

Photocatalytic Reactions in the 2,3,7,8,12,13,17,18-Octaethylporphyrinatoiron(III)–Ethanol–Carbon Tetrachloride System†

Andrea Maldotti,* Carlo Bartocci, Rossano Amadelli, and Vittorio Carassiti

Centro di Fotochimica del C.N.R., Dipartimento di Chimica dell'Università di Ferrara, Italy

The photochemistry of ethanol solutions of 2,3,7,8,12,13,17,18-octaethylporphyrinatoiron(III), $[\text{Fe}(\text{oep})]^+$, has been investigated in the presence of CCl_4 and of different amounts of oxygen. Continuous irradiation with 330–440 nm light induces an ethanol-to-oxygen electron transfer occurring with the assistance of an iron(III) porphyrin ethanolate complex. At a partial pressure of oxygen ranging from 0.1 to 1 Torr, the photoproducts, hydroxyethyl radical and superoxide ion O_2^- , give rise to a catalytic process, with >100 turnovers of $[\text{Fe}(\text{oep})]^+$, leading to the reduction of carbon tetrachloride to chloroform and chloride ions and with oxidation of ethanol to acetaldehyde. The rate of the photocatalytic process was observed to depend on the oxygen concentration, excitation wavelength, and the presence of a radical scavenger. A chain mechanism has been formulated involving radical species that can be quenched by oxygen to yield peroxy radicals.

Interest in the interaction of dioxygen with iron porphyrin complexes is increasing in view of its relevance to oxygen activation in many biomimetic catalytic redox processes.^{1–3}

Several studies^{4–10} have indicated that the non-emitting iron(III) porphyrin complexes undergo intramolecular redox photochemistry in the wavelength range 350–450 nm. In each case the primary photochemical act is an axial ligand-to-iron(III) electron-transfer process leading to the reduction of Fe^{III} to Fe^{II} and oxidation, with successive detachment, of the ligand. The consequence of this process is the formation of useful oxidizing agents toward various organic substrates. If the iron(III) porphyrin reactant is in some way regenerated, a catalytic cycle is realized.^{9,11}

The primary photoredox products, *i.e.* iron(II) porphyrin and axial ligand radicals, revert to the initial iron(III) porphyrin complex *via* a fast back electron transfer inside the solvent cage unless oxygen or pyridine is present.^{11,12} It has been assumed that both these species have the function of trapping the iron(II) complex during irradiation.

Recently, we communicated some results on the photochemistry of iron(III) protoporphyrin IX (3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropionic acid) in oxygenated aqueous ethanol solution.¹³ In this system, the reaction of oxygen with the photochemically formed iron(II) complex results in the reoxidation of Fe^{II} and in the formation of superoxide ion, O_2^- . A peculiar aspect of the overall process is that the iron(III) porphyrin complex is found unmodified at the end of the reaction, while oxygen is reduced to superoxide and ethanol is oxidized to hydroxyethyl radical. Both these products can effectively react with CCl_4 : the O_2^- radical *via* a nucleophilic attack to give CCl_3O_2^- and Cl^- ,¹⁴ the α -hydroxyethyl radicals *via* an electron-transfer process giving $^{\bullet}\text{CCl}_3$ and Cl^- .^{15,16}

In the present work these reactions are catalytically performed by irradiating ethanol solutions of iron(III) 2,3,7,8,12,13,17,18-octaethylporphyrin $[\text{Fe}(\text{oep})]^+$ in the presence of CCl_4 and oxygen. The interest in this type of reaction arises from the implications for the cytochrome P-450 mediated toxicity of halogenated compounds,¹⁷ as well as in degradation of CCl_4 in wastes.¹⁸

Experimental

Materials and Apparatus.—Octaethylporphyrinatoiron(III) chloride was purchased from Porphyrin Products Inc., and

phenyl-*t*-butylnitrone [benzylidene(*t*-butyl)amine oxide] (pbn) from Aldrich. Solvents were of spectroscopic grade and were dried and purified by standard methods.

