Photo-decarboxylation of iron(III) porphyrin–amino acid complexes in aqueous solution

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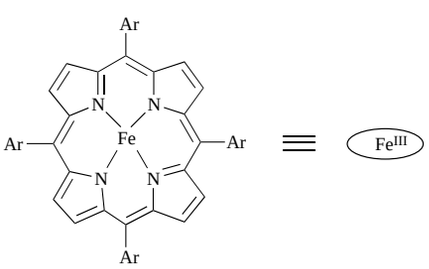
Irradiation (λ > 390 nm) of acidic anaerobic aqueous solutions of iron(III) tetrakis(2-*N*-methylpyridyl)-porphyrin, in the presence of mono- or di-basic amino acids or their *N*-acylated derivatives, generates the iron(II) porphyrin and the corresponding acyloxyl radical; subsequent decarboxylation of the latter gives the corresponding ammonioalkyl or amidoalkyl radical. The rate and course of each reaction have been monitored by UV–VIS spectroscopy and EPR spin-trapping techniques. The large differences in the observed rates of iron(II) porphyrin formation are controlled by two factors: the binding affinity of the carboxy group for the iron(III) porphyrin to form the photoactive complex and the competitive reactions of the acyloxyl radical [decarboxylation and regeneration of the iron(III) porphyrin complex], following photolysis. With cationic carboxylate ligands, such as glycine or L-alanine, charge repulsion with the cationic porphyrin results in the former effect predominating, whereas with neutral ligands, for example *N*-acetylglycine, it is the latter that determines the overall rate of reaction.

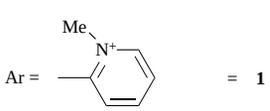
In aqueous base, the amino acids ligate to the iron(III) porphyrin *via* the amino rather than the carboxy group. Subsequent irradiation brings about an electron transfer from the ligand to give the iron(II) porphyrin and the amino acid cation–radical which reacts further to give an α-amino radical either by decarboxylation or proton loss.

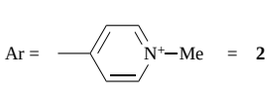
Introduction

The photochemistry of iron(III) porphyrin complexes has been the subject of much recent investigation with particular attention focusing on the photoreduction of iron(III) to iron(II) porphyrin *via* one-electron transfer from an axial ligand.[1] Thus the production of a variety of radical types is possible simply by changing the nature of the ligand, porphyrin and solvent.[2–13] Oxygen-, halogen- and nitrogen-centred radicals have been produced this way and in turn have been used to generate carbon-centred radicals.[2–13] Importantly, these systems can be made catalytic in iron porphyrin when the reactions are undertaken in the presence of an oxidant, normally, but not necessarily, dioxygen.[2–9,11]

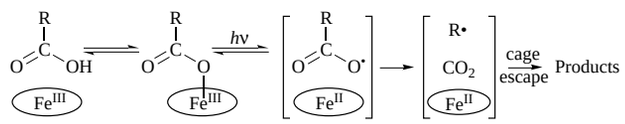
We have established[11–13] that photolysis (using visible light λ > 390 nm) of iron(III) tetrakis(*N*-methylpyridyl)porphyrins (**1** and **2**)–alkyl carboxylic acid complexes in aqueous solution







(pH 3–6) result in the formation of iron(II) porphyrin species and acyloxyl radicals in a solvent cage (Scheme 1); recombination to give the original complex competes with decarboxylation to form the carbon-centred radical R•. Under anaerobic conditions the conversion of iron(III) to iron(II) porphyrin can be conveniently followed by UV–VIS spectroscopy and the rates of iron(II) formation monitored; in parallel EPR experiments, the radicals can be trapped with the water-soluble spin traps, DMPO and DBNBS,† to give spin-adducts [reactions (1) and (2)]. Under aerobic conditions, dioxygen traps any carbon-



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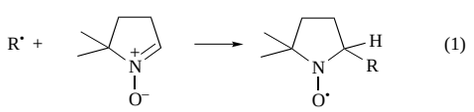
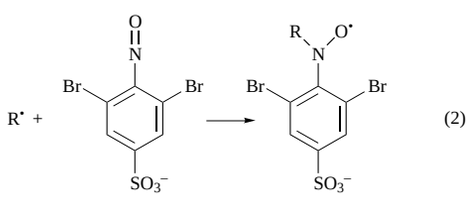
Scheme 1



DMPO



DBNBS

† *Abbreviations*: DMPO, 5,5-dimethylpyrroline *N*-oxide; DBNBS, 3,5-dibromo-4-nitrosobenzene sulfonic acid; porphyrin ligand, T2MPyP, 5,10,15,20-tetrakis(2-*N*-methylpyridyl)porphyrin.

