Photolytic Cleavage of the Iron–carboxyalkyl Ligand Bond in some Iron(III) Tetra(*N*-methylpyridyl)porphyrins: Evidence for Reversible Photodecomposition and Fragmentation from EPR and UV Spectroscopy

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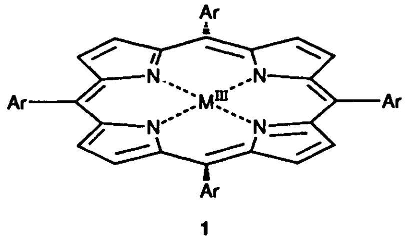
EPR spectroscopy, in conjunction with spin-trapping and spin-scavenging techniques, has been employed together with UV–VIS spectroscopy to establish that iron(III) tetra(*N*-methylpyridyl)porphyrins ligated to carboxylate anions undergo ready photodissociation with light in the visible region of the spectrum. Studies conducted as a function of pH and for a variety of carboxylic acids provide evidence for initial photodecomposition to give Fe^{II} and acyloxyl radicals, for which recombination competes with decarboxylation to give alkyl radicals. The roles of oxygen and the structure of the initial complex have been explored.

The incorporation of iron and certain other transition-metal ions into porphyrins and other related macrocyclic ligands leads to the formation of molecules with a variety of remarkable chemical and biological properties involving ligand binding (*e.g.*, haemoglobin),[1] redox reactions (*e.g.*, peroxidases and cytochrome P-450 monooxygenases)[2] and photochemical decomposition (*e.g.*, the use of porphyrin derivatives in phototherapy).[3]

Our particular interests have largely concerned the reaction of iron porphyrins with hydroperoxides (*e.g.*, to distinguish free radical and ionic processes)[4] and their activation of oxygen or other oxidants (as models for enzyme reactions),[5] as well as in the development of catalytic systems for oxidation involving the Fe^{III}–Fe^{IV} couple[6] (in contrast with the Fe^{II}–H_2O_2 reaction in which Fe^{II} and Fe^{III} are believed to be involved).

The study to be described here involves an investigation of the stability and photochemical decomposition of a variety of iron porphyrin complexes $PFe^{III}X$, (**1**) [Fe^{III}T4NMPyP and Fe^{III}T2NMPyP] in which a carboxylate ligand is bound to the iron centre ($X = O_2CR$). On the basis of the finding that irradiation in the visible region can result in the cleavage of an iron–ligand bond in some related porphyrins with a chlorine, hydroxy or alkoxy ligand (**2**) [*cf.* reaction (1)],[7] we proposed that the corresponding carboxyl derivatives should undergo ready photodecomposition and set out to explore the occurrence and mechanism of such reactions, utilizing the techniques of EPR-spin trapping and spin-scavenging, in conjunction with UV–VIS spectroscopy.



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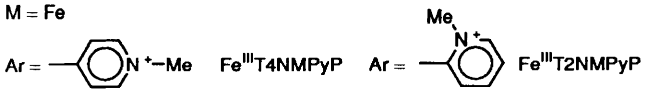


$$PFe^{III}\text{–}X \xrightarrow{h\nu} PFe^{II} + X^{\bullet} \qquad (1)$$

2 $X = Cl, OH, OR$

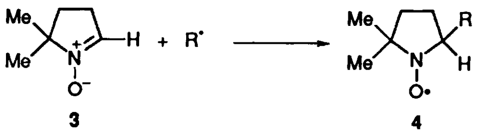
Results and Discussion

Experiments were carried out using the iron(III) porphyrins (**1**) with water-soluble carboxylic acid ligands [$X = O_2CR$; $R = (CH_3)_3C$, $(CH_3)_2CH$, CH_3CH_2, CH_3, $CH_2{=}CHCH_2$; $CH_2{=}C(CH_3)$, $PhCH_2$, Ph] which are expected to ligate axially to the iron porphyrin; structures of the complexes (as a function of pH) were examined by UV–VIS spectroscopic studies. EPR and UV–VIS methods were utilized to study the intermediates obtained on exposure of the complexes to visible radiation (λ > 390 nm) supplied by a 300 W xenon arc lamp.