Irradiations were carried out with a Hanau Q 400 mercury lamp. The required wavelength ranges were selected using glass cut-off filters. When necessary, monochromatic light was obtained with Corning filters.

U.v.–visible spectra were recorded with a Kontron model Uvikon 860 spectrophotometer, X-band e.s.r. spectra with a Bruker 220 SE spectrometer which was calibrated using $\alpha\alpha'$ -diphenylpicrylhydrazyl. Potentiometric titrations were performed using a Amel model 337 pH meter, and gas chromatographic analysis by a Perkin-Elmer model F 17 gas chromatograph with a Chromosorb 102 column (80–100 mesh).

Procedures.—The complex $[\text{Fe}(\text{oep})]^+$ was dissolved in anhydrous ethanol and the solutions obtained were placed in 0.2-, 1-, or 4-cm spectrophotometric cells or a quartz e.s.r. capillary, and used within 24 h.

When deaeration was required, reaction vessels were connected to a vacuum line and solutions degassed to less than 10^{-5} Torr (*ca.* 1.33×10^{-3} Pa) by means of at least five vacuum-line freeze-thaw pump cycles. When necessary, oxygen was let into the reaction vessel until the desired pressure was reached.

The $[\text{Fe}(\text{oep})]^+$ solutions were irradiated at the appropriate wavelength at $22 \pm 1^\circ\text{C}$, and the photoreaction monitored by u.v.–visible spectroscopy. The light intensity was measured by the ferrioxalate actinometric method.¹⁹ The analysis of Cl^- was performed by potentiometric titration with AgNO_3 after dilution of the reaction mixture with $0.02 \text{ mol dm}^{-3} \text{ HNO}_3$.

Irradiations in the e.s.r. cavity in the presence of pbn were performed at room temperature with light of wavelength higher than 350 nm, to avoid photolysis of the trap. In the absence of pbn, $[\text{Fe}(\text{oep})]^+$ solutions were irradiated at $\lambda > 310 \text{ nm}$. After irradiation for 10 min the solutions were cooled to 100 K.

Results

U.v.–Visible Spectral Changes.—When photolysis ($\lambda = 405 \text{ nm}$) of ethanol solutions of $[\text{Fe}(\text{oep})]^+$ containing $1 \text{ mol dm}^{-3} \text{ CCl}_4$ was carried out at a partial pressure of oxygen ranging from 0.2 to 1 Torr (5×10^{-7} – $2.5 \times 10^{-6} \text{ mol dm}^{-3}$), the u.v.–visible spectrum of the porphyrin changed from curve (a) to curve (b) of Figure 1. Spectra (a) and (b) can be ascribed to the charged species (1) and to neutral species (2) respectively.²⁰

† Non-S.I. units employed: $G = 10^{-4} \text{ T}$.

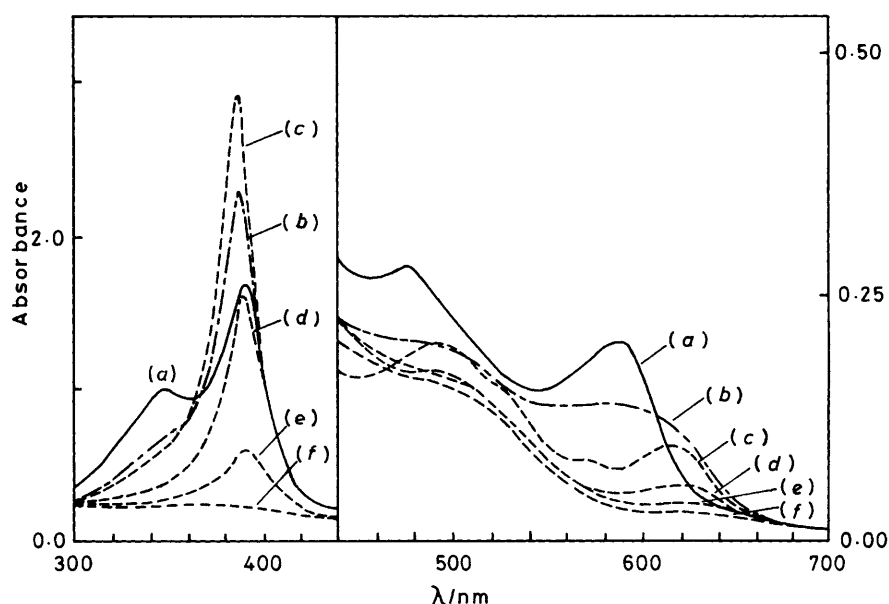
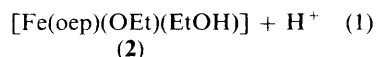
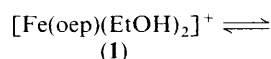


