Reactions of carboxyl radicals generated by the photocleavage of complexes of iron(III) tetra(2-*N*-methylpyridyl)porphyrin with unsaturated and aromatic carboxylic acids in aqueous solution

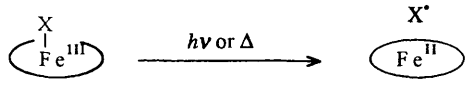
Bruce C. Gilbert,*,[a] John R. Lindsay Smith,*,[a] Philip MacFaul[a] and Philip Taylor[b]

[a] *Department of Chemistry, University of York, York, UK Y01 5DD*
[b] *Decorative Research and Development Department, ICI Paints plc, Wexham Road, Slough, Berkshire, UK SL2 5DS*

Anaerobic aqueous solutions of the complexes of iron(III) tetra(2-*N*-methylpyridyl)porphyrin with carboxylate anions, benzoate, phthalate and 2- and 4-methylbenzoate, have been photolysed with visible light (λ > 390 nm) to give solvent-caged iron(II) porphyrin and aroyloxyl radicals. Evidence is presented that the rate of build-up of the iron(II) porphyrin in the reaction is dependent on the partitioning of the caged aroyloxyl radicals between product formation (decarboxylation and hydrogen abstraction from the methyl group) and regeneration of the starting complex. The fastest reaction occurs with 2-methylbenzoate for which intramolecular hydrogen abstraction converts the initially formed 2-methylbenzoyloxyl into 2-carboxybenzyl radicals. The photolysis of the iron(III) porphyrin complexes of acrylic, methacrylic and dimethylacrylic acids shows analogous behaviour, with the extra possibility that the carboxyl radicals may also add to the alkenic group of the substrate molecules in the solvent cage. The rapid decarboxylation of phenylacetoxyl radicals results in the fast photoreduction of the iron(III) porphyrin by phenylacetic acid to iron(II) porphyrin and to benzyl radicals. Under aerobic conditions the reoxidation of the iron(II) to iron(III) allows the system to become photocatalytic in iron porphyrin. The stability of the catalyst to oxidative destruction is moderate but can be dramatically improved by anchoring the charged iron porphyrin by electrostatic interaction to a silica support.

Iron porphyrins catalyse a wide range of biological and chemical oxidations either as mono-oxygen-transfer or electron-transfer agents.[1] Much current interest lies in those reactions which utilise clean oxidants, such as dioxygen or hydrogen peroxide, to bring about selective oxidation. In this respect the recent reports of iron(III) porphyrin-catalysed autoxidation and photooxidation of hydrocarbons are of particular importance.[2]

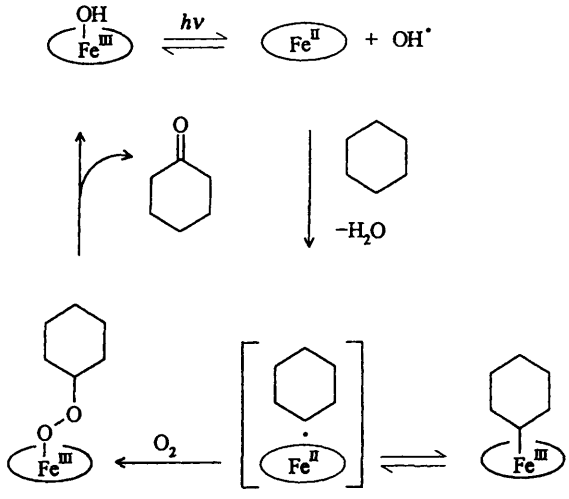
Iron(III) porphyrins can undergo both thermal[2h,3] and photochemical[4] reduction by one-electron transfer from an axial ligand to the metal atom [reaction (1)]. In hydrocarbon



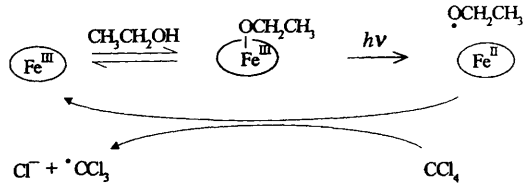
(1)

solvents, the rate of photoreduction of iron(III) porphyrin depends on the C–H bond dissociation energy of the solvent, suggesting that hydrogen abstraction by the ligand radical (probably within a solvent cage) is required for the reaction to proceed. In the absence of an easily abstractable hydrogen, the initially formed photoproducts recombine to regenerate the original iron(III) complex.[4c] This reaction has been developed into a photooxidation of cyclohexane by dioxygen in which iron(III) tetramesitylporphyrin with a hydroxide ligand is the catalyst (Scheme 1).[2g] The success of this system relies on the rapid reoxidation of the iron(II) by dioxygen. In another related system, alcohols have been photooxidised *via* their alkoxide complexes with iron(III) porphyrins using tetrachloromethane as the oxidant to recycle the iron(II) back to iron(III) (Scheme 2).[2f,5]

In a recent paper we described the photocleavage of the complexes of alkyl carboxylic acids with iron(III) tetra(*N*-methylpyridyl)porphyrins in aqueous solution.[6] Using spin-trapping and spin-scavenging EPR techniques and UV–VIS



Scheme 1



$$CH_3CH_2O^{\bullet} + CH_3CH_2OH \longrightarrow CH_3CH_2OH + CH_3\dot{C}HOH \quad (2)$$

$$CH_3CH_2O^{\bullet} + CCl_4 \longrightarrow CH_3CHO + Cl^- + {}^{\bullet}CCl_3 \quad (3)$$

$$CH_3\dot{C}HOH + CCl_4 \longrightarrow CH_3CHO + Cl^- + {}^{\bullet}CCl_3 \quad (4)$$

$$CH_3CH_2OH + {}^{\bullet}CCl_3 \longrightarrow CH_3\dot{C}HOH + HCCl_3 \quad (5)$$

Scheme 2

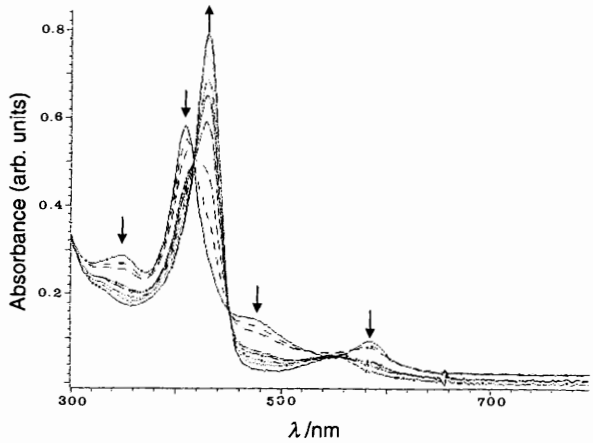


Fig. 1 UV–VIS spectral changes observed on irradiation of Fe^{III}T2MPyP and 2-methylbenzoic acid. Spectra were recorded at 5 min intervals for 35 min: 1×10^{-5} mol dm^{-3} Fe^{III}T2MPyP and 0.1 mol dm^{-3} 2-methylbenzoic acid, pH 5.5.