(*a*) *EPR Experiments: Spin-trapping.*—Initial experiments were carried out with the *in-situ* photolysis of aqueous solutions of Fe^{III}T4NMPyP and pivalic acid in the presence of the spin trap DMPO **3** (5,5-dimethyl-1-pyrroline *N*-oxide). A strong signal could be detected: optimum concentrations were found to be [Fe^{III}T4NMPyP], 1×10^{-4} mol dm^{-3}, [Me_3CCO_2H], 0.1 mol dm^{-3}, [DMPO], 5×10^{-2} mol dm^{-3}. Under these conditions the six-line EPR spectrum, with $g = 2.0060$ a(N) 1.625, a(H) 2.320 mT, was observed to build up quickly and decay (Fig. 1 shows the spectrum recorded over a period of *ca.* 4 min after onset of photolysis). This spectrum is attributed to a relatively long-lived nitroxide spin-adduct (**4**; $R = Bu^t$) of the trap and a carbon-centred radical:[8] it is believed to characterize formation of the *tert*-butyl radical formed as in reactions (2), (3) and (4).

$$PFe^{III}\text{–}O_2CR \overset{h\nu}{\rightleftharpoons} PFe^{II} + RCO_2^{\bullet} \qquad (2)$$

$$RCO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2 \qquad (3)$$



(4)

3 **4**

(*i*) In a series of related experiments we discovered that the rate of build-up and decay of this signal depended upon the length of time for which the acid was allowed to equilibrate with the porphyrin: the longer the equilibration time the faster the signal built up and then decayed.

(*ii*) When the solution was deoxygenated with nitrogen before photolysis a more intense signal was obtained, although a steady decay was still observed (see also Fig. 1). Closer

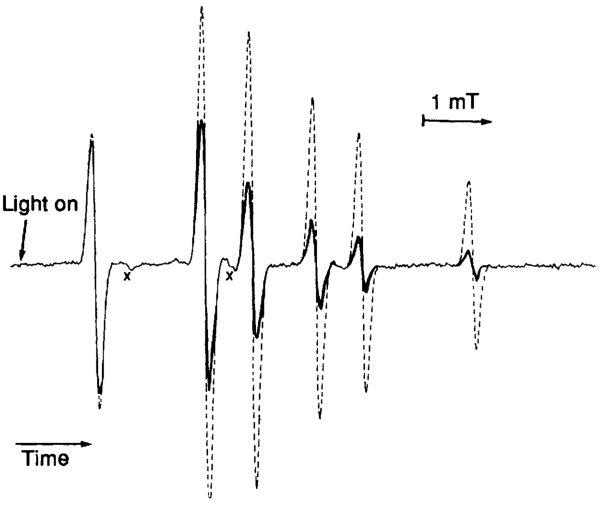


Fig. 1 EPR spectrum of the spin-adduct **4**, R = Bu^t, recorded during the photolysis ($\lambda > 390$ nm) of Fe^{III}T4NMPyP and pivalic acid in aqueous solution in the presence of the spin-trap DMPO (**3**) (concentrations given in the text): ——, in the presence of dioxygen; – – – –, in the absence of dioxygen. Signals marked × all believed to be due to traces of alkoxyl adducts (see the text).

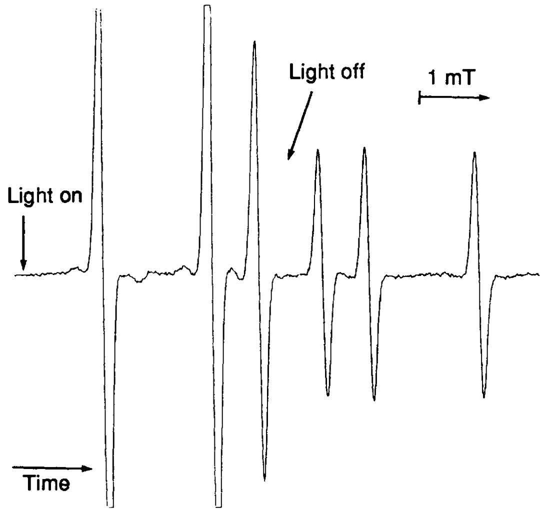


Fig. 2 EPR spectrum of the spin-adduct **4**, R = Bu^t, recorded during the photolysis ($\lambda > 390$ nm) of Fe^{III}T4NMPyP and pivalic acid in aqueous solution in the presence of the spin trap DMPO (**3**), showing the effect of cessation of photolysis (concentrations given in the text)

