

# Photo-decarboxylation of substituted alkylcarboxylic acids brought about by visible light and iron(III) tetra(2-*N*-methylpyridyl)-porphyrin in aqueous solution

Bruce C. Gilbert,<sup>a</sup> George R. Hodges,<sup>a</sup> John R. Lindsay Smith,<sup>\*,a</sup> Philip MacFaul<sup>a</sup> and Philip Taylor<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of York, York, UK YO1 5DD

<sup>b</sup> Decorative Research and Development, ICI Paints plc, Wexham Road, Slough, Berks, UK SL2 5DS

The complexes of iron(III) tetra(2-*N*-methylpyridyl)porphyrin with vinyl acetic acid and a selection of  $\alpha$ -halo and  $\alpha$ -hydroxycarboxylic acids,  $\alpha$ -,  $\beta$ - and  $\gamma$ -ketoacids,  $\beta$ -dicarboxylic acids and polyacrylic acid have been photolysed ( $\lambda > 390$  nm) in an anaerobic aqueous solution. UV-VIS spectroscopy shows that the primary reaction is photoreduction of the iron(III) atom by the axial carboxylate ligand to give a solvent-caged carboxyl radical and iron(II) porphyrin.

The rate of iron(II) formation is determined by the competitive reactions of the carboxyl radical in the solvent cage: recombination with the iron(II) porphyrin to regenerate the starting complex *versus* decarboxylation. EPR spin-trapping methods have been used to detect the carbon radicals arising from decarboxylation.

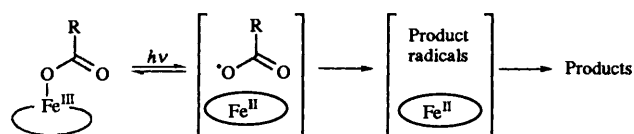
Vinylacetic and  $\alpha$ -hydroxycarboxylic acids lead to a rapid rate of iron(II) porphyrin formation; with the latter this is partly due to the one-electron reduction of the iron(III) porphyrin by the  $\alpha$ -hydroxyalkyl radicals from the photo-decarboxylation. By contrast the build-up of iron(II) porphyrin from the photoreactions of the  $\alpha$ -haloacids is slow and does not go to completion since the iron(III) porphyrin is regenerated by reaction of the halo-substrate with the iron(II) compound.

Ketoacids show an unusual variety of reactions, depending on structure. The  $\alpha$ -ketoacids give acyl and, by decarbonylation, alkyl radicals and the iron(II) porphyrin CO complex, whereas with  $\beta$ -ketoacids the photoreaction is catalytic, since, following decarboxylation of the carboxyl radical, the iron(III) porphyrin is rapidly regenerated by oxidation of the iron(II) porphyrin by the  $\alpha$ -keto radical.  $\gamma$ -Ketoacids behave in a similar fashion to alkylcarboxylic acids.

The photoreactions of  $\beta$ -dicarboxylic acids resemble those of their monocarboxylic analogues. With polyacrylic acid the rate of iron(II) formation is slow and this is attributed to the polyacid encouraging recombination of iron(II) porphyrin and carboxyl radical.

The well established photoredox chemistry of iron(III) porphyrins provides a simple route into a diverse set of radical reactions.<sup>1</sup> The most widely studied reaction involves a photoreduction of the iron(III) porphyrin by the axial ligand. By controlling the nature of the axial ligand, the substituents on the porphyrin and the solvent, access to oxygen-, halogen- and nitrogen-centred radicals is possible which, by further reactions, can be used to generate carbon-centred radicals.<sup>2-8</sup> In the presence of dioxygen, or some other oxidant that can regenerate the iron(III) porphyrin, these reactions can be developed into systems that are catalytic in iron porphyrin.<sup>2-7</sup>

Our earlier studies have concentrated on the photocleavage of the complexes of iron(III) tetra(*N*-methylpyridyl)porphyrins with alkyl- and aryl-carboxylates and acrylates in aqueous solution.<sup>9-10</sup> These follow the general reaction scheme shown in Scheme 1 and provide a new selective source of carbon radicals.



Scheme 1

Absorption of visible light by the metalloporphyrin initiates electron transfer from the carboxylate ligand to the iron(III) porphyrin to give a solvent-caged iron(II) porphyrin and

carboxyl radical.<sup>1</sup> Subsequent reactions involve a partition of these caged species between product-forming processes and recombination to regenerate the starting iron(III) porphyrin-carboxylate complex. Under aerobic conditions dioxygen traps any carbon radicals formed and, more importantly, reoxidises the iron(II) to iron(III) allowing the system to be catalytic in iron porphyrin.

We have now extended the range of this reaction to include a selection of substituted aliphatic acids, with a view to exploring its scope and limitations. This study reveals that the initial photocleavage is a general phenomenon of the iron(III)-carboxylate complexes in aqueous solution. However, the fate of the carboxyl radical is very dependent on the nature of the substituent, particularly in reactions where the decarboxylated radical is sensitive to oxidation or reduction by the transition metal ions.