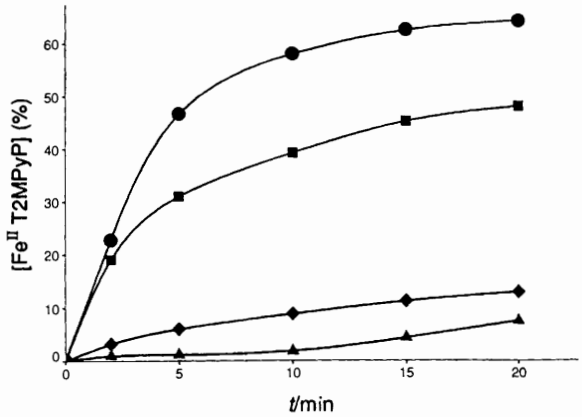
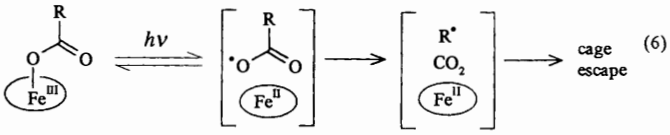
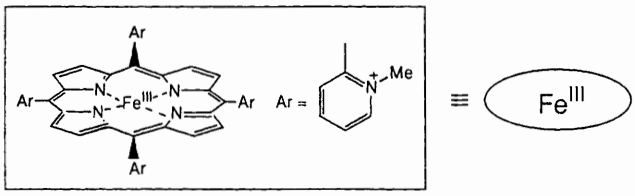


Fig. 2 Build-up of iron(II) porphyrin, as a function of total irradiation time, observed in the anaerobic photolysis of Fe^{III}T2MPyP with selected aromatic carboxylic acids in aqueous solution: (▲), phthalic acid, pH 6.5; (◆), benzoic acid, pH 4.8; (■), 4-methylbenzoic acid, pH 6.2; (●), 2-methylbenzoic acid, pH 5.5. 1×10^{-5} mol dm^{-3} Fe^{III}T2MPyP and 0.1 mol dm^{-3} [carboxylic acid].

spectroscopy, we demonstrated that the initial photoreduction generates an acyloxyl radical and iron(II) porphyrin within a solvent cage. Further reaction occurs within the cage and involves competition between recombination to regenerate the initial complex and, following decarboxylation, the formation of an alkyl radical which with the iron(II) porphyrin escapes into the solution [reaction (6)]. This mechanism accounts for



the radicals detected and explains the relative rates of photoreduction of the carboxylate complexes largely in terms of the relative rates of decarboxylation of the acyloxyl radicals. In this paper we have extended our investigations to include the photoreactions of iron(III) tetra(2-*N*-methylpyridyl)porphyrin **1** (Fe^{III}T2MPyP)† complexes of aromatic and alkenic carboxylic



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acids and, by making use of the rapid oxidation of iron(II) to iron(III) porphyrins by dioxygen, we have developed a photocatalytic oxidative decarboxylation process. Supporting the catalyst in the latter system leads to a dramatic improvement in catalyst stability.

Results

Benzoic and substituted benzoic acids

Photolysis (25 min, $\lambda > 390$ nm) of aqueous solutions (pH 5.5) of Fe^{III}T2MPyP (1×10^{-5} mol dm^{-3}) and 2-methylbenzoic acid (0.1 mol dm^{-3}), in the absence of dioxygen, leads to the disappearance of the absorption of the Soret band (λ_{max} 414 nm) in the UV–VIS spectrum of the iron(III) porphyrin and the appearance of a new peak at 428 nm (Fig. 1). These changes, which are also accompanied by the replacement of the $\alpha\beta$ bands at 486 and 598 nm by a single absorption at 550 nm, arise from the conversion of the iron(III) into the iron(II) porphyrin. Very comparable spectral changes were observed with aliphatic carboxylic acids in our previous study.[6] When the photolysis was repeated using 4-methylbenzoic acid the photoreduction was slower and those of benzoic and phthalic acid were significantly slower still (Fig. 2).

In parallel experiments, the photolyses were carried out in the presence of the spin trap DMPO and monitored by EPR spectroscopy. This led to the detection of weak signals from nitroxide radicals assigned to carbon-centred radical adducts of the trap [reaction (7)] with the hyperfine splittings shown in

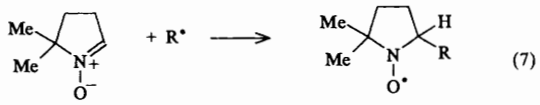
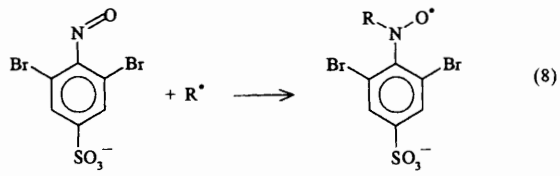


Table 1; the most intense signal was obtained from 2-methylbenzoic acid (Fig. 3). In all the reactions a weak signal from the hydroxyl radical adduct was also detected. The intensity of the latter did not alter with photolysis. The spin trap DBNBS was also employed in an attempt to identify the carbon-centred radicals formed in the photolyses [reaction (8)].



