Dioxygen Activation in the Photochemistry of some Oxo-metalloporphyrin Complexes

Paola Bergamini, Silvana Sostero, and Orazio Traverso
Centro di Fotochimica del C.N.R., Dipartimento di Chimica, Università di Ferrara, 44100 Ferrara, Italy
Paola Deplano*,† **and Lon J. Wilson**
Department of Chemistry, P.O. Box 1892, William Marsh Rice University, Houston, Texas 77251, U.S.A.

Ultraviolet irradiation of the peroxo-complexes [Ti(O_2)(tpp)] and [Mo(O_2)(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinate) induces elimination of O_2 and generation of the corresponding oxometalloporphyrins [TiO(tpp)] and [MoO(tpp)]. Reductive elimination of O_2 from [{Fe(tpp)}$_2$O] also occurs upon irradiation of argon-purged solutions. Studies using spin traps in e.s.r. experiments, together with quenching experiments, indicate that photolysis of the peroxo-complexes produces O_2 in the $^1\Delta_g$ excited state. For [{Fe(tpp)}$_2$O] the results differ with the conditions used. In aerated CH_2Cl_2 solutions, $^1O_2$ is produced in the quenching process of the excited states by O_2. In degassed CH_2Cl_2 solutions apparently $^1O_2$ is not formed in the photoinduced deoxygenation reaction, but rather, studies using spin traps for e.s.r. investigations have indicated the formation of the superoxide ion O_2^-. The attack on solvent by $^1O_2$ and of photogenerated O_2^-, involving radical formation, is also discussed.

The interaction of O_2 with metalloporphyrins has been the subject of continued intense study. In this connection, several dioxygen complexes of iron(II), titanium(IV), and molybdenum(VI) poprhyrins have been extensively investigated.[1–3] Transition-metal oxoporphyrin complexes are useful intermediates of dioxygen activation and play a key role in many selective oxidations of organic substrates.[4–7]

In spite of the large number of known oxygen–porphyrin complexes and their importance in catalysis, relatively few photochemical investigations have been conducted on these compounds. In 1979, Ledon *et al.*[8] reported that photolysis of bis(peroxo)molybdenum(VI) porphyrin complexes in benzene produced the related *cis*-dioxo-complex [Mo(O)$_2$(ttp)]·C_6H_6 (ttp = 5,10,15,20-tetra-*p*-tolylporphyrinate). Moreover, it was observed that oxygen-atom transfer from [Mo(O)$_2$(ttp)]·C_6H_6 occurred readily to PPh_3. In 1980, Boreman *et al.*[6] showed that photolysis of benzene solutions of the peroxotitanium(IV) porphyrins [Ti(O_2)(tpp)] and [Ti(O_2)(tmtp)] (tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate) led to the corresponding oxotitanium(IV) porphyrins. The system is particularly interesting, since the reaction occurs through photoinduced elimination of $^1O_2$, thus making the oxometalloporphyrin complexes potential candidates for particular oxidizers of various organic substrates in photo-oxidation processes. Richman and co-workers[9] have shown that u.v. irradiation of degassed benzene solutions of [{Fe(tpp)}$_2$O] with an excess of PPh_3 results in the formation of [Fe(tpp)(PPh_3)] and P(O)Ph_3, probably *via* a photodisproportionation process involving production of the ferryl complex [FeO(tpp)] as a reactive intermediate.

Because of the importance of oxometalloporphyrin complexes in photoassisted activation of dioxygen, we have undertaken an investigation of the photochemical properties of this class of compounds. The first objective is to test (*i*) the generality of the photoinduced elimination of O_2 from stable peroxo- and μ-oxo-porphyrin complexes of transition metals and (*ii*) the potential of these compounds in dioxygen activation.

The photochemistry of [Ti(O_2)(tpp)], [Mo(O_2)(tpp)], and [{Fe(tpp)}$_2$O] and an investigation designed to clarify the mechanism of the observed photoinduced dioxygen evolution are reported herein.