Figure 1. Electronic spectra of an ethanol solution of $4 \times 10^{-6} \text{ mol dm}^{-3}$ $[\text{Fe}(\text{oep})]^+$ containing 1 mol dm^{-3} CCl_4 in the presence of 1 Torr of oxygen: (a) before irradiation; (b) immediately after irradiation for 120 s at 405 nm; (c)–(f) 15, 30, 45, and 60 min respectively in the dark at 22°C , after irradiation. A 4-cm optical length spectrophotometric cell was used in each case



The complex $[\text{Fe}(\text{oep})]^+$ in ethanol/ CCl_4 (2:3) presents the spectrum (b) in Figure 1 even before irradiation. This can be attributed to the increase in polarity of the mixed solvent which is expected to favour the shift toward the protonated form in equilibrium (1). The spectral changes observed upon irradiation suggest that the spontaneous axial protonation process is in some how favoured by the dissociation process caused by the photoinduced ethanolate-to-iron electron transfer.

Spectral changes in time were followed in the dark, after a few seconds of irradiation. The result was that, after a further displacement toward the protonated form [Figure 1, curve (b)], an absorbance decrease over the whole u.v.-visible range occurred indicating an irreversible modification of the iron porphyrin complex which can be attributed to ring opening. This behaviour suggests that the photolysis induces a chain process in which radical intermediates attack the porphyrin ring yielding small colourless fragments. Strikingly, only negligible spectral changes were observed either in carefully deaerated solution or at a partial pressure of oxygen higher than 1 Torr.

Efficiency of the Photocatalytic Process.—Potentiometric titrations indicated that the bleaching process observed in the presence of small amounts of oxygen is accompanied by a non-stoichiometric disappearance of CCl_4 leading to the formation of chloride ions. So long as CCl_4 is in large excess in comparison with the secondary halogenated products, we can calculate the turnover of $[\text{Fe}(\text{oep})]^+$ (equivalents of Cl^- per equivalent of porphyrin consumed). These conditions were fulfilled when the irradiated solutions contained 1 mol dm^{-3} CCl_4 and $[\text{Fe}(\text{oep})]^+$ in the concentration range 10^{-6} – $10^{-5} \text{ mol dm}^{-3}$. Indeed, after complete bleaching of the solution, the chloride concentration never exceeded $5 \times 10^{-3} \text{ mol dm}^{-3}$; then, also the amount of CCl_4 reacted should be negligible in comparison with its initial concentration.