## Results and discussion

### Vinylacetic acid

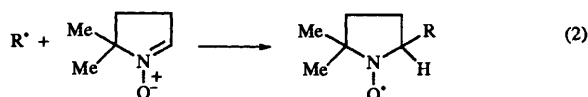
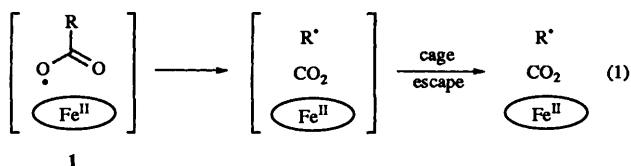
The photoreaction of vinylacetic acid illustrates well the general mechanism of the photolysis of iron(III) porphyrin-carboxylate complexes. Thus UV-VIS spectroscopy shows that 5 min irradiation ( $\lambda > 390$  nm) of an anaerobic aqueous solution (pH 2.9) of Fe<sup>III</sup>T2MPyP and vinylacetic acid leads to the complete conversion of the iron(III) porphyrin [ $\lambda_{\text{max}}$  394 (Soret), 496 and 608 nm] to the corresponding iron(II) species [ $\lambda_{\text{max}}$  428 (Soret) and 540 nm]. The rate of this reaction is very similar to that of

**Table 1** Assignments and hyperfine splittings of the radical adducts to DMPO and DBNBS from the photoreactions of Fe<sup>III</sup>T2MPyP with aliphatic carboxylic acids in anaerobic aqueous solution: <sup>a</sup> 1 × 10<sup>-4</sup> mol dm<sup>-3</sup> Fe<sup>III</sup>T2MPyP, 0.1 mol dm<sup>-3</sup> carboxylic acid and 5 × 10<sup>-2</sup> mol dm<sup>-3</sup> spin trap, pH 2.9

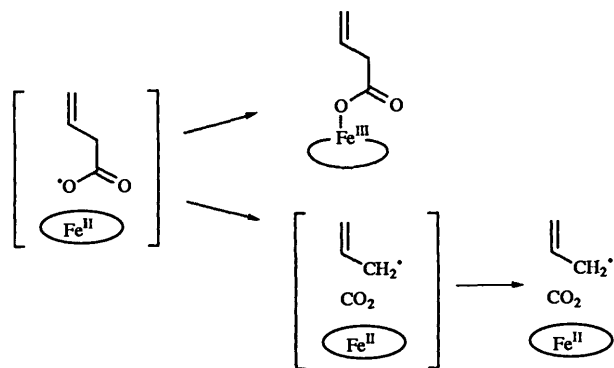
Carboxylic acid	Spin trap	Assignment of trapped radical	Hyperfine splittings/mT <sup>b</sup>	
			a <sub>N</sub>	a <sub>H</sub>
Acetic	DMPO	CH <sub>3</sub> <sup>•</sup>	1.615	2.295
Vinylacetic	DMPO	CH <sub>2</sub> =CHCH <sub>2</sub> <sup>•</sup>	1.589	2.247
Phenylacetic	DMPO	PhCH <sub>2</sub> <sup>•</sup>	1.600	2.240
Glycolic	DMPO	HOCH <sub>2</sub> <sup>•</sup>	1.561	2.247
Glycolic	DBNBS	HOCH <sub>2</sub> <sup>•</sup>	1.342	0.904
			0.063	
2-Hydroxy-2-methylpropanoic	DMPO	HOCMe <sub>2</sub> <sup>•</sup>	1.561	2.356
2-Bromopropanoic	DMPO	BrCHMe <sup>•</sup>	1.562	2.301
2-Bromo-2-methylpropanoic	DMPO	BrCMe <sub>2</sub> <sup>•</sup>	1.553	2.180
2-Chloropropanoic	DMPO	ClCHMe <sup>•</sup>	1.562	2.274
3-Methyl-2-oxobutanoic	DMPO	Me <sub>2</sub> CHC <sup>•</sup> O	1.507	1.849
		Me <sub>2</sub> CH <sup>•</sup>	1.616	2.438
3-Phenyl-2-oxopropanoic	DMPO	PhCH <sub>2</sub> C <sup>•</sup> O	1.567	1.863
		PhCH <sub>2</sub> <sup>•</sup>	1.589	2.192
3-Oxopentanedioic	DMPO	HO <sub>2</sub> CCH <sub>2</sub> COCH <sub>2</sub> <sup>•</sup>	1.424	2.384
4-Oxopentanoic	DMPO	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> <sup>•</sup>	1.589	2.274
Malonic	DMPO	HO <sub>2</sub> CCH <sub>2</sub> <sup>•</sup>	1.534	2.301
2,2-Dimethylmalonic	DMPO	HO <sub>2</sub> CCMe <sub>2</sub> <sup>•</sup>	1.534	2.630

<sup>a</sup> g-Value 2.0060 ± 0.0001. <sup>b</sup> ± 0.005 mT.

phenylacetic acid, whereas that of acetic acid is only 55% complete after 30 min.<sup>9,10</sup> Parallel experiments, in the presence of the spin trap 5,5-dimethylpyrroline *N*-oxide (DMPO), give EPR spectra of aminoxyl radicals, assigned to the spin-adducts of the carbon-centred radicals, allyl, benzyl and methyl, arising from the decarboxylation of vinylacetic, phenylacetic and acetic acid, respectively [Table 1, reactions (1) and (2)].