Experimental

Materials and Apparatus.—The compounds under consideration were prepared as previously described.[6,8,10] Purity was checked by elemental analysis and by spectroscopic (i.r. and u.v.–visible characteristic absorptions) analysis. Solvents were of spectroscopic grade and were dried with molecular sieves and/or by distillation over P_2O_5 under nitrogen. Electronic absorption spectra were measured on Cary 210 and Perkin-Elmer 323 spectrophotometers. E.s.r. studies were carried out on a Bruker ER 2000 *X*-band or a Varian E112 spectrometer. The concentration of paramagnetic species was determined by double integration of the e.s.r. signal relative to a standard diphenylpicrylhydrazyl calibrant. Infrared spectra were recorded on a Perkin-Elmer 225 i.r. spectrophotometer using KBr pellets or in 0.1-mm path length NaCl liquid i.r. cells. Mass spectra were recorded with an AEI MS 902 mass spectrometer. Proton and ^{31}P n.m.r. spectra were recorded with a Bruker n.m.r. spectrometer.

General Irradiation Procedures.—Irradiations were conducted at 404 nm using a 450-W Hanovia medium-pressure Hg lamp, equipped with Corning filters, or a Bruker 400-W Hg lamp (cut off λ = 400 nm). The compound to be studied was dissolved in benzene or CH_2Cl_2 and the solution was placed in either an evacuable quartz u.v. cell, which was degassed by freeze–pump—thaw cycles, or under argon sealed in e.s.r. tubes. The solution was then irradiated with the appropriate lamp and the electronic and e.s.r. spectra were periodically recorded. Lamp intensities were measured with ferrioxalate, K_3[Fe(C_2O_4)$_3$]·3H_2O, actinometry. The quantum yield of O_2 eliminated from a degassed CH_2Cl_2 solution of [{Fe(tpp)}$_2$O] was determined by irradiating with 404 nm and monitoring the increase in absorbance at 690 nm due to formation of [Fe(tpp)Cl].

Studies of Dioxygen Evolution.—A sample of the peroxo-complexes was placed in a quartz reaction vessel fitted with a

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† *Present address:* Istituto di Chimica Generale, Inorganica ed Analitica, Università di Cagliari, 09100 Cagliari, Italy.

stopcock, and the solvent condensed into the vessel at 77 K under vacuum. The solution was warmed to room temperature and photolysed as above, the vessel was then connected to the gas inlet system of the mass spectrometer, the solution cooled to 77 K, and the gas phase admitted to the mass spectrometer.

Photolysis of $[M(O_2)(tpp)]$ $[M = Ti$ **(1)** *or* Mo **(2)**$]$.—A degassed benzene solution (6×10^{-5} mol dm^{-3}) of **(1)** was irradiated with $\lambda = 404$ nm for 2 h. Mass spectrometric analysis of the gases above the irradiated solution demonstrated the production of O_2. Toepler pump analysis of an exhaustively photolysed benzene solution of **(1)** indicated that 0.4 mol of O_2 was released per mol of irradiated complex. Removal of solvent yielded [TiO(tpp)] **(1a)** ($\lambda_{max.} = 421$, 482, 512, 552, and 590 nm). Photolysis of a degassed benzene solution of **(2)** for 2 h ($\lambda = 404$ nm) followed by removal of solvent yielded [MoO(tpp)] **(2a)** ($\lambda_{max.} = 430$, 514, 553, and 592 nm). This method gave nearly quantitative conversion to the corresponding oxometalloporphyrins **(1a)** and **(2a)**, based on reacted dioxometal complexes **(1)** and **(2)**, although small amounts of $[\{Mo(tpp)\}_2O]$ were sometimes present.

Photolysis of $[\{Fe(tpp)\}_2O]$ **(3)**.—Sample solutions of complex **(3)** were prepared in the appropriate solvent. The sample solutions were subjected to short-term photolysis (< 5 min) for mechanistic experiments or prolonged photolysis for mass spectroscopic analysis of the gases above the irradiated solutions.