The turnover of $[\text{Fe}(\text{oep})]^+$ was measured as a function of

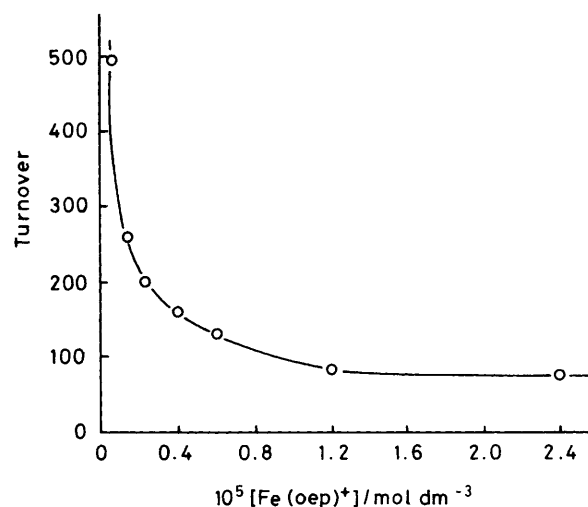


Figure 2. Dependence of the turnover of $[\text{Fe}(\text{oep})]^+$ on the initial concentration

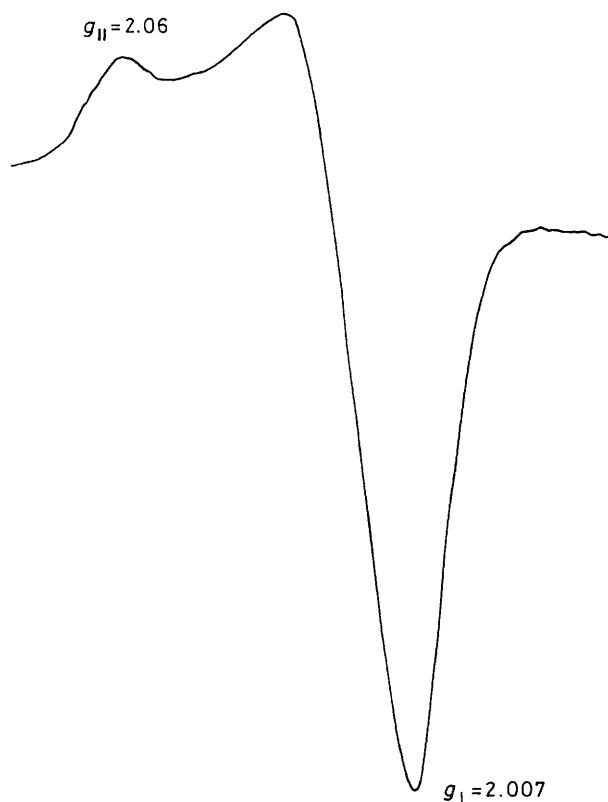
the initial porphyrin concentration. The results are reported in Figure 2. Qualitatively similar results were obtained over all the wavelength range 330–440 nm. Conversely, the rate of the photocatalytic process is strongly dependent on the excitation wavelength.

The Table reports the turnover and the turnover per min of $[\text{Fe}(\text{oep})]^+$ at different irradiation wavelengths and absorbed light intensities. In all the experiments the porphyrin concentration was $4 \times 10^{-6} \text{ mol dm}^{-3}$; the reaction was allowed to proceed until the solution was completely bleached. The lowest amount of photons which must be absorbed to allow experimental measurement of the rate of the photocatalytic process was $4.5 \times 10^{-8} \text{ mol min}^{-1}$ at 405 nm. At this wavelength, the quantum yield, given as the ratio of the chloride concentration to the number of photons absorbed, was estimated to be 1.5×10^5 .

Since the turnover of $[\text{Fe}(\text{oep})]^+$ is high at low porphyrin concentration, in order to accumulate organic products in

Table. Turnover values at different irradiation wavelengths and absorbed light intensities *