The two methylbenzoic acids gave weak signals from adducts of primary carbon radicals (*cf.* benzyl radicals, see below) (Table 1), but no signals from radical adducts derived from benzoic or phthalic acid were detected. With all the aromatic acids an EPR signal consisting of a triplet of triplets (a_N = 1.246 mT, a_{2H} = 0.055 mT), attributed to the $SO_3^{\bullet -}$ adduct of DBNBS,[7] was obtained.

Alkenic carboxylic acids

The photolysis of an anaerobic aqueous solution of Fe^{III}T2MPyP in the presence of methacrylic acid was shown by UV–VIS spectroscopy to lead to complete reduction to the iron(II) complex within 15 min. The equivalent reactions of acrylic, crotonic, (*Z*)-2,3-dimethylacrylic and 3,3-dimethyl-

† Abbreviations: T2MPyP, 5,10,15,20-tetra(2-*N*-methylpyridyl)porphyrin ligand; T4MPyP, 5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrin; DMPO, 5,5-dimethylpyrroline *N*-oxide; DBNBS, 3,5-dibromo-4-nitrosobenzenesulfonic acid. Si-Fe^{III}T2MPyP, Fe^{III}T2MPyP supported on silica.

Table 1 Assignments and hyperfine splittings of the spin-trap radical-adducts formed in the photoreactions of $Fe^{III}T2MPyP$ with aromatic and unsaturated carboxylic acids in anaerobic aqueous solution: 1×10^{-4} mol dm^{-3} $Fe^{III}T2MPyP$, 0.1 mol dm^{-3} carboxylic acid and (5–10) $\times 10^{-2}$ mol dm^{-3} spin trap; pH 6.0 for benzoic acids and 3.0 for phenylacetic and acrylic acids

Carboxylic acid	Spin trap	Assignment of trapped radical[a]	Hyperfine splittings[b] a_N/mT	a_H/mT
Benzoic	DMPO[c]	R•	1.589	2.301
Phthalic	DMPO[c]	R•	1.603	2.424
4-Methylbenzoic	DMPO[c]	R•	1.602	2.438
	DBNBS[d]	4-(•CH_2)$C_6H_4CO_2H$	1.436	1.128
2-Methylbenzoic	DMPO[c]	R•	1.589	2.328
	DBNBS[d]	2-(•CH_2)$C_6H_4CO_2H$	1.424	0.986
Phenylacetic	DMPO[e]	R•	1.600	2.240
	DBNBS[f]	$PhCH_2$•	1.438	1.178
				0.068[g]
Acrylic	DMPO[c]	R•	1.589	2.274
Methacrylic	DMPO[c]	R•	1.589	2.329
Crotonic	DMPO[c]	R•	1.589	2.301
(*Z*)-2,3-Dimethylacrylic	DMPO[c]	R•	1.589	2.542
3,3-Dimethylacrylic	DMPO[c]	R•	1.589	2.301
	DBNBS[d]	CH_3>C=C<H, •CH_2, CO_2H	1.397	1.041

[a] R• is a carbon-centred radical [reactions (7) and (8)]. It is believed that the radical trapped with DBNBS is the same as that trapped with DMPO. [b] ± 0.005 mT; *g*-values 2.0060 ± 0.0001. [c] Photolysis for up to 10 min. [d] Photolysis for 15 min. [e] Photolysis for 30 s. [f] Photolysis for 2 min. [g] Splittings from *meta*-hydrogens on spin trap.

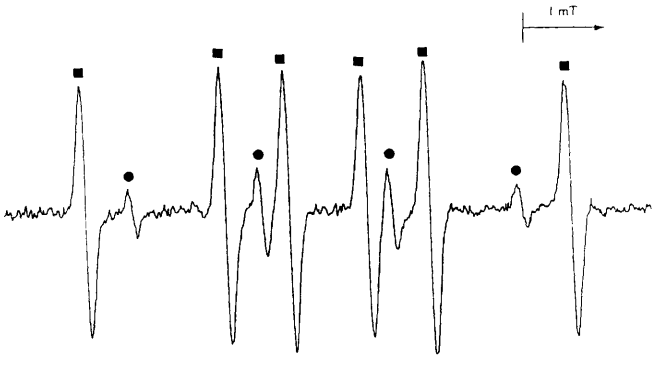


Fig. 3 EPR spectrum of the carbon-centred radical (■) and the hydroxyl radical (●) DMPO spin-adducts; recorded after 4 min anaerobic irradiation of $Fe^{III}T2MPyP$ and 2-methylbenzoic acid in aqueous solution: 1×10^{-4} mol dm^{-3} $Fe^{III}T2MPyP$, 0.1 mol dm^{-3} 2-methylbenzoic acid and 8×10^{-2} mol dm^{-3} DMPO, pH 6

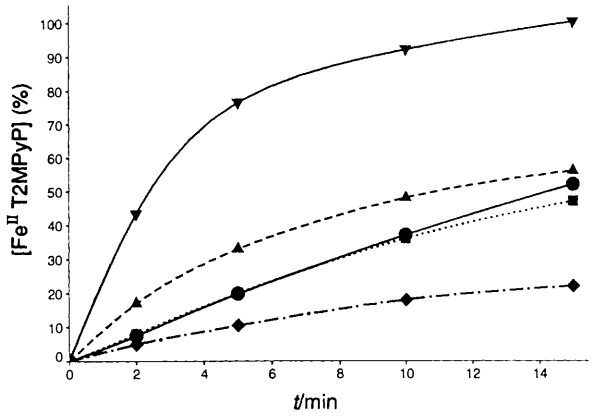
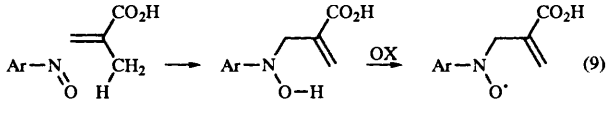


Fig. 4 Build-up of iron(II) porphyrin, as a function of total irradiation time, observed in the anaerobic photolysis of $Fe^{III}T2MPyP$ with selected alkenic carboxylic acids in aqueous solution: (▼) methacrylic, (▲) crotonic, (●) (*Z*)-2,3-dimethylacrylic, (■) 3,3-dimethylacrylic and (◆) acrylic acid; 1×10^{-5} mol dm^{-3} $Fe^{III}T2MPyP$ and 0.1 mol dm^{-3} carboxylic acid, pH 2.9

acrylic acids were investigated and each gave the iron(II) porphyrin, although the rate of reduction was markedly dependent on the structure of the carboxylic acid (Fig. 4). These differences in rates were shown not to be due to the presence of the commercial inhibitor in the reaction mixtures since removal of the inhibitor before photolysis had no effect on the rate of photoreduction.