Preparation of $[Fe(py)_2(tpp)]$.—A degassed benzene–pyridine (py) (1:1 v/v) solution (50 cm^3) containing **(3)** (5×10^{-4} mol) and excess PEt_3 (5×10^{-3} mol) was irradiated ($\lambda = 404$ nm) for 2 h. After the solvent was removed *in vacuo*, n-hexane was added. The resulting heterogeneous mixture was filtered to yield $[Fe(py)_2(tpp)]$ ($\lambda_{max.} = 425$, 490, 529, and 560 nm).

E.S.R. and Quenching Experiments.—Solutions of **(3)** (5×10^{-4} mol dm^{-3}) in the appropriate solvent were introduced into a cylindrical quartz e.s.r. tube in the dark and deoxygenated by bubbling with a slow stream of argon for 30 min. They were then introduced into the e.s.r. cavity and directly photolysed with $\lambda = 404$ nm. The spin traps used were 5,5-dimethylpyrrolidine *N*-oxide (dmpo) and *N*-benzylidene-t-butylamine *N*-oxide (bbao) in 5×10^{-3} mol dm^{-3} concentration. The $^1O_2$ quenchers used were 2,2,6,6-tetramethylpiperidine (tmp), 1,4-diazabicyclo[2.2.2]octane (dabco), and 1,3-diphenylisobenzofuran (dpbf). The spin traps and quenchers were obtained from Aldrich Chemical Co.

Results and Discussion

Photolysis of degassed benzene solutions of the peroxometalloporphyrin complexes $[M(O_2)(tpp)]$ $[M = Ti^{IV}$ **(1)** or Mo^{IV} **(2)**$]$ leads to the corresponding oxometalloporphyrins [MO(tpp)] $[M = Ti^{IV}$ **(1a)** or Mo^{IV} **(2a)**$]$. Mass spectroscopic analysis of the gases above the irradiated solutions showed only the presence of O_2. The final electronic absorption spectra are identical to those of [MO(tpp)]. Removal of O_2 during irradiation does not affect the course of reaction. This suggests that O_2 is not involved in the formation of [MO(tpp)].

The mechanism shown in Scheme 1, first proposed by Marchon and co-workers[6] in the photoinduced deoxygenation of peroxotitanium(IV) porphyrins, may be suggested as the most plausible one for the photoinduced elimination of O_2 from $[M(O_2)(tpp)]$.

$$[M^{IV}(O_2)(tpp)] \xrightarrow{h\nu} [M^{II}(tpp)] + O_2$$

$$[M^{II}(tpp)] + [M^{IV}(O_2)(tpp)] \longrightarrow 2[M^{IV}O(tpp)]$$

Scheme 1.

The μ-oxo complex $[\{Fe(tpp)\}_2O]$ **(3)**, which binds oxygen in the framework of the Fe–O–Fe bond and cannot be readily deoxygenated thermally, undergoes photoinduced evolution of dioxygen as indicated by mass spectroscopic analysis of the gases above irradiated benzene solutions.

The photoelimination reactions only proceeded to a significant extent if the solutions were purged with an inert gas (argon) before and during irradiation.

A solution of **(3)** in benzene–pyridine (1:1 v/v) was irradiated in the presence of PEt_3. The compound $P(O)Et_3$ was detected in the irradiated solutions by its ^{31}P n.m.r. spectrum, which showed a singlet resonance at δ 42 p.p.m. After irradiation for 2 h the bis(pyridine) adduct $[Fe(py)_2(tpp)]$ was isolated and identified by its electronic spectrum and elemental analysis. The isolation of $[Fe(py)_2(tpp)]$ and the concomitant formation of $P(O)Et_3$ only occurred when the solutions were photolysed. Thus the overall reaction [equation (1)] represents a photoinduced oxygen-atom transfer from the μ-oxo-di-iron complex to a phosphorous centre.

$$[\{Fe(tpp)\}_2O] \xrightarrow[py,\,PEt_3]{h\nu} 2[Fe(py)_2(tpp)] + P(O)Et_3 \quad (1)$$

E.S.R. Experiments and Quenching Results.—Experiments have been performed to determine whether photolysis of the oxoporphyrin complexes **(1)**—**(3)** produces O_2 in its triplet ground state ($^3O_2$) or in the excited singlet state $^1\Delta_g$.