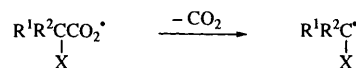
The relative rates of iron(II) formation in these reactions can be accounted for by considering the rates of decarboxylation of the solvent-caged carboxyl radicals. Thus decarboxylation of the vinylacetoxyl and phenylacetoxyl radicals, which probably occur at comparable rates (*k* for PhCH<sub>2</sub>CO<sub>2</sub><sup>•</sup>, 5 × 10<sup>9</sup> s<sup>-1</sup>),<sup>11</sup> is faster than that of the acetoxyl radical (*k* for CH<sub>3</sub>CO<sub>2</sub><sup>•</sup>, 1.3 × 10<sup>9</sup> s<sup>-1</sup>),<sup>11</sup> and consequently they compete more effectively with the regeneration of the iron(III) porphyrin-carboxylate complex (Scheme 2).



Scheme 2

### α-Hydroxy- and α-halo-substituted carboxylic acids

The anaerobic irradiation of the Fe<sup>III</sup>T2MPyP complexes of glycolic, 2-hydroxy-2-methylpropanoic, 2-bromopropanoic, 2-bromo-2-methylpropanoic and 2-chloropropanoic acids, in the presence of DMPO, all lead to the formation of spin-adducts of carbon-centred radicals (Table 1). By analogy with our earlier studies of alkylcarboxylates,<sup>9</sup> these are assigned to the substituted alkyl radicals from decarboxylation of the carboxyl radicals (Scheme 3). In agreement with these assignments, the



R<sup>1</sup> and R<sup>2</sup> = H or Me; X = Br, Cl or OH

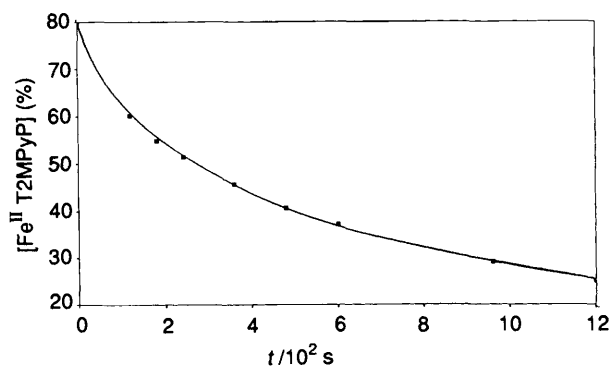
Scheme 3

reaction of glycolic acid was also carried out in the presence of 3,5-dibromo-4-nitrosobenzenesulfonic acid (DBNBS) and an EPR spectrum of a primary alkyl spin-adduct, assigned to hydroxymethyl, was obtained (Table 1).

The formation of iron(II) porphyrin in the photoreactions of the hydroxyacid complexes was fast and complete reduction occurred in 2 min for Me<sub>2</sub>C(OH)CO<sub>2</sub>H and in 5 min for HOCH<sub>2</sub>CO<sub>2</sub>H. In contrast the reactions of the haloacids were slower and did not lead to the total reduction of the iron(III) porphyrin. Thus for example, 12 min photolysis of Fe<sup>III</sup>-T2MPyP with 2-bromo-2-methylpropanoic acid achieved a 58% yield of the iron(II) porphyrin and this value remained essentially unchanged after a further 30 min of irradiation.

Decarboxylation of the α-hydroxycarboxyl radicals should, as observed, be favoured over those of their alkylcarboxyl analogues since they form the relatively stable α-hydroxyalkyl radicals. Furthermore, as we reported previously,<sup>9</sup> their rates will be effectively doubled since each α-hydroxyalkyl radical formed in the photoreaction can rapidly reduce a further iron(III) porphyrin in a non-photochemical process [reaction (3)]. In agreement with the latter conclusion, the rate constants for the oxidation of Me<sub>2</sub>C<sup>•</sup>OH by iron(III) deuterioporphyrin<sup>12</sup> and by iron(III) protoporphyrin (IX)<sup>13</sup> [reaction (3)] have been





**Fig. 1** Time dependent oxidation of Fe<sup>II</sup>T2MPyP by 2-chloropropanoic acid in anaerobic aqueous solution: Fe<sup>II</sup>T2MPyP generated by photolysis of  $1 \times 10^{-5} \text{ mol dm}^{-3}$  Fe<sup>III</sup>T2MPyP with  $0.1 \text{ mol dm}^{-3}$  2,2-dimethylpropanoic acid in aqueous solution ( $3 \text{ cm}^3$ );  $10 \mu\text{l}$  2-chloropropanoic acid

reported to be  $3.7 \times 10^8$  and  $2.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. The expected rate constant for this oxidation by Fe<sup>III</sup>T2MPyP should be greater than these values since the electron-withdrawing 2-*N*-methylpyridyl groups should favour the reduction of iron(III) [cf. the half-wave potentials *vs.* SCE for reduction of iron(III) deuterioporphyrin in *N,N'*-dimethylformamide (DMF),  $-0.30 \text{ V}$ ,<sup>14</sup> iron(III) protoporphyrin (IX) in DMF,  $-0.27 \text{ V}$ <sup>14</sup> and iron(III) tetra(2-*N*-methylpyridyl)porphyrin at pH 9.0,  $-0.12 \text{ V}$ <sup>15</sup>].