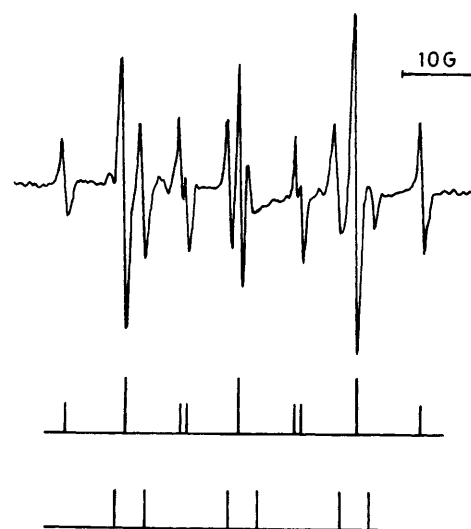
λ nm	Absorbed light intensity/ Einstein min^{-1}	Turnover	Turnover min^{-1}
335	1.5×10^{-7}	160	5.5
365	1.5×10^{-7}	185	6.1
405	1.5×10^{-7}	171	1.4
440	1.5×10^{-7}	175	0.6
405	4.5×10^{-8}	185	0.5
405	2.0×10^{-6}	180	3.0

* Initial concentrations of $[\text{Fe}(\text{oep})]^+$: $4 \times 10^{-6} \text{ mol dm}^{-3}$.**Figure 3.** E.s.r. spectrum of $5 \times 10^{-4} \text{ mol dm}^{-3}$ aerated ethanol solution of $[\text{Fe}(\text{oep})]^+$ containing $1 \text{ mol dm}^{-3} \text{ CCl}_4$, recorded at 100 K, after irradiation for 5 min with light of $\lambda > 315 \text{ nm}$ at room temperature

a detectable amount the reaction was carried out stepwise. Namely, successive portions of porphyrin were added in the course of the reaction to the same solution. In each step the concentration was maintained not higher than $10^{-6} \text{ mol dm}^{-3}$. When the chloride concentration was $1.3 \times 10^{-2} \text{ mol dm}^{-3}$, gas chromatographic analysis indicated the presence of $4 \times 10^{-3} \text{ mol dm}^{-3}$ acetaldehyde and $8 \times 10^{-3} \text{ mol dm}^{-3}$ chloroform.

Experiments, performed in ethanol solutions of $[\text{Fe}(\text{oep})]^+$ containing $1 \text{ mol dm}^{-3} \text{ CHCl}_3$, gave over the whole range of irradiation wavelength (330–440 nm) the following results: (i) bleaching of $[\text{Fe}(\text{oep})]^+$ did not occur in the dark, after irradiation; (ii) no appreciable formation of Cl^- was observed. These results indicate that, in the CCl_4 –ethanol– $[\text{Fe}(\text{oep})]^+$ system, CHCl_3 does not undergo further reaction, and can be considered the final product of the photoinduced chain reaction.

E.S.R. and Quenching Experiments.—In order to verify that paramagnetic species are formed during irradiation, solutions of

**Figure 4.** Experimental spectrum, with stick diagram, obtained after irradiation of a $5 \times 10^{-4} \text{ mol dm}^{-3}$ ethanol solution of $[\text{Fe}(\text{oep})]^+$ in the presence of $5 \times 10^{-2} \text{ mol dm}^{-3}$ pbn for 2 min at 298 K

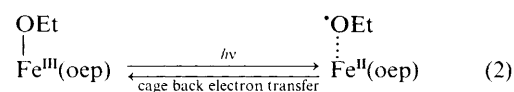
$[\text{Fe}(\text{oep})]^+$ were irradiated in the presence of oxygen at room temperature inside the e.s.r. cavity and then cooled to 100 K. Under these conditions, the spectrum in Figure 3 was obtained. It consists of an asymmetric singlet which is typical of the O_2^- radical.²¹

Irradiations were also conducted in the presence of pbn which can trap radicals to give more stable nitroxides.²² With solutions containing 1 Torr of oxygen, the e.s.r. spectrum shown in Figure 4 was obtained at room temperature. This can be interpreted as resulting from the superimposition of two distinct signals. One consisting of a 1:1:1 triplet of 1:2:1 triplets is characteristic of spin adduct $\text{PhCH}_2\text{N}(\text{O}^*)\text{Bu}^t$ (3) ($a_N = 16.0$, $a_H = 8.5$). The other, consisting of a 1:1:1 triplet of doublets, presents hyperfine splitting constants typical of nitroxide $\text{PhCH}[\text{CHMe}(\text{OH})]\text{N}(\text{O}^*)\text{Bu}^t$ (4) ($a_N = 15.8$, $a_H = 4.0$).²³ No evidence of formation of paramagnetic radical adducts with pbn was obtained when the same experiment was performed in carefully deaerated solutions.