Table 1 EPR parameters of alkyl radical-adducts to DMPO, obtained from the photolysis of carboxylate derivatives of iron(III) tetra(*N*-methylpyridyl)porphyrins in aqueous solution[a]

	Hyperfine splittings/mT[b]	
Acid	a_N	a_H
Pivalic	1.625	2.320
Isobutyric	1.625	2.425
Propionic	1.615	2.310
Acetic	1.615	2.295
Phenylacetic	1.600	2.240

[a] *g*-Value 2.0060 ± 0.0001. [b] ±0.005.

inspection of the EPR spectra obtained after a short photolysis time (*ca.* 30 s) in experiments in the presence of dioxygen shows the presence of relatively low concentrations of spin-adducts from an oxygen-centred radical [with splittings *a*(N) 1.465 mT, *a*(H) 1.635 mT]. These observations suggest that when dioxygen is present, first-formed alkyl radicals may be scavenged by dioxygen, to give peroxyl radicals which can subsequently form the corresponding alkoxyl radicals which are then trapped.[4,9]

(*iii*) In experiments in which the irradiation was interrupted the intensity of the alkyl-radical's adduct-signal remained constant (see, *e.g.*, Fig. 2).

(*iv*) When experiments were carried out as a function of pH it was found that similar strong signals were observed between pH *ca.* 3 and pH 6.5. No signals were observed at pH 1.5 or at pH 9.

(*v*) Successful experiments were similarly carried out for other carboxylic acids; details of the EPR parameters of the appropriate spin-adducts are collected in Table 1. For a series of simple alkanoic acids, the relative intensities of the EPR adducts **4** were in the following order:

$$R = Bu^t > Pr^i > Et > Me$$

Other types of acid were also studied. Whereas no signals at all could be obtained from benzoic, vinyl acetic and methacrylic acids, signals (presumably from the benzyl radical adduct) were observed with phenylacetic acid.

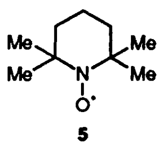
(*vi*) In parallel experiments with the porphyrin Fe^{III}T2-NMPyP we found that the EPR signals of the adducts were essentially identical with those observed with the 4-*N*-methylpyridine analogue, that they showed the same order of signal intensity as a function of structure and had similar decay characteristics, but were considerably stronger.

Our EPR spin-trapping results establish that when a carboxylic acid is ligated to certain iron(III) tetra(*N*-methylpyridyl)porphyrins the iron–oxygen bond can be homolytically cleaved by visible irradiation to produce an alkyl radical (*presumably* formed by rapid decarboxylation of a first-formed acyloxyl radical) and, we suggest, the corresponding Fe^{II} porphyrin (see Scheme 2 and later). The radical can react with dioxygen or, in our experiments, become trapped to give aminoxyl adducts which are relatively stable in the *absence* of further photolysis. These aminoxyls do not therefore readily disproportionate or react with Fe^{III} porphyrins, but they do disappear when the light is incident.

(*b*) *Spin-scavenging Experiments*.—To account for the disappearance of the aminoxyl spin-adducts in *photolytic* experiments we propose that the continual generation of radicals eventually leads to the consumption of DMPO and reduction in the adduct concentration *via* the occurrence of reaction (5) (which can be referred to as spin-scavenging).[10]

$$R_2NO^\bullet + R'^\bullet \longrightarrow R_2NOR' \qquad (5)$$

In order to obtain further evidence for this reaction we carried out EPR experiments as described above but with the addition of the stable aminoxyls TEMPO (**5**) or TEMPOL (**6**) in place of DMPO (at various concentrations in the range 10^{-3}–10^{-4} mol dm^{-3}). When photolysis commenced, signals from the aminoxyl were quickly removed. These aminoxyls did not react with the acids themselves, with the porphyrin complexes or with the oxoiron(IV) porphyrin (prepared as described later). We therefore believe that the occurrence of reaction (5) is responsible, in a significant part at least, for the removal of aminoxyl signals.