Complexes **(1)** and **(2)** were irradiated in degassed benzene solutions containing tmp as scavenger of $^1O_2$. The absorption spectra of the complexes did not change upon addition of tmp indicating the absence of a thermal reaction. However, irradiation of these solutions induced electronic spectral variations (two well defined isosbestic points in the region 400—600 nm) indicating conversion of **(1)** and **(2)** to **(1a)** and **(2a)** respectively. Monitoring the photolysis in the e.s.r. cavity revealed the spectrum of the tmp nitroxide radical, formed by reaction of tmp with $^1O_2$ ($g = 2.0059$, hyperfine coupling = 16.15 G). In the photolysis of **(1)** and **(2)**, the formation of $^1O_2$ was confirmed by the following results: (*i*) the addition of dabco, a non-reactive quencher for $^1O_2$, effectively suppressed formation of the nitroxide radical[11,12] [dabco with $k_q = 1.4 \times 10^7$ dm^3 mol^{-1} s^{-1} scavengers $^1O_2$ more efficiently than does tmp ($k_q = 10^5$ dm^3 mol^{-1} s^{-1})] and (*ii*) the peculiar photo-oxidation behaviour previously observed for complex **(1)**.[6] Cyclohexene was oxidized to a mixture of cyclohex-2-en-1-ol, cyclohex-2-en-1-one, and cyclohexane oxide.[6]

Apparently $^1O_2$ is not formed in the photoinduced deoxygenation of $[\{Fe(tpp)\}_2O]$ **(3)**. When this complex was photolysed in the presence of tmp no e.s.r. signal of the tmp nitroxide radical was observed. This is in agreement with the observed thermal and photochemical inertness of **(3)** as an oxidizing agent of typical organic substrates.[13]

Solvent Dependence.—In CH_2Cl_2 complexes **(1)** and **(2)** undergo photochemical reactions very similar to those observed in benzene. In degassed CH_2Cl_2 solutions, **(3)** exhibits the following features. (*i*) As irradiation ($\lambda = 404$ nm) proceeded a smooth decrease in intensity of the bands at 570 and 610 nm occurred and new bands appeared and grew at 506.8, 656, and 687.6 nm. The new bands were identical in position and shape to those displayed by [Fe(tpp)Cl] (Figure 1). (*ii*) Degassed solutions of **(3)** in CH_2Cl_2–py (1:1 v/v) were irradiated at 404 nm. Mass spectroscopic analysis of the gases above the irradiated solutions showed only the presence of O_2. Exhaustive photolysis indicated that 0.44 mol of O_2 was released per mol of complex irradiated. Evaporation of the solvent from the irradiated (2 h) solution gave $[Fe(py)_2(tpp)]$. Compound **(3)** did not show any thermal reaction with pyridine. (*iii*) Upon brief irradiation of a degassed CH_2Cl_2 solution of **(3)** in the

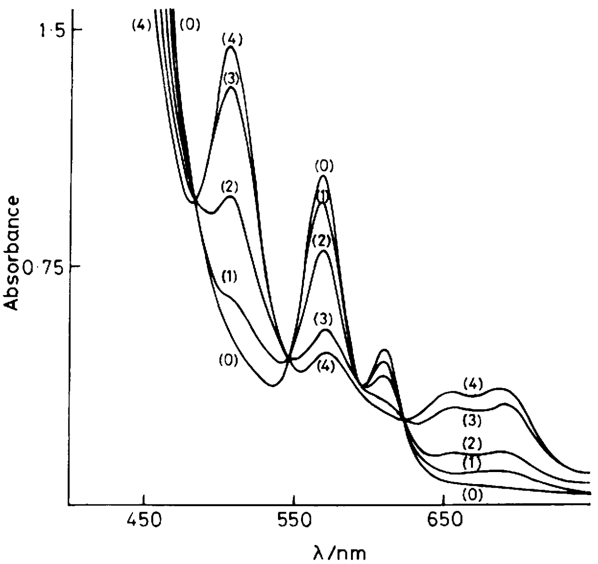

Figure 1. Photochemically induced visible spectral changes of [{Fe(tpp)}$_2$O] (6.5×10^{-6} mol dm^{-3} in CH_2Cl_2):(0), initial spectrum; (1), (2), (3), (4) after 5, 10, 20, 35 min of irradiation (λ = 404 nm)