Experiments were carried out to verify that the radical scavenger pbn was able to inhibit the photocatalytic process. As expected, in the presence of pbn no changes in the electronic spectrum were observed during the irradiation, as well as in the dark after irradiation. At the same time, there was no evidence of Cl^- formation.

Discussion

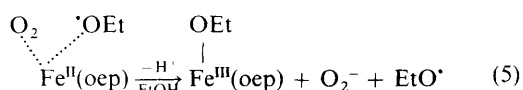
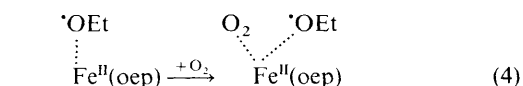
The primary photoreduction process [equilibrium (2)] leads to the formation of ethoxy radicals. In spin-trapping e.s.r. experiments these radicals were not trapped as such by pbn. The only paramagnetic adducts observed were hydroxyethyl radicals and hydrogen atoms. Hydroxyethyl radicals are formed according to equation (3).



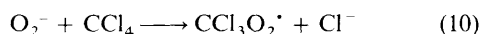
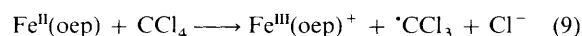
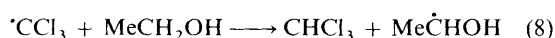
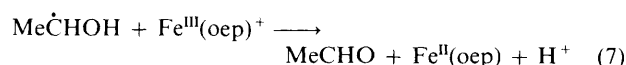
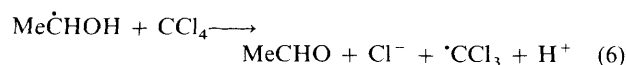
As reported in previous work,¹² the trapping of H^{\bullet} can be ascribed to the strong tendency of ethoxy radicals to be oxidized to acetaldehyde giving a hydrogen atom to the spin trap. This

phenomenon is made possible by the strong interaction of EtO^\bullet with the metal.

The experimental results show that radical adducts are observed only when the solution contains oxygen. This indicates that interaction with oxygen strongly competes with cage reoxidation [equation (2), reverse reaction], allowing the ethoxy radical either to diffuse away undergoing rapid conversion into hydroxyethyl radical or to react with the radical scavenger (pbn) giving an H atom adduct and acetaldehyde. Oxygen can prevent cage reoxidation by reacting with Fe^{II} when this is still bound to some degree to the ethoxy radical [equations (4) and (5)].^{12,13} Other authors, previously, took into account the possibility of an involvement of this type of intermediate in anion-promoted auto-oxidation processes of haemoproteins.^{2,14}



The e.s.r. spectrum obtained at low temperature (Figure 3) gives experimental evidence that the photochemically induced oxidation of ethanol is accompanied by the reduction of oxygen to give the superoxide ion [equations (4) and (5)]. The species O_2^- and MeCHOH formed in reactions (5) and (3) can be considered the initiators of the observed catalytic process. The successive chain propagation steps, described by equations (6)–(10) explain the observed formation of MeCHO , CHCl_3 ,



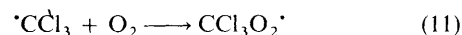
and Cl^- . According to equation (6), MeCHOH reacts with CCl_4 to give Cl^- and CCl_3^\bullet .^{15,16} The latter can, in turn, abstract an α -hydrogen from EtOH yielding CHCl_3 and, again, MeCHOH .