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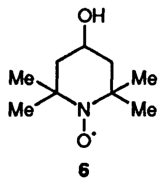

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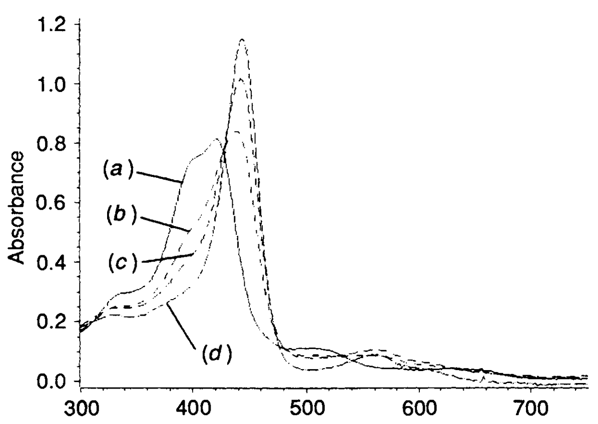


Fig. 3 UV–VIS spectrum (*a*) of Fe^{III}T4NMPyP in the presence of pivalic acid in aqueous solution. Spectra (*b*), (*c*) and (*d*) were recorded after a total photolysis time of 15, 30 and 60 s, respectively ($\lambda > 390$ nm; [Fe^{III}T4NMPyP] 1×10^{-5} mol dm^{-3}; [pivalic acid] 0.1 mol dm^{-3}).

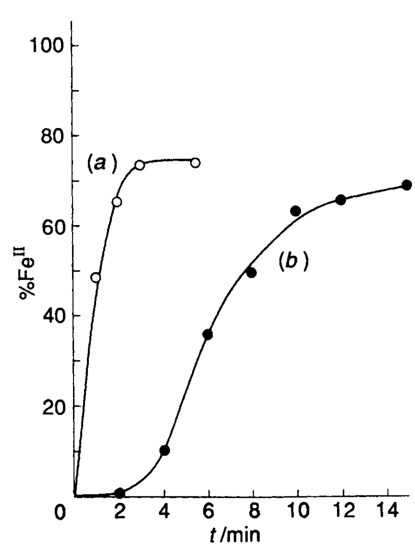


Fig. 4 The build-up of Fe^{II} porphyrin, as a function of total irradiation time, observed in the photolysis ($\lambda > 390$ nm) of (*a*) Fe^{III}T2NMPyP and (*b*) Fe^{III}T4NMPyP, in the presence of propionic acid in aqueous solution. [Fe^{III}T2NMPyP] 1×10^{-5} mol dm^{-3}; [Fe^{III}T4NMPyP] 1×10^{-5} mol dm^{-3}, [propionic acid] 0.1 mol dm^{-3}. For the method of calculation of % Fe^{II} porphyrin, see the Experimental section.

(*c*) *UV–VIS Spectroscopic Studies of the Iron*(III) *Porphyrins.*—Parallel experiments to those described above were conducted in which changes induced by photolysis were followed by UV–VIS spectroscopy.

The UV–VIS spectrum of a solution of Fe^{III}T4NMPyP (1×10^{-5} mol dm^{-3}) in aqueous pivalic acid (0.1 mol dm^{-3} at pH 1.5) contains a peak with λ_{max} at 404 nm (the Soret band) and a shoulder at *ca.* 420 nm. As the pH is raised, the intensity of the peak at 404 nm decreases and that of the shoulder increases, until above pH 2.5 the Soret band's λ_{max} lies at 422 nm with a shoulder at *ca.* 400 nm (see Fig. 3): there are two small bands at 510 and 630 nm. The shoulder decreases in intensity at higher pH values and at pH 6 and above a single peak ($\lambda_{max} = 426$ nm) is observed, with small bands at *ca.* 600 and 634 nm.

In experiments at pH *ca.* 3 in the absence of dioxygen we found that irradiation leads to a shift of the Soret peak to 440 nm with an increase in the intensity, together with the formation of a less intense broad band at 570 nm (see Fig. 3). We believe that this is characteristic of the corresponding Fe^{II} porphyrin.[11] On aeration of the solution the original spectrum was regenerated. This reaction was observed to occur in the pH range 3–6, but not at more acid (1.5) or alkaline (9–11) conditions.

The rate of build up of Fe^{II} porphyrin from the Fe^{III} porphyrin was also followed for the same series of carboxylate derivatives of Fe^{III}T4NMPyP as before, in a series of experiments at pH *ca.* 3. The results can be summarized as follows.