Photolysis of dioxygen-free aqueous solutions of the iron(III) porphyrin and the vinyl carboxylic acids in the presence of DMPO gave weak signals from carbon-centred radical adducts that built up in intensity during 5 min continual irradiation. The use of DBNBS to identify the carbon-centred radicals formed in the photoreactions was severely limited by the thermal side reactions of some of the carboxylic acids with the spin trap. These gave rise to intense EPR signals from aminoxyl radicals formed from the ene reaction between the spin trap and the unsaturated acid followed by oxidation of the hydroxylamine product by the nitroso compound [reaction (9)].[8] 3,3-Dimethylacrylic acid which does not react directly with DBNBS was used to study the photoreduction of $Fe^{III}T2MPyP$; this gave the EPR spectrum of an adduct of a radical of the type RCH_2•. The hyperfine splittings and suggested assignments of all the carboxylic acid derived radical-adducts of DMPO and of DBNBS are shown in Table 1.



The presence of methanol in the photoreaction of methacrylic acid had a significant influence on the rate of iron(II) formation. Increasing the alcohol concentration up to 1×10^{-3} mol dm^{-3} led to an increase in rate whereas higher concentrations resulted in a slower reaction. The maximum initial rate (in the presence of 1×10^{-3} mol dm^{-3} methanol), was approximately twice that in the absence of alcohol. Ethanol gave an identical rate enhancement to methanol, propan-2-ol was less effective and 2-methylpropan-2-ol showed a slight inhibition. An EPR study of the photoreaction in the presence of methanol using the spin trap DMPO gave two carbon-centred radical adducts; the first (a_N 1.534 mT, a_H 2.247 mT), formed within a few seconds of irradiation, was replaced by the second (a_N 1.589 mT, a_H 2.329 mT) after photolysis for approximately a further minute.

Table 2 Catalyst turnovers observed during the photoreaction of phenylacetic acid with $Fe^{III}T2MPyP$, $Fe^{III}T4MPyP$ and Si–$Fe^{III}T2MPyP$: 1×10^{-5} mol dm^{-3} catalyst, 0.1 mol dm^{-3} phenylacetic acid and solvent 3 cm^3

			Yield/catalyst turnovers[a]			
Catalyst	Solvent	Time/min	$PhCH_2OH$	PhCHO	$PhCH_2CH_2Ph$	Total
$Fe^{III}T2MPyP$	H_2O	60[b]	15	133	2	152
$Fe^{III}T4MPyP$	H_2O	30[b]	8	42	—	50
$Fe^{III}T2MPyP$	CH_3CN	60[b]	—	387	—	387
Si–$Fe^{III}T2MPyP$[c]	CH_3CN	720[d]	27	932	—	959

[a] Moles of product/moles of catalyst. [b] Catalyst > 90% photobleached. [c] 5 mg of Si–$Fe^{III}T2MPyP$ equivalent to 1.6×10^{-5} mol dm^{-3} of homogeneous catalyst. [d] UV–VIS spectroscopy, although not quantitative, indicates negligible photobleaching has occurred.

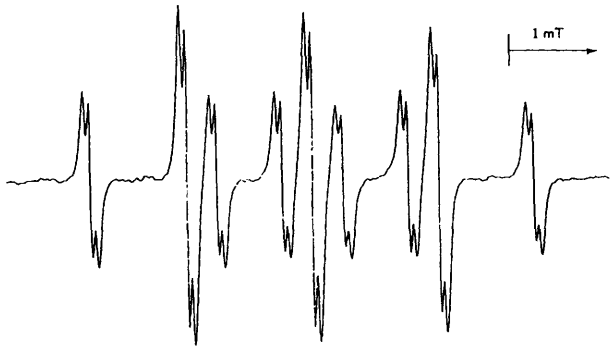


Fig. 5 EPR spectrum of the benzyl radical spin-adduct with DBNBS, observed after 2 min anaerobic irradiation of $Fe^{III}T2MPyP$ and phenylacetic acid in acetonitrile: 1×10^{-4} mol dm^{-3} $Fe^{III}T2MPyP$, 0.1 mol dm^{-3} phenylacetic acid, and a saturated solution of DBNBS

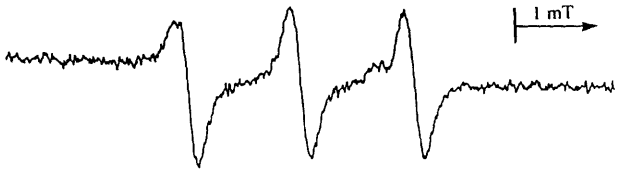


Fig. 6 EPR spectrum of the *tert*-butyl radical-adduct of DBNBS, recorded after 150 s anaerobic photoreaction of Si–$Fe^{III}T2MPyP$ with 2,2-dimethylpropanoic acid in acetonitrile solution: 3.3 mg Si–$Fe^{III}T2MPyP$, 0.1 mol dm^{-3} 2,2-dimethylpropanoic acid, saturated solution of DBNBS and 2 cm^{-3} acetonitrile

Phenylacetic acid

Photolysis of $Fe^{II}T2MPyP$ in the presence of phenylacetic acid in anaerobic aqueous or acetonitrile solution brings about the rapid formation or $Fe^{II}T2MPyP$. In contrast, under aerobic conditions photolysis leads to the complete oxidative bleaching of the metalloporphyrin after 1 h irradiation. EPR studies of the anaerobic reactions with the spin traps DMPO and DBNBS gave signals assigned to adducts of primary carbon-centred radicals ($PhCH_2^{\bullet}$) (*e.g.* Fig. 5 and Table 1). GC analysis of the aerobic reaction in aqueous solution revealed that the major product formed was benzaldehyde together with small amounts of benzyl alcohol and bibenzyl (Table 2). No toluene was detected. The total number of catalyst turnovers achieved by the iron(III) porphyrin was calculated to be 152, where turnover is defined as the number of moles of products per mole of catalyst. When the reaction was carried out in acetonitrile, instead of water, benzaldehyde was the sole product and the total number of turnovers was 387 (Table 2). UV–VIS analysis revealed that in the latter reaction the $Fe^{III}T2MPyP$ was > 90% bleached. For comparison the experiment in aqueous solution was repeated with $Fe^{III}T4MPyP$; in this case the catalyst was totally bleached in less than 30 min and the total number of turnovers was 50 (Table 2).

