hydrophobic Fe(TPP), Fe(TTP), and Fe(TMP). In fact, under these conditions, the $CH_3CH_2O^{\bullet}$ radical has less chance to react with ethanol and, at the same time, cyclohexane is not expected to react so efficiently with the $CH_3CH_2O^{\bullet}$ radical as to compete with the cage reoxidation reaction (process 5, Scheme I). The consequence is that less $Fe^{II}(P)$ diffuses into the solution bulk. The decrease of Φ_{red} by increasing the cyclohexane/ethanol ratio (Table I) gives further evidence of the above described microsolvation effect.

In a previous paper[26] we have reported that pbn and dmpo were able to remove a hydrogen atom from the alkoxy radical formed during the irradiation of pyridine–water–ethanol solutions of iron protoporphyrin IX (Fe(PPIX)). The result was explained by supposing that the hydrogen abstraction was occurring when the $CH_3CH_2O^{\bullet}$ radical was still interacting so strongly with the iron to be inhibited from diffusing away as such. The results obtained in the present work give evidence of a more complex behavior of the two nitrones in radical trapping during the irradiation of meso-substituted iron porphyrins. Dmpo traps hydrogen and, presumably, $CH_3\dot{C}HOH$ radicals in all cases whereas pbn behaves like dmpo in the case of Fe(TPP) (Figure 2a) and Fe(TTP), but traps only $CH_3CH_2O^{\bullet}$ and $CH_3\dot{C}HOH$ radicals during the irradiation of Fe(TPFPP), Fe(TMP), and Fe(TDCPP) (Figure 2b). With the last two compounds, the approach of the bulky pbn to the CH_3CH_2O ligand is hindered because the first coordination sphere of iron is sterically protected by four methyl groups or four chlorine atoms, respectively. As a consequence, pbn can only trap free-radical species that have diffused away from the first coordination sphere, i.e., $CH_3CH_2O^{\bullet}$ and/or $CH_3\dot{C}HOH$ (see process 6 in Scheme I). The steric hindrance is not sufficient to forbid dmpo to approach the $CH_3CH_2O^{\bullet}$ radical and, thus, to remove from it a hydrogen atom. Obviously, both bpn and dmpo abstract hydrogen from $CH_3CH_2O^{\bullet}$ in the case of the not sterically protected Fe(TPP) and Fe(TTP). The behavior of the spin traps is illustrated in Scheme II. Sequence 1 refers to trapping of hydrogen. The most plausible hypothesis is that of a concerted mechanism in which the electron transfer from the CH_3CH_2O ligand to iron leads to weakening of the C–H bond, favoring the hydrogen abstraction by nitrone. Sequence 2 represents the case in which steric hindrance forbids pbn to approach the ethoxy ligand and, consequently, to remove from it hydrogen atoms. Equations 3–5 indicate the fate of the $CH_3CH_2O^{\bullet}$ radical after diffusion outside the coordination sphere of iron.

Scheme II



$$CH_3CH_2O^{\bullet} + \text{nitrone} \xrightarrow{3} CH_3CH_2O^{\bullet}\text{–nitrone}$$

$$CH_3CH_2O^{\bullet} + CH_3CH_2OH \xrightarrow{4} CH_3CH_2OH + CH_3\dot{C}HOH$$

$$CH_3\dot{C}HOH + \text{nitrone} \xrightarrow{5} CH_3\dot{C}HOH\text{–nitrone}$$

The behavior of Fe(TPFPP) does not agree with the above explanation because, despite the fact that the fluorine atoms do not constitute a serious obstacle to the approach of pbn to the CH_3CH_2O ligand, no experimental evidence for pbn–hydrogen adducts was observed. A possible explanation for this anomalous behavior should be found in the existence of hydrogen bonds between ethanol and fluorine atoms of Fe(TPFPP) preventing easy access of pbn to the iron proximity.

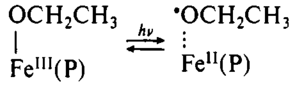
Photoreduction of CCl_4. The instability of iron porphyrins during the irradiation is the most important obstacle met in the use of these compounds as catalysts for haloalkane photoreduction.[18] Preliminary results reported in a recent communication[19] show that Fe(TDCPP) is a good catalyst for the photoreduction of CCl_4 and, at the same time, exhibits good stability under irradiation. The results obtained in the present paper (Table II) indicate that the stability and the good catalytic properties of Fe(TDCPP) are also presented by Fe(TMP). On the contrary, Fe(TPP), Fe(TPFPP), and Fe(TTP) undergo rapid irreversible modification and degradation when irradiated in ethanol solutions containing CCl_4. These results prove that the hindrance of the ortho phenyl substituents plays an important role in protecting the meso positions of the porphyrin ring against the attack of free-radical species produced during the photocatalytic process.