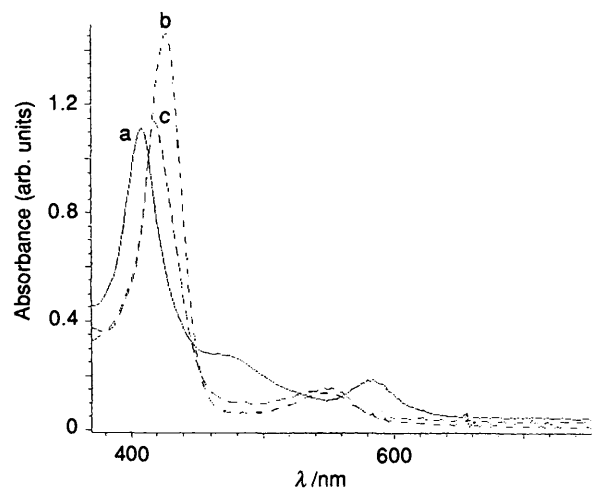
The behaviour of the haloacids suggests that these systems reach a photoequilibrium such that the rate of formation of the iron(II) porphyrin equals its rate of oxidation. In agreement with this conclusion, leaving the photolysed solutions to stand in the dark led to the regeneration of Fe<sup>III</sup>T2MPyP. The reproducibility of the above reactions indicates that the oxidant in these systems was not adventitious dioxygen; an alternative explanation is that the iron(II) porphyrin was oxidised by unreacted substrate. This was subsequently confirmed by the addition of the haloacids to aqueous solutions of iron(II) porphyrin, from the anaerobic photoreaction of Fe<sup>III</sup>T2MPyP with 2,2-dimethylpropanoic acid. Each haloacid led to the formation of the iron(III) porphyrin (*e.g.* Fig. 1) with the fastest reaction occurring with 2-chloropropanoic acid. The mechanism of this reduction was not investigated further; however, it is likely that it takes place by an electron-transfer or ligand-transfer process.<sup>16</sup> Although these photoreactions are catalytic in iron porphyrin, their synthetic potential is clearly limited by the mixed nature of the products obtained from the concurrent decarboxylation and reduction of the haloacids.

#### $\alpha$ -Ketoacids

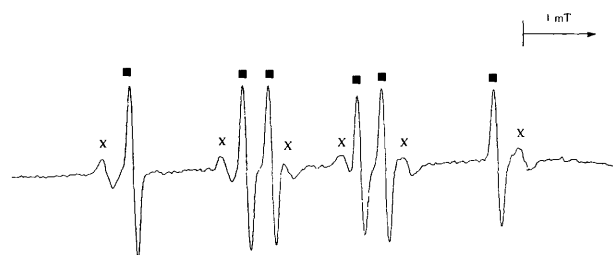
The anaerobic photoreactions of the Fe<sup>III</sup>T2MPyP with 3-methyl-2-oxobutanoic and 3-phenyl-2-oxopropanoic acid were unusual. The former initially gave the expected shift in the UV-VIS Soret peak to 426 nm after 2 min of irradiation; however, this changed after a further 15 min photolysis to give a new porphyrin species with a Soret peak at 418 nm (Fig. 2). In contrast, irradiation of Fe<sup>III</sup>T2MPyP in the presence of 3-phenyl-2-oxopropanoic acid immediately gave the 418 nm species. UV-VIS spectroscopy showed that allowing air into both reactions containing the 418 nm absorbing species led to the regeneration of the initial iron(III) porphyrin.

EPR spin-trapping experiments with DMPO indicate the presence of two carbon-centred radicals in the reactions of each  $\alpha$ -ketoacid (Table 1). These are assigned to an alkyl and, by comparison with published data, to an acyl radical.<sup>17</sup> With 3-methyl-2-oxobutanoic acid the DMPO-acyl radical adduct gave the more intense EPR signal (Fig. 3), whereas with 2-oxo-3-phenylpropanoic acid the alkyl-radical adduct was dominant.