The redox potential of MeCHOH makes it able to reduce $[\text{Fe}(\text{oep})]^+$ in accordance with equation (7).¹⁵ The reactant iron(III) porphyrin can then be regenerated by direct electron transfer to CCl_4 [equation (9)].^{17,25} Finally the nucleophilic attack of O_2^- on CCl_4 leads to the formation of Cl^- and peroxy radicals $\text{CCl}_3\text{O}_2^\bullet$ [equation (10)].^{14,18}

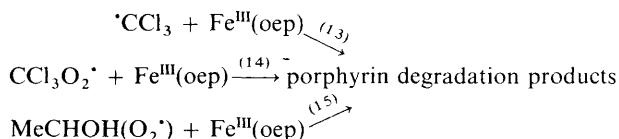
The $[\text{Fe}(\text{oep})]$ formed by equation (7) is known to reduce CCl_4 much faster than it binds and, successively, reduces oxygen.¹⁷ On the other hand, the iron(II) intermediate formed in the primary photochemical reduction [equation (2)] exhibits such strong ability to bind [equation (4)] and then reduce oxygen [equation (5)] as to prevent the CCl_4 reduction. As a consequence, while under irradiation reaction (10) is an efficient way for the reduction of CCl_4 , when the irradiation is stopped it does not occur appreciably.

Our experimental results indicate that the catalytic chain process is suppressed by the presence of radical scavenger

(pbn), by an oxygen partial pressure higher than 1 Torr, and by a high initial concentration of $[\text{Fe}(\text{oep})]^+$. This behaviour can be interpreted in terms of reactions (11)–(15). The effect of pbn is as expected, because of its strong ability to scavenge radical intermediates. Oxygen is known to react effectively with MeCHOH and CCl_3^\bullet radicals to give peroxy radicals.^{26,27} Thus at an oxygen partial pressure higher than 1 Torr, reactions (11) and (12) prevent the chain process from proceeding.



All the radical species involved in the chain process can attack $[\text{Fe}(\text{oep})]^+$ to give porphyrin degradation products [equations (13)–(15)]. The above degradation processes involve the porphyrin ring and can be initiated by hydrogen abstraction, addition reactions, and electron transfer.^{16,17,20} At higher concentrations of $[\text{Fe}(\text{oep})]^+$ reactions (13) can be so efficient as to prevent CCl_3^\bullet from working as a chain carrier. The trend of the turnover as a function of the initial concentration of $[\text{Fe}(\text{oep})]^+$ is in agreement with the above statement.



As far as the dependence of the rate of the photocatalytic process on excitation wavelength is concerned, it may be remarked that, for the same amount of absorbed photons, the turnover per min increases with decreasing irradiation wavelength in the range 330–440 nm, and flattens out at short wavelengths. This behaviour parallels the general trend previously observed for the photoreduction quantum yields of iron porphyrin complexes.^{3,10}

The results presented herein indicate that an electron transfer from ethanol to oxygen is realized with the photoassistance of $[\text{Fe}(\text{oep})]^+$. We would point out that the oxidation of the axial ligand is in itself an interesting process from the viewpoint of the conversion of organic and inorganic molecules. Furthermore, we have shown that the photochemically formed radical species can induce a catalytic chain process which leads to the reduction of CCl_4 to CHCl_3 and Cl^- with a mechanism which bears a close relationship with that reported to explain the cytochrome P-450 mediated toxicity of halogenated compounds. A peculiar aspect of the present investigation is that, by keeping the $[\text{Fe}(\text{oep})]^+$ concentration at catalytic concentrations, it is possible to allow the reaction to proceed to complete conversion of CCl_4 into CHCl_3 and Cl^- . This appears to be very promising in view of the employment of iron porphyrin catalysts in the sunlight-assisted degradation or transformation of halogenated hydrocarbons in wastes.

Acknowledgements

Financial support by the Ministry of Education is gratefully acknowledged. Thanks are also due to Mr. Luciano Righetti for his contribution to the experimental work.