The free-radical origin of the iron porphyrin consumption under irradiation in ethanol solution containing CCl_4 is shown by the fact that, in the presence of a radical scavenger (pbn), Fe(TPP), Fe(TTP), and Fe(TPFPP) are much more resistant to degradation (Figure 3). The net reaction photoactivated by iron porphyrins is indicated in eq 1. If one reasonably assumes that all the

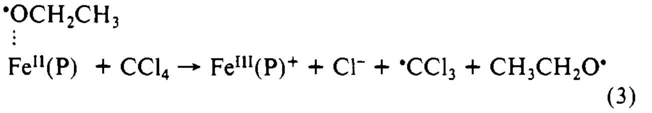
$$CCl_4 + CH_3CH_2OH \xrightarrow[Fe(P)]{h\nu} Cl^- + CHCl_3 + CH_3CHO + H^+ \qquad (1)$$

acetaldehyde diethyl acetal detected in the analysis of the products (see Results) is formed by reaction of acetaldehyde with ethanol, due to the acidic environment produced by reaction 1, Cl^-, CH_3CHO, and $CHCl_3$ are formed in a molar ratio of 1:1:1, which is consistent with the stoichiometry of reaction 1. This indicates that each "photoactivated" ethanol molecule reduces one molecule of CCl_4 to Cl^- and $CHCl_3$, oxidizing itself to acetaldehyde.

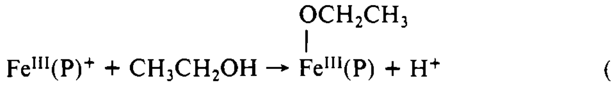
A reaction mechanism well fitting the experimental results is shown in eqs 2–7. The $Fe^{II}(P)$ formed through an intramolecular electron transfer from the axial ethanolate ligand to iron (eq 2)



$$\begin{array}{c}OCH_2CH_3\\|\\Fe^{III}(P)\end{array} \overset{h\nu}{\rightleftharpoons} \begin{array}{c}{}^{\bullet}OCH_2CH_3\\\vdots\\Fe^{II}(P)\end{array} \qquad (2)$$



$$\begin{array}{c}{}^{\bullet}OCH_2CH_3\\\vdots\\Fe^{II}(P)\end{array} + CCl_4 \rightarrow Fe^{III}(P)^+ + Cl^- + {}^{\bullet}CCl_3 + CH_3CH_2O^{\bullet} \qquad (3)$$



$$Fe^{III}(P)^+ + CH_3CH_2OH \rightarrow \begin{array}{c}OCH_2CH_3\\|\\Fe^{III}(P)\end{array} + H^+ \qquad (4)$$

$$CH_3CH_2O^{\bullet} + CH_3CH_2OH \rightarrow CH_3CH_2OH + CH_3\dot{C}HOH \qquad (5)$$

$${}^{\bullet}CCl_3 + CH_3CH_2OH \rightarrow CHCl_3 + CH_3\dot{C}HOH \qquad (6)$$

$$CH_3\dot{C}HOH + CCl_4 \rightarrow CH_3CHO + {}^{\bullet}CCl_3 + Cl^- + H^+ \qquad (7)$$

is oxidized to Fe^{III}(P) by CCl_4 (eq 3), which is reduced to Cl^- and the $^\bullet CCl_3$ radical. In turn, Fe^{III}(P), depending on its stability, can react with ethanol, giving the original catalyst, or undergo destroying attack by free-radical species. The $CH_3CH_2O^\bullet$ radical rapidly reacts, as expected, with ethanol to give the $CH_3\dot{C}HOH$ radical (eq 5). The rapid scavenging of this radical by CCl_4 (eq 7) prevents the secondary reduction of Fe^{III}(P), which is observed to occur in the absence the carbon tetrachloride (process 7 in Scheme I). The higher value of Φ_{Cl} (2.7×10^{-2}) (Table II) as compared with the Φ_{red} obtained in the presence of a radical scavenger (0.8×10^{-2}) (Table I) indicates that the reaction of CCl_4 with ethanol (eq 1) occurs to a great extent (70%) via thermal processes initiated by $CH_3\dot{C}HOH$ and $^\bullet CCl_3$ radicals (eqs 5-7). The free-radical thermal processes are suppressed by adding a suitable amount of pbn. Accordingly, acetaldehyde and chloroform are formed in negligible amounts. Thus, since in the presence of scavengers the reduction of CCl_4 occurs only by reaction with Fe^{II}(P) (eq 2), $\Phi_{Cl} = \Phi_{red}$.[32]

Conclusions

The results obtained from the investigation on the photoredox properties of iron *meso*-tetraarylporphyrins in ethanol show that the substituents on the meso-phenyl groups are observed to have negligible influence on the energy and reactivity of the excited state responsible for the primary photoreduction process. In cyclohexane-ethanol mixed solvent, important effects of the microsolvation in proximity to the central iron are observed.