We assign the iron porphyrin species with  $\lambda_{\text{max}}$  418 nm to the CO complex of Fe<sup>II</sup>T2MPyP formed by the reaction of the



**Fig. 2** UV-VIS spectrum of Fe<sup>III</sup>T2MPyP in the presence of 3-methyl-2-oxobutanoic acid in anaerobic aqueous solution, (a) before photolysis, (b) and (c) after 2 and 17 min photolysis:  $1 \times 10^{-5} \text{ mol dm}^{-3}$  Fe<sup>III</sup>T2MPyP and  $0.1 \text{ mol dm}^{-3}$  3-methyl-2-oxobutanoic acid



**Fig. 3** EPR spectrum of radical-adducts of DMPO formed during the photolysis of Fe<sup>III</sup>T2MPyP with 3-methyl-2-oxobutanoic acid in anaerobic aqueous solution:  $1 \times 10^{-4} \text{ mol dm}^{-3}$  Fe<sup>III</sup>T2MPyP,  $0.1 \text{ mol dm}^{-3}$  3-methyl-2-oxobutanoic acid and  $5 \times 10^{-2} \text{ mol dm}^{-3}$  DMPO, pH 2.9; scan time 2 min. ■, Me<sub>2</sub>CHCO•; X, Me<sub>2</sub>CH•

iron(II) porphyrin with the CO released in the decarboxylation. In agreement with this conclusion CO gas, when bubbled into an anaerobic aqueous solution of Fe<sup>II</sup>T2MPyP (from the photolysis of Fe<sup>III</sup>T2MPyP with 2,2-dimethylpropanoic acid), brought about a shift in the Soret absorption from 426 to 418 nm. Furthermore, introducing air into this system regenerated the iron(III) porphyrin UV-VIS spectrum.

Scheme 4 presents a mechanism for the photoreaction of the two  $\alpha$ -ketoacids. Initial photolysis is followed by rapid decarboxylation to give solvent-caged acyl radical-iron(II) porphyrin. For 3-methyl-2-oxobutanoic acid the acyl radical is trapped by the iron(II) porphyrin to give an acyl-iron(III) porphyrin complex (Soret  $\lambda_{\text{max}}$  426 nm). Further irradiation is then required to cleave this acyl complex leading to an alkyl radical and the Fe<sup>II</sup>T2MPyP-CO complex. However, with 2-oxo-3-phenylpropanoic acid the decarboxylation of the acyl radical is very fast (for PhCH<sub>2</sub>CO•,  $k = 10^7$ - $10^8 \text{ s}^{-1}$  compared with  $5 \times 10^4 \text{ s}^{-1}$  for Me<sub>2</sub>CHCO•)<sup>18</sup> effectively preventing the formation of an acyl-iron(III) complex and leading directly to the benzyl radical and Fe<sup>II</sup>T2MPyP-CO complex.

The aerobic photolysis of 2-oxo-3-phenylpropanoic acid was also briefly examined. Under these conditions dioxygen traps the benzyl radical and by regenerating the iron(III) porphyrin makes the system catalytic. This is closely analogous to the equivalent reaction of phenylacetic acid which was discussed in the previous paper.<sup>10</sup> However, the catalytic efficiency of the photooxidation of 2-oxo-3-phenylpropanoic acid was significantly greater (Table 2).

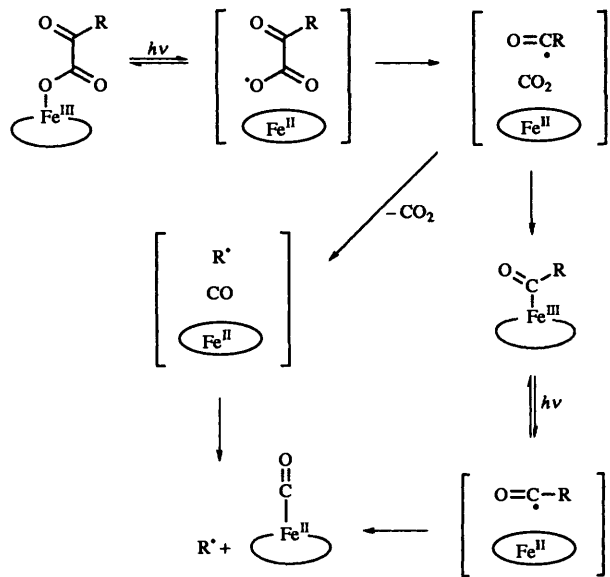
#### $\beta$ -Ketoacids

The anaerobic photoreaction (1 min) of 3-oxopentanedioic acid with Fe<sup>III</sup>T2MPyP in the presence of DMPO in aqueous solution gave an EPR signal which we assign to the

**Table 2** Catalyst turnovers observed during the photoreaction of 2-oxo-3-phenylpropanoic and phenylacetic acid with Fe<sup>III</sup>T2MPyP in aqueous solution<sup>a</sup>: 1 × 10<sup>-5</sup> mol dm<sup>-3</sup> Fe<sup>III</sup>T2MPyP and 0.1 mol dm<sup>-3</sup> carboxylic acid

Substrate	Time/min	Catalyst destruction	Yield/catalyst turnovers <sup>a</sup>		
			PhCHO	PhCH <sub>2</sub> OH	PhCH <sub>2</sub> CH <sub>2</sub> Ph
PhCH <sub>2</sub> COCO <sub>2</sub> H	5	30	317	—	—
PhCH <sub>2</sub> CO <sub>2</sub> H	60	> 90	133	15	2

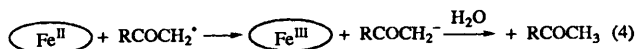
<sup>a</sup> Moles of product/moles of catalyst. <sup>b</sup> Results from ref. 10.