The quantum yield of the photo-oxidation of phenylacetic acid catalysed by $Fe^{III}T2MPyP$ in aqueous solution was determined to be 1.1×10^{-2}.[9]

Photoreactions with $Fe^{III}T2MPyP$ supported on silica

The UV–VIS spectrum of a suspension of the supported catalyst (Si–$Fe^{III}T2MPyP$) (loading 10.4 mg per g of silica)[10] in acetonitrile gave a Soret peak with λ_{max} 414 nm which after irradiation for 15 min in the presence of 2,2-dimethylpropanoic or phenylacetic acid, under anaerobic conditions, shifted to 434 nm. The original spectrum of Si–$Fe^{III}T2MPyP$ was subsequently regenerated by allowing air into the system. Irradation of the supported catalyst in the absence of the carboxylic acids led to no changes in the UV–VIS spectrum. Reduction of Si–$Fe^{III}T2MPyP$ with hydrazine gave Si–$Fe^{II}T2MPyP$ which had a UV–VIS spectrum that was almost identical to that obtained from the anaerobic photolysis experiment.

An EPR study of the photoreaction of 2,2-dimethylpropanoic and phenylacetic acid with Si–$Fe^{III}T2MPyP$ and the spin trap DBNBS in anaerobic acetonitrile gave signals which were assigned to the *tert*-butyl and the benzyl radical adducts, respectively (*e.g.* Fig. 6). In air the 2,2-dimethylpropanoic acid reaction with either $Fe^{III}T2MPyP$ or Si–$Fe^{III}T2MPyP$ gave no EPR signals due to the methyl radical adduct of DBNBS.

Product analysis of the aerobic reaction of phenylacetic acid showed that benzaldehyde was the dominant product (> 97%) with a small amount of benzyl alcohol; neither bibenzyl nor toluene was detected (Table 2). The photooxidation with the supported catalyst was slower than with the homogeneous analogue, however, most significantly there was no evidence of catalyst bleaching even after nearly 1000 turnovers. The photo-oxidation with Si–$Fe^{III}T2MPyP$ was also investigated in a flow system in which the supported catalyst was irradiated in a flow cell through which the acetonitrile solution of phenylacetic acid was passed. After five cycles of the reaction solution and a total of 54 min irradiation there had been 50 turnovers and there was no detectable catalyst bleaching.

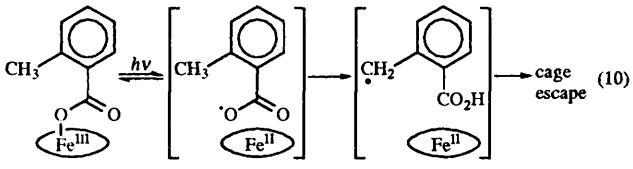
Discussion

(*a*) Benzoic acids

In the anaerobic photolysis of simple alkylcarboxylate complexes of iron(III) porphyrins, the rate of formation of iron(II) porphyrin depends on the relative rates of the competitive reactions of the initially formed acyloxyl radicals within the solvent cage.[6] Thus the faster the rate of decarboxylation the better the forward reaction is able to compete with recombination to regenerate the starting complex. For this reason it was expected that the low rate of decarboxylation of the aroyloxyl radicals (*ca.* $2–6 \times 10^6$ s^{-1}) relative to those of alkylcarboxyl radicals (*ca.* $10^9–10^{10}$ s^{-1})[11] would lead to a very slow photoreduction of the iron(III) porphyrin by benzoic and substituted benzoic acids. The photoreduction with benzoic acid is indeed slow although the fact that it is observed at all suggests that for benzoic acid either the photocleavage may be more efficient or the back reaction less favourable. This aspect of the reaction is currently under investigation.

Based on the rates of decarboxylation, the photoreduction with 4-methylbenzoic acid should be slower than that of benzoic acid,[11b] on the contrary, the reactions with 4-methylbenzoic and, more particularly, 2-methylbenzoic acid are relatively fast. We believe that the differences in the rates of the reactions of benzoic and methylbenzoic acids can be accounted for by considering the possible reactions of the aroyloxyl radicals within the solvent cage (see below).

EPR spin-trapping experiments with DMPO demonstrate that carbon-centred and not carboxyl radical adducts are obtained with all the benzoic acids. For benzoic and phthalic acids, we believe that these arise from the phenyl and 2-carboxyphenyl radicals, respectively, derived from the decarboxylation of the aroyloxyl radicals: thus the hyperfine splittings of the radical adduct from phthalic acid (Table 1) are very similar to those assigned to the 2-carboxyphenyl adduct from the transition metal-catalysed decomposition of magnesium monoperoxyphthalate (a_N 1.575 mT, a_H 2.400 mT).[12] By contrast 2- and 4-methylbenzoic acids give 2- and 4-carboxybenzyl radicals (identified as DBNBS adducts), suggesting that both the initially formed aroyloxyl radicals must undergo rapid hydrogen abstraction. For 2-methylbenzoic acid, this will evidently occur by an intramolecular reaction for which the rate constant is 1.7×10^7 s^{-1} at 25 °C [reaction (10)].[13] However,



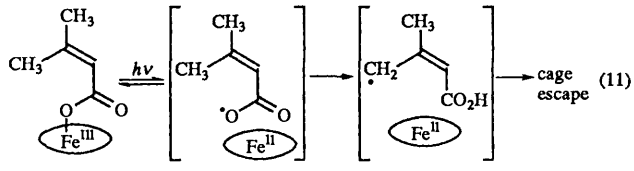
for the 4-isomer such a process is not possible and we propose that the carboxybenzyl radical arises from an intermolecular reaction with the substrate, present as carboxylate counterions to the cationic *N*-methylpyridyl groups on the porphyrin ring within the solvent cage (Scheme 3). Allowing for the atropisomeric mixture of Fe^{III}T2MPyP, it is likely that on average two carboxylate anions will be present on the side of the porphyrin ring on which the aroyloxyl radical is formed. Furthermore, the counterions should be well placed for intermolecular hydrogen abstraction since the positive charges on the pyridyl rings in the 2-positions are close to the reaction centre.