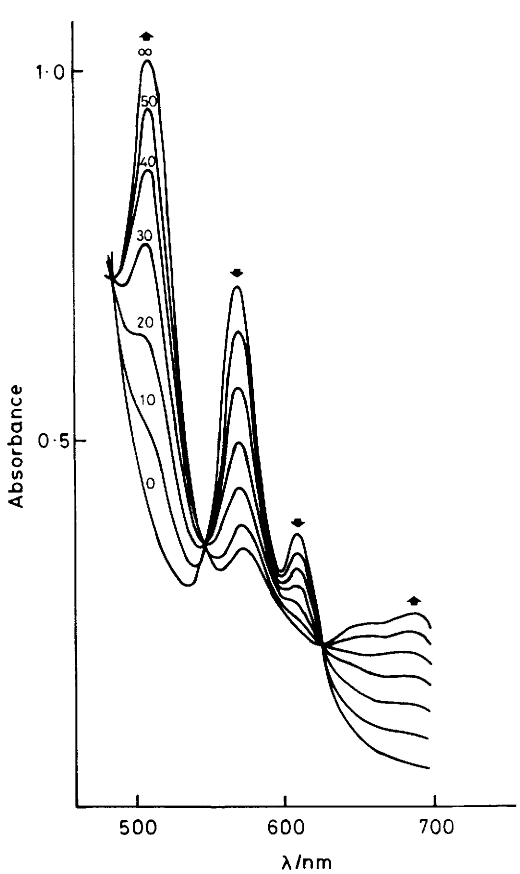

Figure 2. Spectral changes occurring during irradiation (λ = 410 nm) of a 4.5×10^{-5} mol dm^{-3} O_2-saturated solution of [{Fe(tpp)}$_2$O] in CH_2Cl_2 containing 6% CH_3OH. (0), initial spectrum; ∞, final spectrum. Values refer to the irradiation time in min

e.s.r. cavity in the presence of the spin trap dmpo, a signal with a hyperfine splitting pattern characteristic of the O_2^-–dmpo adduct was observed.[14] The characteristic 12-line spectrum of the O_2^-–dmpo adduct was unaffected by addition of the $^1O_2$ quencher dabco, indicating that the superoxide does not arise *via* $^1O_2$. Analysis of the electronic spectra of irradiated solutions of (**3**) in CH_2Cl_2 containing dmpo showed the absence of signals associated with the formation of [Fe(tpp)Cl]. (*iv*) The rate of molar production of [Fe(tpp)Cl] was twice the rate of loss of (**3**). (*v*) Photoreaction of CH_2Cl_2 solutions of (**3**) was affected by the presence of O_2 (see results reported in the next section) which functions as a quencher [15,16] of the excited triplet state of [{Fe(tpp)}$_2$O] (which may be taken as a diradical).

On the basis of these results we propose the mechanism shown in Scheme 2.

$$[\{Fe(tpp)\}_2O] \xrightarrow{h\nu} [\{Fe(tpp)\}_2O]^* \qquad (a)$$

$$[\{Fe(tpp)\}_2O]^* \longrightarrow Fe(tpp)^\bullet + FeO(tpp)^\bullet \qquad (b)$$

$$FeO(tpp)^\bullet + [\{Fe(tpp)\}_2O] \longrightarrow [\{Fe(tpp)\}_2(O_2)] + Fe(tpp)^\bullet \qquad (c)$$

$$2[\{Fe(tpp)\}_2(O_2)] \longrightarrow 2[\{Fe(tpp)\}_2O] + O_2 \qquad (d)$$

$$Fe(tpp)^\bullet + O_2 \longrightarrow [Fe(tpp)^+, O_2^{\bullet -}] \qquad (e)$$

$$[Fe(tpp)^+, O_2^{\bullet -}] + CH_2Cl_2 \longrightarrow [Fe(tpp)Cl] + O_2 + \underset{\substack{\downarrow \\ \text{products}}}{CH_2Cl^\bullet} \qquad (f)$$

Scheme 2.