Scheme 4

HO<sub>2</sub>CCH<sub>2</sub>COCH<sub>2</sub> spin adduct (Table 1). Surprisingly, however, in the absence of the spin trap, UV-VIS analysis showed negligible iron(II) porphyrin was formed during 25 min of irradiation. Despite the absence of iron(II) porphyrin there was extensive formation of gas bubbles in the photolysis cell which, by displacement with nitrogen into calcium hydroxide, were identified as carbon dioxide. A control experiment showed no carbon dioxide was formed in the absence of Fe<sup>III</sup>T2MPyP.

The decarboxylation of HO<sub>2</sub>CCH<sub>2</sub>COCH<sub>2</sub>CO<sub>2</sub> should be rapid since the product radical, HO<sub>2</sub>CCH<sub>2</sub>COCH<sub>2</sub>•, is resonance stabilised. Confirmation for the resonance stabilisation comes from the smaller α-proton hyperfine splitting of the acetone radical (1.92 mT) than that of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>• (2.2 mT),<sup>19</sup> the smaller C-H bond dissociation energy of acetone (385 kJ mol<sup>-1</sup>) compared with ethane (421 kJ mol<sup>-1</sup>),<sup>20</sup> and the barrier to rotation around the •CH<sub>2</sub>-COR bond of ca. 38 kJ mol<sup>-1</sup>.<sup>19</sup> The spin-trapping EPR study and the formation of CO<sub>2</sub> support the formation of an α-keto radical from 3-oxopentanedioic acid. We believe that the absence of iron(II) porphyrin arises from its efficient oxidative trapping by the α-keto radical in the solvent cage. This regenerates the Fe<sup>III</sup>T2MPyP and leads to a photocatalytic decarboxylation system [reaction (4), Scheme 5].



#### γ-Ketoacids

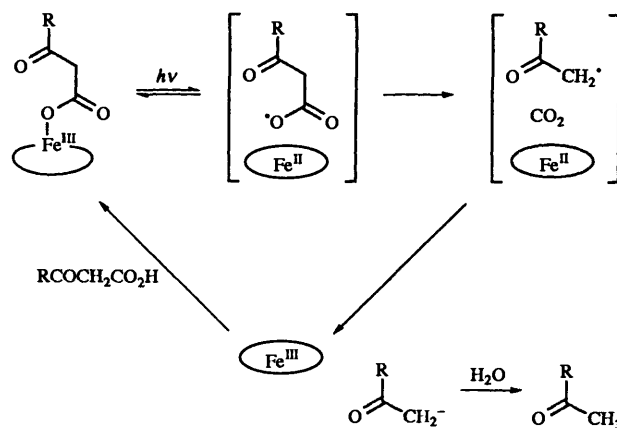
The anaerobic photolysis of 4-oxopentanoic acid with Fe<sup>III</sup>T2MPyP in aqueous solution led to the formation of the iron(II) porphyrin and, in the presence of DMPO, gave an EPR spectrum which we assign to the spin-adduct of the 3-oxobut-1-yl radical (Table 1). The rate of this photolysis was significantly lower than those of the α- and β-ketoacids and comparable with those of acetic and propanoic acids, since the carbonyl group is

sufficiently removed from the radical centre to have little influence on its stability.

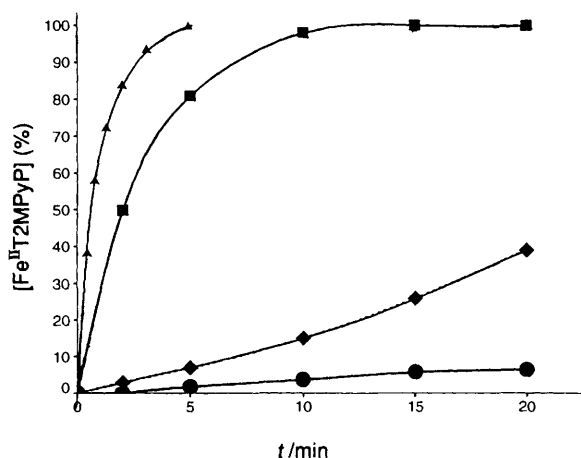
#### β-Dicarboxylic acids

EPR signals from carbon-centred radical adducts were observed from the anaerobic photoreactions of malonic and dimethylmalonic acid in the presence of Fe<sup>III</sup>T2MPyP and DMPO. The splitting constants and assignments of the trapped radicals are given in Table 1.