The relative rates of photoreduction of Fe^{III}T2MPyP by the benzoic acids can also be accounted for by the reactions described above. Assuming that the rates of formation and recombination of the caged aroyloxyl radical and iron(II) porphyrin from the initial photolysis are the same for each of the benzoic acids, the observed rates of photoreduction will depend on the rates of the forward reactions of the carboxyl radicals within the solvent cage. With benzoic and phthalic acids this is the relatively slow decarboxylation (2×10^6 s^{-1} for benzoic acid),[11a] whereas for the methylbenzoic acids the faster hydrogen abstraction occurs (1.7×10^7 s^{-1} for 2-methylbenzoic acid), with the intramolecular reaction of the 2-methylbenzoic acid being significantly faster than the intermolecular process of the 4-isomer.

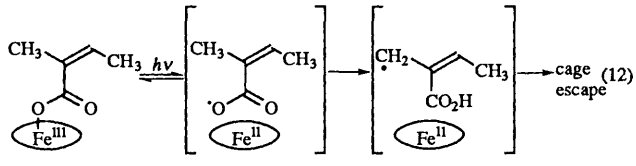
(*b*) Acrylic acids

As we observed with the benzoic acids, the photolysis of the Fe^{III}T2MPyP complexes of the acrylic acids in the presence of DMPO gives adducts of carbon-centred radicals with no evidence for carboxyl radical adducts. However, the identification of these radicals, using DBNBS, was severely limited by the ene reaction between the acrylic acid and the trap.[8] Only with 3,3-dimethylacrylic acid was it possible to obtain an EPR spectrum from a DBNBS adduct from the photolysis. Consequently the mechanism of the reactions of the acrylic acids are less well characterised than those of the benzoic acids.

By analogy with the methylbenzoic and benzoic acids, the photoreduction of the iron(III) porphyrin by each of the methyl- and dimethyl-acrylic acids was found, as expected, to be faster than the parent compound. For 3,3-dimethylacrylic acid the initially formed carboxyl radical rapidly undergoes an intramolecular hydrogen abstraction, in preference to decarboxylation, to generate the primary radical trapped by DBNBS [reaction (11)]. The photoreduction of Fe^{III}T2MPyP with



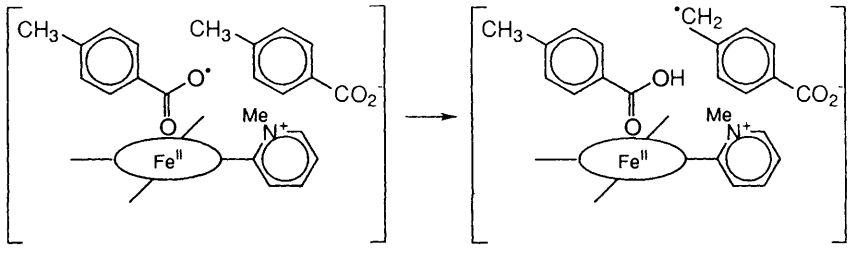
isomeric (*Z*)-2,3-dimethylacrylic acid occurs at a very similar rate and we conclude that here also the rapid 1,5-hydrogen shift takes place, although the alternative 1,4-hydrogen shift is another possibility [reaction (12)].



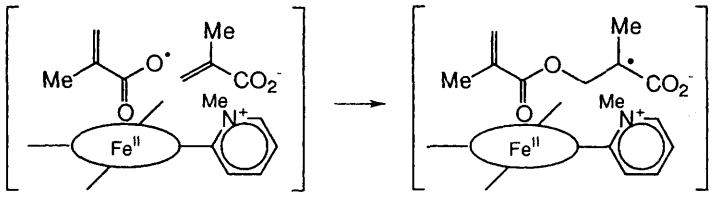
Methacrylic acid is surprisingly a more effective photoreductant than 2,3-dimethylacrylic acid although only an intramolecular 1,4-hydrogen shift is possible. This we interpret as arising from the participation of an extra reaction of the caged carboxyl radical of the former substrate that competes with regeneration of the iron(III) porphyrin–carboxylate complex. We suggest this may be addition of the carboxyl radical to methacrylate counterions of the porphyrin within the solvent cage [Scheme 4; *cf.* the intermolecular reaction of 4-methylbenzoic acid (Scheme 3)].

(*c*) Acrylic acids in the presence of alcohols

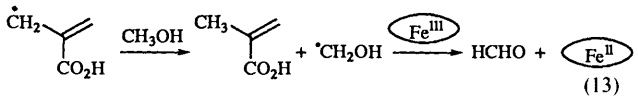
The photoreactions of methacrylic acid in the presence of methanol suggest that the carbon radicals, which escape from the solvent cage, may abstract a hydrogen atom from the alcohol to produce a hydroxymethyl radical which subsequently rapidly reduces an iron(III) to an iron(II) porphyrin [reaction (13)].[14] Such a mechanism leads to a predicted doubling of the



Scheme 3



Scheme 4



(13)