(*i*) For the simple alkanoic acids described earlier, the rapid build-up of Fe^{II} could be followed and observed to be quickly complete (within less than 3 min for pivalic and isobutyric acids).

(*ii*) Conversion into Fe^{II}T4NMPyP was observed for all the carboxylate derivatives studied except for those of acetic and benzoic acids. Thus, the reaction appears to proceed with vinylacetic and methacrylic acid derivatives, although no alkyl radical-adducts were observed in the corresponding EPR experiments.

(*iii*) The rate of production of iron(II) porphyrin was enhanced when acid complexes of Fe^{III}T2NMPyP were used (see Fig. 4). The larger EPR signals and the faster reaction for experiments with Fe^{III}T2NMPyP may be due to the fact that the Fe^{II} is less easily oxidized back to Fe^{III} than it is for the corresponding 4-*N*-methylpyridylporphyrin,[12] so that if the Fe–O bond is initially cleaved, recombination to regenerate the starting complex is less likely (see later). A steric effect, due to the *N*-methyl group being in the *ortho* position, may also disfavour the back reaction.

(*d*) *UV–VIS Spin-scavenging Experiments.*—To examine the effect of added aminoxyl on the appearance of the Fe^{II} porphyrin, the photolyses were repeated in the presence of up to a tenfold excess of **6** over Fe^{III}T4NMPyP. This resulted in an induction period during which very little Fe^{II} porphyrin could be observed (presumably until all the aminoxyl had been removed), after which the formation of Fe^{II} porphyrin proceeded as before (see Fig. 5). The removal of a tenfold excess indicates that cycling of the porphyrin must be occurring, and therefore various experiments were carried out to determine which porphyrin species was reactive towards the aminoxyl.

(*i*) We considered the possibility that the oxoiron(IV) porphyrin [PFe^{IV}=O] may be present due to reaction of the iron(II) porphyrin with any dioxygen in the system.[13] However, experiments involving addition of the aminoxyl **6** to PFe^{IV}=O [prepared by addition of *tert*-butyl hydroperoxide to Fe^{III}-T2NMPyP)],[6] established that this species does not react with the aminoxyl [there was no change in the UV–VIS spectrum of the oxoiron(IV) porphyrin].

(*ii*) The addition of an equivalent amount of the aminoxyl **6** to a sample of Fe^{II} porphyrin generated photolytically resulted in the regeneration of the Fe^{III} porphyrin (see Fig. 6). The sharp isosbestic points in the spectra show that the photoreduction and subsequent oxidation leads to no detectable loss of the iron porphyrin.

These results strongly suggest that the removal of the aminoxyl signal observed in EPR spin-trapping experiments with DMPO is due to both spin-scavenging of the aminoxyl adducts by radicals and by the iron(II) porphyrin.

Conclusions

The results provide evidence that irradiation of carboxylate derivatives of iron(III) porphyrins with visible light in aqueous solution leads to the production of acyloxyl radicals, and hence alkyl radicals (detected by EPR spin-trapping) and iron(II) porphyrins, as shown by spectrophotometry. The major factors which affect the reaction appear to be the pH, the structure of the carboxylic acid, and the nature of the porphyrin.

In aqueous solution, the porphyrin species present depends on the pH.[11,14] In our experiments where a carboxylic acid is present, we believe, on the basis of changes in the UV–VIS spectra, that at low pH (< 2) a protonated ligand is present (see

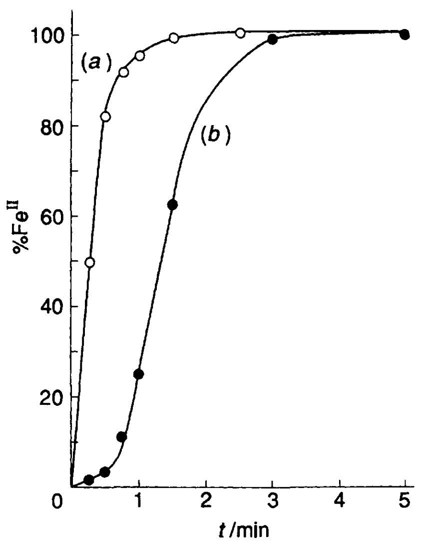


Fig. 5 The build up of Fe^{II} porphyrin, as a function of total irradiation time, observed in the photolysis (λ > 390 nm) of Fe^{III}T2NMPyP and pivalic acid in aqueous solution (*a*), and also in the presence of a tenfold excess of the aminoxyl TEMPOL (**6**) (*b*). ([Fe^{III}T2NMPyP] 1 × 10^{-5} mol dm^{-3}; [pivalic acid] 0.1 mol dm^{-3}; [TEMPOL] 1 × 10^{-4} mol dm^{-3}). For the method of calculation of % Fe^{II}T2NMPyP, see the Experimental section.