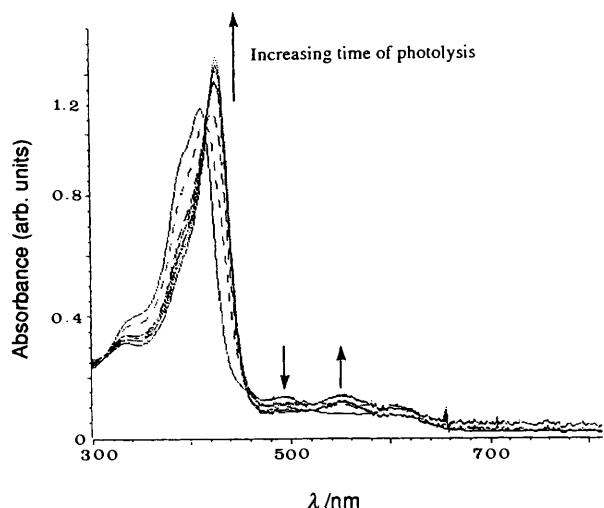
The time-dependent formation of iron(II) porphyrin in these anaerobic photolyses, in the absence of DMPO, are recorded in Fig. 4 together with those of 2-methylpropanoic and acetic acids for comparison. These results show the rates of iron(II) formation are comparable, although somewhat lower than those of their monocarboxylate analogues and the introduction of two methyl groups leads to a marked increase in the rate of photoreduction by dimethylmalonic acid compared with malonic acid. We suggest this effect is caused by an increased rate of decarboxylation arising from steric effects in the



Scheme 5



**Fig. 4** Time dependent formation of Fe<sup>II</sup>T2MPyP during the photolysis of Fe<sup>III</sup>T2MPyP with malonic (●), 2,2-dimethylmalonic (■), 2-methylpropanoic (▲) and acetic acid (◆): 1 × 10<sup>-5</sup> mol dm<sup>-3</sup> Fe<sup>III</sup>T2MPyP and 0.1 mol dm<sup>-3</sup> carboxylic acid, pH 2.9



**Fig. 5** Time dependent changes in the UV-VIS spectrum of  $\text{Fe}^{\text{III}}\text{T2MPyP}$  in an anaerobic aqueous solution of polyacrylic acid. Spectrum recorded every 4 min for 20 min:  $1 \times 10^{-5} \text{ mol dm}^{-3}$   $\text{Fe}^{\text{III}}\text{T2MPyP}$  and polyacrylic acid equivalent to  $0.1 \text{ mol dm}^{-3}$  of the monomer, pH 1.9.

carboxyl radical and/or increased stability in the alkyl radical formed on decarboxylation. A similar argument was proposed previously to account for the rates of the photoreactions of simple alkylcarboxylate-iron(III) porphyrin complexes.<sup>9</sup>

Interestingly, the photoreactions of the  $\beta$ -dicarboxylic acids, unlike that of the  $\beta$ -ketoacid, do not show evidence for cycling of the iron(II)-iron(III) porphyrin. It appears that whereas the  $\alpha$ -keto radical is rapidly reduced by  $\text{Fe}^{\text{II}}\text{T2MPyP}$ , the corresponding  $\alpha$ -carboxyalkyl radicals are not, suggesting that the greater stabilising influence ( $-M$  effect) of the ketone group on the forming anion is critical for this reaction.<sup>21</sup>

#### Polyacrylic acid

The amount of polyacrylic acid used in the photolysis experiments was adjusted such that the concentration of the monomer units was the same ( $0.1 \text{ mol dm}^{-3}$ ) as that used for the monocarboxylic acid studies. This solution was then stirred overnight with  $\text{Fe}^{\text{III}}\text{T2MPyP}$  to ensure complete equilibration and complexation of the iron(III) porphyrin with the polymer acid.<sup>22</sup> The anaerobic irradiation of this solution resulted in the slow formation of the iron(II) porphyrin (Fig. 5).

Intuitively the rate of the photoreduction of the iron(III) in the polymer complex might be expected to be similar to that of 2-methylpropanoic acid; however, it was significantly lower. We attribute this predominantly to the encapsulation of the iron(III) porphyrin by the polyacrylic acid.<sup>22</sup> This has the effect of holding the carboxyl radical close to the iron(II) porphyrin, analogous to a restrictive solvent cage, which favours recombination and regeneration of the starting iron(III) porphyrin.

Changing the pH of the reaction over a range of values from 1.5 to 5.2 showed that the optimum rate occurred close to pH 1.9. At higher or lower pH values the rate of iron(II) formation decreased. This pH optimum of the polymer acid photoreaction is lower than that of 2,2-dimethylpropanoic acid with  $\text{Fe}^{\text{III}}\text{T2MPyP}$ . We suggest that the reactivity depends on a balance between there being a sufficient concentration of the ionised carboxylate groups to give the photoreactive iron(III) carboxylate complex and minimising electrostatic interactions between polymer and porphyrin that encourage recombination of the carboxyl radical and iron(II) porphyrin.

After photolysis the reaction at pH 1.9 gave a fine precipitate. We believe this arises from decarboxylation of the polymer which decreases its hydrophilicity sufficiently to cause precipitation.