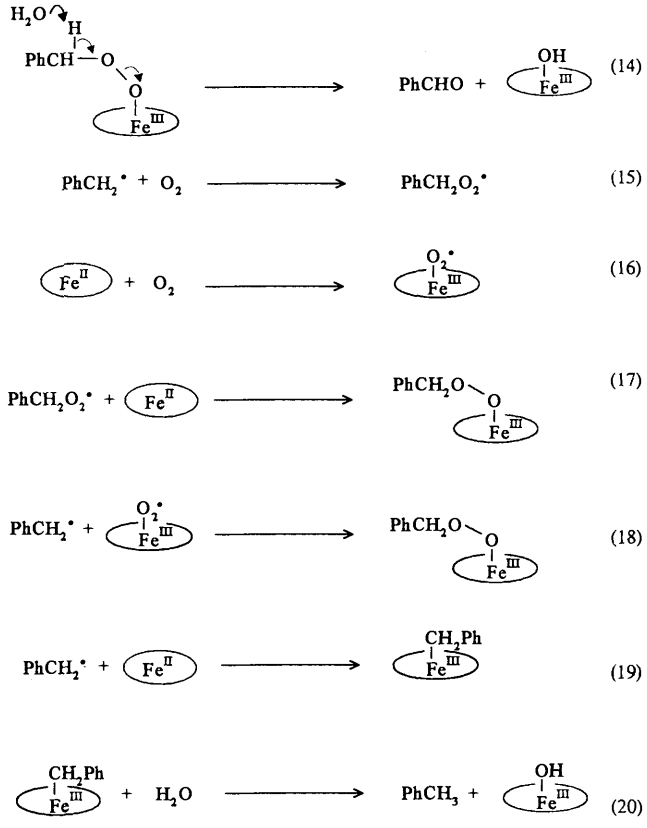
rate of formation of Fe^{II}TMPyP if all the carbon radicals are trapped by methanol. This maximum effect was observed when the methanol concentration was increased to 1×10^{-3} mol dm^{-3}. Above this concentration the rate of reduction is lower; we interpret this as arising from the alcohol competing with the carboxylate as a ligand for the iron(III) porphyrin. Consistent with this, both ethanol and propan-2-ol, which have readily abstractable α-hydrogens, behave similarly to methanol whereas 2-methylpropan-2-ol, with no such hydrogens, does not show a rate enhancement. To prove the identity of the radical trapped first by DMPO from the photoreaction in the presence of methanol, we also examined the photodecarboxylation of the hydroxyacetate–iron(III) porphyrin complex. This system gave an adduct, presumably from the hydroxymethyl radical, with very similar hyperfine splittings (a_N = 1.561 mT, a_H = 2.247 mT) to the initial radical formed in the photoreaction of methacrylate with Fe^{III}T2MPyP and methanol. The adduct that develops later in the latter reaction is identical with that obtained in the absence of methanol.

(*d*) Phenylacetic acid

The photoreduction of Fe^{III}T2MPyP by phenylacetic acid was selected to examine the possibility of generating a photocatalytic system using the fast *in situ* oxidation of the iron(II) to iron(III) porphyrin with air. The anaerobic photolysis is rapid, comparable in rate to that of isobutyric acid (in agreement with the similar rates of decarboxylation of the carboxyl radicals of the two acids, 5×10^9 and 6.5×10^9 s^{-1}, respectively[15]), and considerably faster than those of benzoic or the methylbenzoic acids. Furthermore the expected products from the benzyl radical are easily separated and analysed by GC.

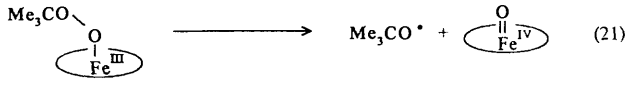
Benzyl radicals, generated from the decarboxylation of phenylacetoxyl radicals, and Fe^{II}T2MPyP are efficiently trapped and oxidised by dioxygen (Scheme 1). We propose that the major product, benzaldehyde, is formed from benzylperoxyiron(III) porphyrin by heterolytic elimination [reaction (14)].[16] This is analogous to the pathway suggested by Balch and co-workers for the conversion of cyclohexylperoxyiron(III) tetramesitylporphyrin into cyclohexanone.[16] The former arises from the very rapid reaction of dioxygen with the benzyl radicals ($k = 2 \times 10^9$ dm^3 mol^{-1} s^{-1})[17] [reaction (15)] or with iron(II) porphyrin [reaction (16)] followed by reactions (17) or (18), respectively.[18] The formation of a benzyliron porphyrin intermediate in these reactions appears to be ruled out [reaction (19)]. In aqueous solution such a species would be expected to be hydrolytically cleaved to the hydroxyiron(III) porphyrin and toluene [reaction (20)][19] and the latter was not detected in the reaction products. The minor oxidation product, benzyl alcohol, is most likely formed by the self-reaction of benzylperoxyl radicals[20] and the trace of bibenzyl from the dimerisation of benzyl radicals.

The quantum yield obtained for the Fe^{III}T2MPyP-photocatalysed oxidative decarboxylation of phenylacetic acid (1.1×10^{-2}) is small although it is significantly larger than the values reported for the photoreaction of the chloride complex



of Fe^{III}TPP in benzene or cyclohexane, $< 1 \times 10^{-4}$ and 5.1×10^{-4}, respectively.[2g,21] The low value in the present study could arise from a number of causes, but must in part be due to the rapid recombination of the initial photoproducts within the solvent cage.

Changing the reaction solvent from water to acetonitrile has no effect on the radical trapped by DBNBS from the photoreaction of phenylacetic acid. Interestingly, however, the same change with the reaction of 2,2-dimethylpropanoic acid, under aerobic conditions, gave the EPR spectrum of only the *tert*-butyl radical adduct of DBNBS whereas in aqueous solution the methyl radical adduct was also detected.[6] We interpret this solvent effect to the faster rate of fragmentation of the *tert*-butoxyl radicals, from the homolytic breakdown of *tert*-butylperoxyiron(III) porphyrin complex [reaction (21)],[22]



in aqueous solution ($k = 1.4 \times 10^6$ s^{-1})[23] than in acetonitrile (estimated[24] $k = 1 \times 10^5$ s^{-1}).

(*e*) Photocatalysis with Fe^{III}TMPyP supported on silica

We have explored the catalytic potential of the iron(III) porphyrin anchored, by electrostatic interactions, to silica (Si–Fe^{III}T2MPyP) by examining the photolysis of a stirred suspension of Si–Fe^{III}T2MPyP in the presence of phenylacetic and of 2,2-dimethylpropanoic acid. Under anaerobic conditions

this behaves in an analogous manner to Fe^{III}T2MPyP in homogeneous solution. Thus the formation of benzyl and *tert*-butyl radicals and Si–Fe^{II}T2MPyP were detected using the EPR spin-trap DBNBS and UV–VIS spectroscopy, respectively. Furthermore air reoxidises the supported iron(II) porphyrin. However, it takes longer for the heterogeneous reaction to go to completion, presumably because the suspended catalyst is less effective at absorbing the irradiation. A brief study with a flow system shows that the photosystem might be adapted for use in a continuous photooxidation in which the carboxylic acid solution is passed over the illuminated heterogeneous catalyst.