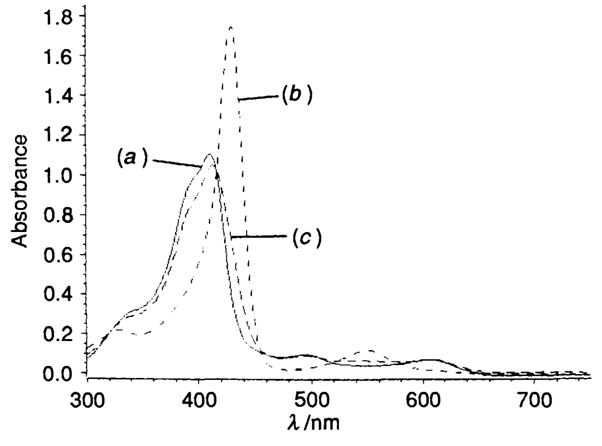
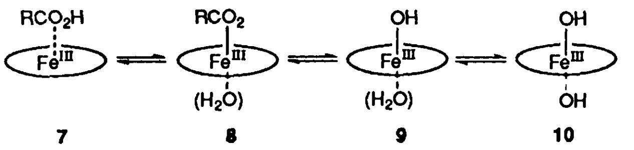


Fig. 6 (*a*) UV–VIS spectrum of Fe^{III}T2NMPyP in the presence of pivalic acid in aqueous solution. (*b*) UV–VIS spectrum of Fe^{III}-T2NMPyP and pivalic acid after 3 min photolysis (λ > 390 nm). (*c*) UV–VIS spectrum after addition of TEMPOL (**6**) to the photolysed solution. For (*a*)–(*c*), [Fe^{III}T2NMPyP] 1 × 10^{-5} mol dm^{-3}; [pivalic acid], 0.1 mol dm^{-3}; [TEMPOL] 1 × 10^{-5} mol dm^{-3}.

7). Between pH 2 and 6 deprotonation of this ligand occurs to give the carboxylate derivative of the porphyrin (complex **8**). At higher pH (> 6) it appears that replacement of the carboxy ligand by hydroxy group occurs (complex **9**). The presence of a second water as a sixth ligand in these species is debatable;[14] however, this should not essentially affect the mechanism of the photoreduction. At very high pH (> 11) two hydroxy ligands are believed to be present (complex **10**).[11,14] These changes in the porphyrin species would explain the observed pH-dependence of the reaction if it is assumed that it is complex **8** that undergoes photolysis.