The proposed mechanism for production of [Fe(tpp)Cl] includes a prior rate-limiting electron-transfer process. The formation of an ion pair in step (e) is central to Scheme 2.

While intermediates are not detected, the necessity of O_2 evolution before it reacts with Fe(tpp)$^\bullet$ is supported by isolation of the adduct [Fe(py)$_2$(tpp)] [result (*ii*)].

According to this mechanism, assuming steady-state concentrations of [{Fe(tpp)}$_2$O]*, Fe(tpp)$^\bullet$, and FeO(tpp)$^\bullet$ and negligible recombination reaction between radicals at low intensities of absorbed light, the rate of production of [Fe(tpp)Cl] is given by $d[Fe(tpp)Cl]/dt = 2\Phi I_a$ and twice the rate of loss of (**3**) as observed experimentally [result (*iv*)]. [I_a is the average number of Einsteins (an Avogadro's number of photons) absorbed by the reactant in unit volume and unit time.]

Effect of Dioxygen.—Initial studies involved photoreaction of [{Fe(tpp)}$_2$O]–CH_2Cl_2 solutions in the presence of small, but variable amounts of O_2. Under these conditions, the photoreaction proceeded in unreproducible fashion with regard to rate, although [Fe(tpp)Cl] was eventually obtained. A reasonable cause for the observed variability of reaction rate is the presence of O_2, which can function as either a quencher [15,16] of excited triplet states of oxoporphyrin complexes or as an initiator of a radical chain process involving a photogenerated superoxide ion.[15]

Thus, experiments were designed to test for these possible O_2 functions and the following results were obtained. (*i*) No photoreaction was observed in an O_2-saturated solution of (**3**) in CH_2Cl_2. (*ii*) Addition of increasing amounts of methanol to the O_2-saturated solution photoinduced loss of O_2 and formation of [Fe(tpp)Cl]. As the photolysis proceeded, the 507, 656, and 688 nm bands of [Fe(tpp)Cl] grew with the isosbestic points at 484, 545, and 623 nm, indicating a smooth conversion of [{Fe(tpp)}$_2$O] to the product [Fe(tpp)Cl] (Figure 2). The rate constant for [Fe(tpp)Cl] formation depended on the CH_3OH concentration. Quantitatively, the CH_3OH dependence is illustrated in Figure 3 by the trend in the quantum yields of

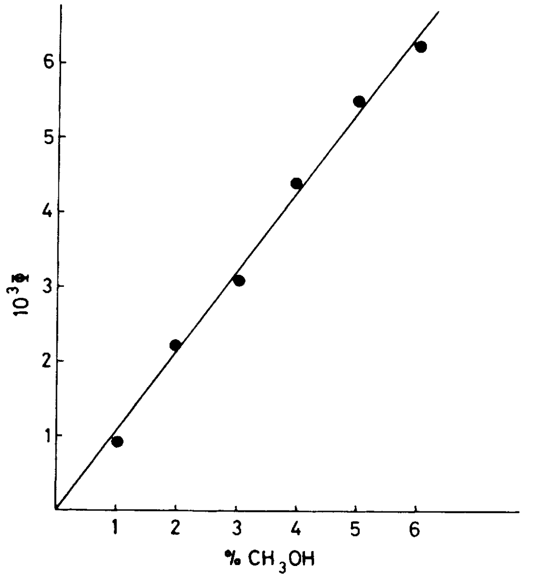

Figure 3. Quantum yields of [Fe(tpp)Cl] formation in CH_2Cl_2 *versus* CH_3OH concentration