The irradiation of an iron porphyrin can induce an intramolecular photoredox reaction giving rise to the formation of reactive species, Fe^{II}(P) and $CH_3CH_2O^\bullet$ radical, which are capable of initiating a catalytic cycle leading to the reduction of CCl_4 to Cl^- and $CHCl_3$ and the oxidation of CH_3CH_2OH to CH_3CHO.

The phenyl substituents play an important role in protecting the porphyrin ring against free-radical attacks, when iron arylporphyrin compounds are used as catalysts for the photoreduction of CCl_4 by ethanol. Chlorine atoms and methyl groups exhibit the most efficient protection due to their steric hindrance on the meso positions.

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Registry No. Fe(TPP)(Cl), 16456-81-8; Fe(TPFPP)(Cl), 36965-71-6; Fe(TDCPP)(Cl), 91042-27-2; Fe(TMP)(Cl), 77439-21-5; Fe(TTP)(Cl), 52155-50-7; CCl_4, 56-23-5; CH_3CH_2OH, 64-17-5; Cl^-, 16887-00-6; CH_3CHO, 75-07-0; $CHCl_3$, 67-66-3.

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[32] The slightly higher value of Φ_{Cl} with respect to Φ_{red} could be ascribed to an incomplete trapping of the $CH_3CH_2O^\bullet$ radicals by pbn.

Contribution from the School of Chemistry,
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Modulation of Valence Orbital Levels of Metalloporphyrins by β-Substitution: Evidence from Spectroscopic and Electrochemical Studies of 2-Substituted Metallo-5,10,15,20-tetraphenylporphyrins

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A new approach for obtaining information about the electronic structure and, in particular, the relative ordering of the frontier and subfrontier orbitals in metalloporphyrin systems is presented. This treatment involves a combination of electrochemical and spectral data. A series of 2-substituted copper(II) 5,10,15,20-tetraphenylporphyrins (**2**–**11**), in which the electronic nature of the substituent has been significantly varied, have been studied. The substituent has a considerable effect on the energies of the two highest occupied molecular orbitals, the a_{2u} and the a_{1u} orbitals, and can even cause the relative order of these orbitals to change. Substantial modulation of the a_{2u}/a_{1u} orbital energies is achieved by variation of the nature of a pyrrolic β-substituent. The effect is, as expected, felt much more strongly on the a_{1u} orbital, which has significant electron density associated with the pyrrolic β-position of metalloporphyrins. Indeed, the relative energy of the a_{1u} orbital in the nitroporphyrin **2** and the aminoporphyrin **11** differs by 0.71 eV; the corresponding difference in the energies of the a_{2u} orbitals is 0.14 eV. In cases where there is a good electron-donating 2-substituent (NH_2, OCH_3, SPh), the "normal" ordering $a_{2u} > a_{1u}$ is reversed. These observations have important consequences in metalloporphyrin systems as their patterns of reactivity, influenced by the electron distribution in the highest filled molecular orbital, will be particularly sensitive to the relative a_{1u}/a_{2u} separation and ordering. A role for pyrrolic β-substituents in the fine tuning of energy levels in porphyrin-based molecular electronic logic and memory devices is suggested.

Introduction

The physical properties and reactivities of metalloporphyrins are widely variable. These differences result from a combination of electronic and steric factors. While steric factors are generally well understood and arise mainly from the environment in which the metalloporphyrin interacts, and from bulky peripheral substituents in the case of 5,10,15,20-tetraarylporphyrins, the electronic structure of the porphyrin ring is subject to a number of influences. For a given metalloporphyrin, however, the major effects on electronic structure should result mainly from the coordinated metal (together with its axial ligands) and the peripheral substituents.[2] Other factors have been noted to give rise to relatively small perturbations of the metalloporphyrin electronic structure. These factors include the effects of aggregation, solvent, polymerization, adsorption onto surfaces, and incorporation into micelles.[3]

It is of particular interest, therefore, to determine how a given metal or peripheral substituent modifies the electronic structure of the porphyrin ring. Several theoretical investigations that involved extensive all-valence electron calculations on porphyrin systems of D_{4h} symmetry have been reported.[4] For more complex systems of this size, however, such calculations are not generally practicable. Fortunately, it is usually found sufficient, for porphyrins of approximate or exact D_{4h} symmetry, to focus attention on the π-electron structure of the ring, and in particular the frontier

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[2] Wang, M.-Y. R.; Hoffman, B. M. *J. Am. Chem. Soc.* **1984**, *106*, 4235.

[3] Shelnutt, J. A.; Ortiz, V. *J. Phys. Chem.* **1985**, *89*, 4733 and references therein.

[4] Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, pp 1-165.