Although the UV-VIS studies show clearly that photoreduction of  $\text{Fe}^{\text{III}}\text{T2MPyP}$  with polyacrylic acid is occurring, all attempts to trap the polymer radical with DMPO or with 2-methyl-2-nitrosopropane were unsuccessful. We assume this is due to steric hindrance of the bulk of the polymer which surrounds the charged porphyrin and, furthermore, anisotropic broadening of the signal would lower the detection level of any adduct formed.

## Experimental

### Materials

The carboxylic acids and DMPO were commercially available and used without further purification. The preparation and purification of DBNBS and  $\text{Fe}^{\text{III}}\text{T2MPyP}$  has been reported previously.<sup>10,23</sup>

### Methods

**Instrumentation.** Details of methods used to monitor reactions (EPR and UV-VIS spectroscopy and GC analysis) have been reported previously.<sup>9,10</sup>

**Photolyses.** The photolyses were carried out using an ILC 302 UV Xenon high-intensity light source (300 W;  $\lambda > 390 \text{ nm}$ ) directed by a liquid light guide (Laser Lines Ltd).<sup>9,10</sup> The solutions were deoxygenated using dioxxygen-free nitrogen.

The iron(II) porphyrin used for reactions with  $\alpha$ -haloacids and with CO was obtained by photolysis of  $\text{Fe}^{\text{III}}\text{T2MPyP}$  ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ) with 2,2-dimethylpropanoic acid ( $0.1 \text{ mol dm}^{-3}$ ) in an anaerobic aqueous solution ( $3 \text{ cm}^3$ ) in a sealed cuvette. When the photoreduction was complete the haloacid ( $10 \mu\text{l}$ ) ( $1 \mu\text{l} = 1 \text{ mm}^3$ ) or CO was introduced into the reaction vessel.

## Acknowledgements

P. M. thanks the SERC and ICI Paints plc for a CASE studentship.

## References

- 1 K. S. Suslik and R. A. Watson, *New J. Chem.*, 1992, **16**, 623.
- 2 A. Tohara and M. Sato, *Chem. Lett.*, 1989, 153.
- 3 C. Bartocci, A. Maldotti, G. Varani, V. Carassiti, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1989, 964.
- 4 Y. Ito, *J. Chem. Soc., Chem. Commun.*, 1991, 622.
- 5 A. Maldotti, C. Bartocci, R. Armadelli, E. Polo, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1991, 1487.
- 6 C. Bartocci, A. Maldotti, G. Varani, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1991, **30**, 1255.
- 7 Y. Ito, K. Kurimoto, S. Miyachi and T. Kako, *Tetrahedron Lett.*, 1991, **32**, 4007.
- 8 M. Hashino, K. Ueda, M. Takahashi, M. Yamaji and Y. Hama, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 405.
- 9 B. C. Gilbert, J. R. Lindsay Smith, P. MacFaul and P. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2033.
- 10 B. C. Gilbert, J. R. Lindsay Smith, P. MacFaul and P. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1996, preceding paper.
- 11 J. W. Hilborn and J. A. Pincock, *J. Am. Chem. Soc.*, 1991, **113**, 2683.
- 12 D. Brault, C. Bizet, P. Morlière, M. Rougee, E. J. Land, R. Santus and A. J. Swallow, *J. Am. Chem. Soc.*, 1980, **102**, 1015.
- 13 H. Goff and M. G. Simic, *Biochim. Biophys. Acta*, 1975, **392**, 201.
- 14 K. M. Kadish, in *Iron Porphyrins*, Part 2, eds. A. B. P. Lever and H. B. Gray, Addison-Wesley, 1983, p. 161.
- 15 K. R. Rodgers, R. A. Reed, Y. O. Su and T. G. Spiro, *Inorg. Chem.*, 1992, **31**, 2688.
- 16 H. O. House, *Modern Synthetic Reactions*, Benjamin/Cummings, Menlo Park, 1972, 2nd edn., p. 158.
- 17 M. J. Davies and T. J. Slater, *Biochem. J.*, 1987, **245**, 167.
- 18 J. A. Howard and J. C. Scaiano in *Landolt-Börnstein: Numerical data and functional relationships in science and technology*, ed. H. Fischer, Springer-Verlag, Berlin, 1984, vol. 13d.
- 19 D. M. Camaioni, H. F. Walter, J. E. Jordan and D. W. Pratt, *J. Am. Chem. Soc.*, 1973, **95**, 7978.

- 20 B. P. Roberts and A. J. Steel, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2155.
- 21 Cf.  $\sigma_{4-X}^-$  values where X = CO<sub>2</sub>R and COMe are 0.74 and 0.82, respectively; O. Exner in *Advances in linear free energy relationships*, eds. N. B. Chapman and J. Shorter, Plenum, London, 1972, ch. 1.
- 22 J. R. Lindsay Smith and R. J. Lower, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2187.
- 23 D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1991, 549.

Paper 5/06443K

Received 2nd October 1995

Accepted 17th October 1995