Aerobic photolyses are catalytic in Si–Fe^{III}T2MPyP and, with phenylacetic acid, give benzaldehyde and benzyl alcohol. Despite the difference in rates between the heterogeneous and homogeneous systems, the former has two important advantages, (*i*) the ease of catalyst recovery and re-use and (*ii*) the very significant increase in stability of the catalyst towards oxidative bleaching (*ca.* 1000 turnovers without significant loss of catalyst). The homogeneous iron(III) porphyrin catalyst has only a moderate stability towards oxidative self-destruction, being virtually completely bleached after 152 turnovers in aqueous solution or *ca.* 400 in acetonitrile. The mechanism of the catalyst destruction is unclear although it probably involves oxyl-radical attack on the porphyrin ring. That site-isolation of the Fe^{III}T2MPyP on silica may prevent the oxidative bleaching suggests that it is intermolecular reactions, probably of intermediates formed in the regeneration of iron(III) from iron(II), which lead to porphyrin destruction. It is well documented, with metalloporphyrin model systems for cytochrome P450, that minimising porphyrin–porphyrin interactions either by the use of bulky meso substituents[25] or by site-isolation[26] increases the stability of the catalyst towards self-oxidation.

Experimental

Materials

All materials were commercially available unless otherwise stated. Iron(III) 5,10,15,20-tetra(2-*N*-methylpyridyl)porphyrin was prepared as described previously[27] and supported on Kieselgel 60 by stirring a suspension of the support (1 g) in a methanol solution of the porphyrin (10 mg) for 24 h. The filtered solid was washed with dichloromethane and acetonitrile and dried at 100 °C/0.1 mmHg. The loading was obtained by quantifying (UV–VIS analysis) the non-loaded metalloporphyrin in the combined reaction solution and washings. The DMPO (Sigma) was purified before use by treatment with activated charcoal. DBNBS was prepared from 3,5-dibromosulfanilic acid following the method of Kaur *et al.*[28] Inhibitor (4-methoxyphenol) was removed from acrylic and methacrylic acids by passing each carboxylic acid through a commercial column (Aldrich) designed for this purpose.

Methods

Instrumentation. Details of methods used to measure EPR and UV–VIS spectra have been reported previously.[6,10b] GC analyses were carried out with a Pye Unicam G.C.D. gas chromatograph (FID) with a glass column packed with DEGA (10%, w/w) on Celite (80–120 mesh). The results were recorded and processed on a Trilab 2000 data station (Trivector Scientific Ltd.). Photolyses were carried out using an ILC 302 UV Xenon high intensity light source (300 W; $\lambda > 390$ nm) directed by a liquid light guide (Laser Lines Ltd.).

Photolyses. The solution photolyses, for EPR studies, were carried out *in situ* in an aqueous sample cell whereas, with Si–Fe^{III}T2MPyP, the photolyses were performed externally and the solid catalyst was removed by filtration prior to the filtrate being placed in the EPR cell. Photolyses of solutions and suspensions for UV–VIS studies used 1 cm pathlength cuvettes. For reactions in the absence of dioxygen the solutions were deoxygenated prior to photolysis using dioxygen-free nitrogen.

In the product studies on the aerobic photolyses of the Fe^{III}T2MPyP–phenylacetic acid system, the extent of reaction was monitored by UV–VIS spectroscopy. For acetonitrile solutions the products were analysed directly by GC, whereas for aqueous reactions they were extracted into diethyl ether prior to analysis.

The flow system photolyses used a specially designed flow cell (1 × 1 × 0.1 cm) filled with 40 mg Si–Fe^{III}T2MPyP and the solution of phenylacetic acid in acetonitrile was irradiated as it passed through the cell. When all the solution had eluted, the reaction mixture was analysed by GC and recycled through the flow cell.

The quantum yield of the photoreaction of Fe^{III}T2MPyP with phenylacetic acid was measured using potassium ferrioxalate actinometry.[9] A solution of iron(III) sulfate (*ca.* 0.2 mol dm^{-3}, standardised by titration against EDTA[29]) in water (100 cm^3) containing sulfuric acid (5.5 cm^3) was prepared. An aliquot (5 cm^3) was removed and mixed with a standard solution of potassium oxalate (5 cm^3, concentration 6 times that of the iron(III) sulfate) and diluted to 100 cm^3 with deionised water to give the stock solution of potassium ferrioxalate. A portion of this solution (3 cm^3) was added to a quartz cuvette (1 cm path length) which was placed behind the cuvette containing the reaction mixture which was irradiated for the required time.

After photolysis the actinometer solution was shaken and an aliquot (1 cm^3) was transferred to a volumetric flask (10 cm^3). A 1,10-phenanthroline solution (0.2% w/w, 2 cm^3) and buffer (0.5 cm^3) [$NaOAc{\cdot}3H_2O$ (8.29 g) and conc. sulfuric acid (1 cm^3) in deionised water (100 cm^3)] were added and the mixture was diluted to 10 cm^3. A blank was prepared by the same method using non-irradiated potassium ferrioxalate. The absorbance of the actinometer solution (λ 510 nm) corrected for the blank (A) was measured and used to calculate the light intensity (I, Einstein min^{-1}) using eqn. (22), where V_1 = volume of aliquot of

$$I = AV_2V_3/\varepsilon\varphi t V_1 \qquad (22)$$

irradiated actinometer solution analysed (1 cm^3), V_2 = volume of actinometer solution irradiated (3 cm^3), V_3 = volume of volumetric flask (10 cm^3), ε = extinction coefficient of iron(II) phenanthroline complex at 510 nm (1.11×10^4 dm^3 mol^{-1} cm^{-1})[9], φ = the quantum yield of the actinometer photoreaction and t = irradiation time in min.

The whole process was repeated with deionised water in place of the reaction mixture. The difference in light intensity between the two experiments, equal to the light absorbed by the iron(III) porphyrin and phenylacetic acid, was used to calculate the quantum yield.

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