References

- 1 D. Mansuy, *Pure Appl. Chem.*, 1987, **59**, 759.
- 2 I. Tabushi, M. Kodaera, and M. Yokayama, *J. Am. Chem. Soc.*, 1985, **107**, 4466.
- 3 J. T. Groves and Y. Watanabe, *J. Am. Chem. Soc.*, 1986, **108**, 7834.
- 4 C. Bartocci, F. Scandola, A. Ferri, and V. Carassiti, *J. Am. Chem. Soc.*, 1980, **102**, 7067.

- 5 C. Bartocci, A. Maldotti, O. Traverso, C. A. Bignozzi, and V. Carassiti, *Polyhedron*, 1982, **2**, 97.
- 6 C. Bartocci, A. Maldotti, V. Carassiti, O. Traverso, and A. Ferri, *Inorg. Chim. Acta*, 1985, **107**, 5.
- 7 C. Bizet, P. Morliere, D. Brault, O. Delgado, M. Bazin, and R. Santus, *Photochem. Photobiol.*, 1981, **34**, 315.
- 8 R. M. Richman and M. W. Peterson, *J. Am. Chem. Soc.*, 1982, **104**, 5795.
- 9 D. N. Hendrickson, M. G. Kinnaird, and K. S. Suslick, *J. Am. Chem. Soc.*, 1987, **109**, 1243.
- 10 Y. Ozaki, K. Iriyama, H. Ogoshi, and T. Kitagawa, *J. Am. Chem. Soc.*, 1987, **109**, 5583.
- 11 M. W. Peterson, D. S. Rivers, and R. M. Richman, *J. Am. Chem. Soc.*, 1985, **107**, 2907.
- 12 A. Maldotti, C. Bartocci, R. Amadelli, and V. Carassiti, *Inorg. Chim. Acta*, 1983, **74**, 275.
- 13 A. Maldotti, C. Bartocci, C. Chiorboli, A. Ferri, and V. Carassiti, *J. Chem. Soc., Chem. Commun.*, 1985, 881.
- 14 D. T. Sawyer and M. J. Gibian, *Tetrahedron*, 1979, 1471.
- 15 V. J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 1971, 458.
- 16 D. Brault, C. Bizet, P. Morliere, M. Rougee, E. J. Land, R. Santus, and A. J. Swallow, *J. Am. Chem. Soc.*, 1980, **102**, 1015.
- 17 D. Brault, *Environ. Health Perspect.*, 1985, **64**, 53.
- 18 J. L. Roberts, jun., and D. T. Sawyer, *J. Am. Chem. Soc.*, 1981, **103**, 712.
- 19 S. L. Murov, in 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973, p. 119.
- 20 D. Brault and P. Neta, *J. Phys. Chem.*, 1984, **88**, 2857.
- 21 M. C. R. Symons, G. W. Eastland, and L. R. Denny, *J. Chem. Soc., Faraday Trans.*, 1980, 1868.
- 22 E. G. Janzen, *Acc. Chem. Res.*, 1971, **4**, 31.
- 23 A. Ledwith, P. J. Russel, and L. M. Sutcliffe, *Proc. R. Soc. London, Ser. A*, 1973, **332**, 151.
- 24 W. J. Wallace, R. A. Houtchens, J. C. Maxwell, and W. S. Cauchey, *J. Biol. Chem.*, 1982, **257**, 4966.
- 25 D. Mansuy, M. Lange, J. C. Chottard, P. Guerin, P. Morliere, D. Brault, and M. Rougee, *J. Chem. Soc., Chem. Commun.*, 1977, 648.
- 26 J. E. Packer, R. L. Wilson, D. Bahenemann, and K. D. Asmus, *J. Chem. Soc., Perkin Trans. 2*, 1980, 296.
- 27 J. Monig, K. D. Asmus, M. Schaeffer, T. F. Slater, and R. L. Willson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1133.

Received 12th April 1988; Paper 8/01420E