[Fe(tpp)Cl]. The quantum yield extrapolated to $[CH_3OH] = 0$ is zero, supporting the results in (*i*) above (Figure 3). (*iii*) The addition of the $^1O_2$ quencher dabco suppressed the formation of [Fe(tpp)Cl] indicating that the photoreaction involves $^1O_2$. That $^1O_2$ arises from the quenching of the metalloporphyrin excited state by O_2, and not *via* direct $^1O_2$ photoevolution, is indicated by the absence of the tmp nitroxide e.s.r. signal in deaerated solution. (*iv*) *In situ* u.v. irradiation of a CH_2Cl_2–CH_3OH (70:30 v/v) solution of (**3**) in the presence of bbao in an e.s.r. cavity gave rise to an e.s.r. spectrum which can be interpreted[17,18] as a superimposition of e.s.r. signals coming from the addition of one hydrogen atom (1:1:1 triplet of 1:2:1 triplets; hyperfine splitting constants $A_N = 16.5$ and $A_H = 9.2$ G) and the methoxy free radical spin adduct respectively (1:1:1 triplets of doublet; hyperfine splitting constants $A_N = 14.4$ and $A_H = 2.95$ G).

These results indicate that the $^1O_2$ produced by quenching of the porphyrin excited state interacts with methanol[19] leading ultimately to the methoxy radicals *via* hydrogen-atom abstraction [equations (2) and (3)].

$$[\{Fe(tpp)\}_2O]^* + O_2 \longrightarrow [\{Fe(tpp)\}_2O] + {}^1O_2 \qquad (2)$$

$$CH_3OH + {}^1O_2 \longrightarrow H^\bullet + CH_3O^\bullet + {}^3O_2 \qquad (3)$$

Reaction of $H^\bullet$ radicals with CH_2Cl_2 will produce HCl [equation (4)] which further reacts with $[\{Fe(tpp)\}_2O]$ to yield [Fe(tpp)Cl] [equation (5)].

$$H^\bullet + CH_2Cl_2 \longrightarrow HCl + {}^\bullet CH_2Cl \qquad (4)$$

$$[\{Fe(tpp)\}_2O] + 2HCl \longrightarrow 2[Fe(tpp)Cl] + H_2O \qquad (5)$$

$${}^\bullet CH_2Cl \longrightarrow \text{products} \qquad (6)$$

Table. Quantum yields of [Fe(tpp)Cl]

Compound	Solvent	Conditions[a]	Φ[b] [Fe(tpp)Cl]
(**3**)[c]	CH_2Cl_2	Degassed	$2.5 \times 10^{\ 3}$
(**3**)	CH_2Cl_2	Atmospheric O_2	0
(**3**)	CH_2Cl_2 + 6% CH_3OH	Atmospheric O_2	$6.5 \times 10^{\ 3}$
(**3**) + dpbf ($10^{\ 5}$ mol dm$^{\ 3}$)	CH_2Cl_2 + 6% CH_3OH	Atmospheric O_2	$4.2 \times 10^{\ 3}$
(**3**) + dpbf ($2 \times 10^{\ 5}$ mol dm$^{\ 3}$)	CH_2Cl_2 + 6% CH_3OH	Atmospheric O_2	$0.8 \times 10^{\ 3}$
(**3**) + dpbf ($4 \times 10^{\ 5}$ mol dm$^{\ 3}$)	CH_2Cl_2 + 6% CH_3OH	Atmospheric O_2	0

[a] Irradiation at 404 nm. [b] Experimental uncertainties are $\pm 0.1 \times 10^{\ 3}$. [c] Concentration of (**3**) is 4.5×10^{-5} mol dm^{-3} in all solutions.

The formation of the $H^\bullet$ radicals in equation (3) is central to the formation of [Fe(tpp)Cl] as indicated by (*a*) the increase in Φ with increasing CH_3OH concentration and (*b*) the decrease in Φ with increase in concentration of the $^1O_2$ acceptor[20] dpbf (Table).

In summary, the results presented herein indicate that photolysis of peroxometalloporphyrin complexes gives rise to evolution of $^1O_2$. For $[\{Fe(tpp)\}_2O]$, it appears that both superoxide O_2^- as well as $^1O_2$ can be obtained in processes of net electron transfer and excitation energy transfer, respectively.

Acknowledgements

The authors wish to thank the Italian Consiglio Nazionale delle Ricerche (C.N.R.), and the Robert A. Welch Foundation for support (to L. J. W.) and the U.S. National Institute of Health for partial support of this work.

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Received 29th July 1985; Paper 5/1300