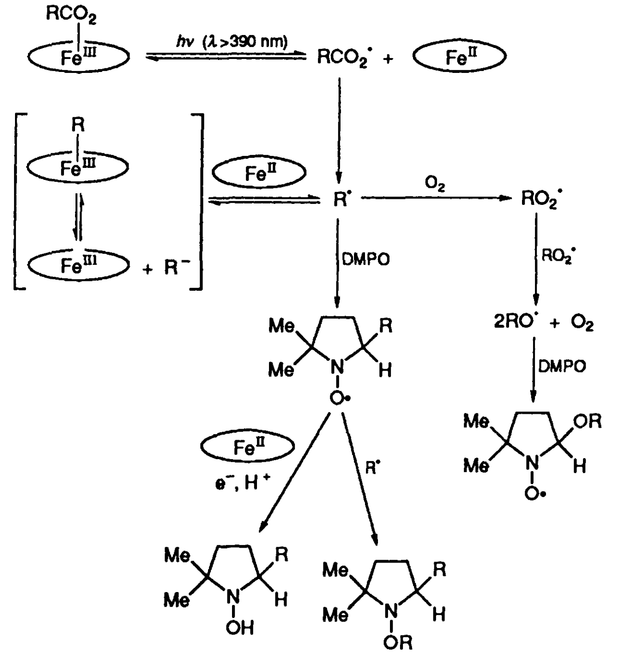
Irradiation with visible light results in the reversible photodecomposition of the ligated porphyrin complex **8**; homolytic cleavage of the iron–oxygen bond evidently produces an iron(II) porphyrin and the corresponding acyloxyl radical. We believe that our results indicate that subsequent recombination of these two species can be avoided if rapid fragmentation of the acyloxyl radical, to give an alkyl radical and carbon dioxide, occurs (see Scheme 2). Our results (and in particular the relative facility of radical generation from a variety of acids) and our interpretations are entirely consistent with the finding that the rate of decarboxylation of acyloxyl radicals increases with the bulk and/or stability of the appropriate alkyl radical (*e.g.*, MeCO$_2^\bullet$ < 1.3 × 10^9 s^{-1}, EtCO$_2^\bullet$, 2 × 10^9 s^{-1}, PhCH$_2$CO$_2^\bullet$, 5 × 10^9 s^{-1}, Bu^{t}CO$_2^\bullet$, 1.1 × 10^{10} s^{-1}).[15]



Scheme 1

We believe that the ease of decarboxylation is also affected by using a porphyrin for which the Fe^{II} state is stabilized, *i.e.*, which is less easily oxidized back to Fe^{III}, hence making the recombination of the acyloxyl radical with the iron(II) porphyrin less favourable [as with Fe^{III}T2NMPyP].

It is known (*e.g.*, from previous EPR experiments) that alkyl radicals rapidly scavenge any dioxygen present to produce peroxyl radicals which react further to give alkoxyl radicals (evidence for which has been obtained) and various degradation products (which have yet to be determined). In the absence of dioxygen the fate of the alkyl radicals is unknown although it is believed that an iron(III) porphyrin and a carbanion, R$^-$ might be formed (see Scheme 2).[16]



Scheme 2

Experimental

All the photolyses were carried out using an ILC 302 UV Xenon high-intensity light source (300 W; λ > 390 nm) directed by a liquid light guide as supplied by Laser Lines Ltd., Banbury, Oxon.

In-situ photolyses were carried out at room temperature using an aqueous sample cell and EPR spectra were recorded with a Bruker ESP 300 spectrometer equipped with 100 kHz modulation, and a Bruker ER 035H gaussmeter for field calibration. Hyperfine splittings were determined directly from the field scan. In experiments carried out in the absence of dioxygen the solutions were deoxygenated prior to photolysis using dioxygen-free nitrogen. UV–VIS spectra were recorded on a Hewlett Packard 8452A diode array spectrometer. Photolyses were carried out in a 1 cm pathlength quartz cuvette which had been stoppered with a Subaseal prior to analysis. Deoxygenation was carried out by bubbling dioxygen-free nitrogen through the reaction solution for 20 min prior to irradiation.

The pH of the iron(III) porphyrin solutions was adjusted by addition of small amounts of NaOH (aq.) or HCl (aq.) as required.

The addition of TEMPOL to $Fe^{II}T2NMPyP$, generated photolytically, was carried out by injecting 5 mm^3 of a deoxygenated solution containing one equivalent of the aminoxyl, into the sealed reaction cuvette. The procedure ensured that both the introduction of dioxygen, and dilution effects were kept to a minimum.

The percentages of iron(II) and iron(III) porphyrin in the photolysed reaction mixtures were calculated using the Hewlett Packard Quant II (multicomponent) analysis program. This involved fitting the UV–VIS spectrum of the reaction mixture using standard spectra for the iron(II) and iron(III) porphyrins of known concentrations. The iron(III) porphyrin standard employed was the spectrum of the reaction mixture prior to photolysis, and the iron(II) porphyrin standard was that of an iron(III) porphyrin and pivalic acid mixture which had been subjected to 5 min photolysis [*i.e.*, 100% conversion into Fe^{II} porphyrin].

The preparations of the iron(III) tetra(*N*-methylpyridyl)-porphyrins have been reported previously.[5b] All the other chemicals were obtained from Aldrich or Sigma, and were used as supplied, with the exception of the spin trap DMPO which was purified before use by treatment with activated charcoal.

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