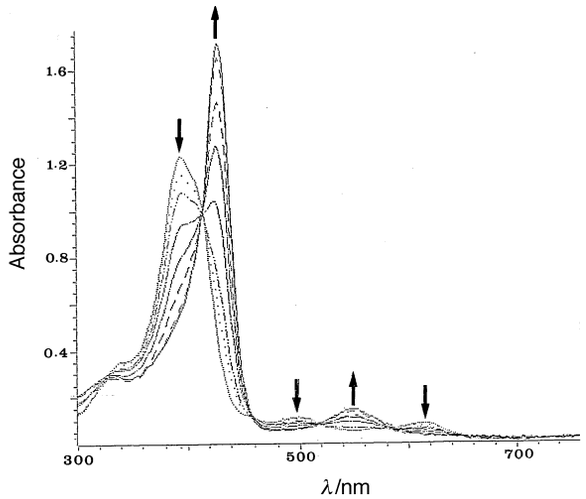
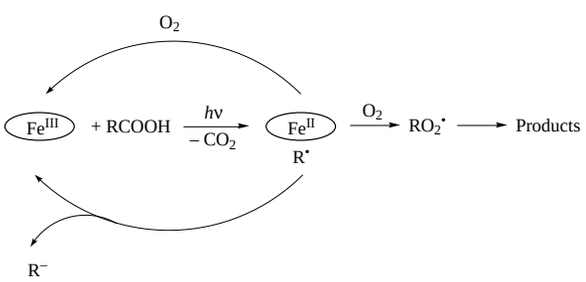


Fig. 1 UV–VIS spectral changes observed on illumination ($\lambda > 390$ nm) of $Fe^{III}T2MPyP$ (10^{-5} mol dm^{-3}) and alanine (0.1 mol dm^{-3}) in anaerobic aqueous acid (pH 3.1). Spectra recorded at 5 min intervals.

centred radicals that escape from the solvent cage and also oxidises iron(II) to iron(III), thus allowing the formation of more starting complex with the acid (Scheme 2). In the absence of



Scheme 2

dioxygen and spin trap, the fate of the radicals is not known; however, in one system at least it was found[13] that iron(II) porphyrin can be oxidised to iron(III) if the radical R$^{\bullet}$ produced has a sufficiently low reduction potential (Scheme 2). This has the advantage of making the system catalytic in the absence of dioxygen.

In our earlier studies we defined the photosystem and described its application to the formation of a variety of carbon-centred radicals directly from iron(III) porphyrin–carboxylic acid complexes. We have now extended this to include the complexes of amino acids (and their *N*-acylated derivatives) with the aim of providing a novel route to nitrogen-containing carbon-centred radicals with potential applications in synthesis.

Results and discussion

The photoreactions of monobasic amino acids in aqueous acid (pH 3–6)

Results. Photolysis ($\lambda > 390$ nm) of an aqueous solution, pH 3.1, of $Fe^{III}T2MPyP$ (1×10^{-5} mol dm^{-3}) and glycine, L-alanine or betaine ($Me_3N^+CH_2CO_2^-$) (0.1 mol dm^{-3}), in the absence of dioxygen, leads to the replacement of the Soret band (λ_{max} 394 nm) in the UV–VIS spectrum by a new band at 430 nm. The α, β bands at 498 and 610 nm are also replaced by a new band at 550 nm (see for example Fig. 1). These spectral changes are consistent with the formation of the iron(II) porphyrin.[11–13] For glycine the reaction required 65 min for 50% conversion to $Fe^{II}T2MPyP$ ($t_{\frac{1}{2}}$) and for betaine and L-alanine, under the same conditions, the reaction was faster, $t_{\frac{1}{2}}$ of 40 and 20 min, respectively. These rates of iron(II) porphyrin formation are very slow when compared with that of the propionic acid–porphyrin

Table 1 Time taken to reduce half of the iron(III) porphyrin ($t_{\frac{1}{2}}$) in the photolysis of $Fe^{III}T2MPyP$ complexes of selected amino acids and their derivatives in aqueous solution at pH 3.1[a]

Acid	Major species at pH 3.1	$t_{\frac{1}{2}}$, time for 50% reduction/s[b]
Glycine	$H_3\overset{+}{N}CH_2CO_2^-$	3900
Betaine	$Me_3\overset{+}{N}CH_2CO_2^-$	2400
N-Acetylglycine	$AcNHCH_2CO_2H$	15
L-Alanine	$H_3\overset{+}{N}CHMeCO_2^-$	1200
4-Aminobutyric acid	$H_3\overset{+}{N}(CH_2)_3CO_2H$	840
4-Acetamidobutyric acid	$AcNH(CH_2)_3CO_2H$	105
6-Aminohexanoic acid	$H_3\overset{+}{N}(CH_2)_5CO_2H$	420
Propionic acid	$CH_3CH_2CO_2H$	90

[a] $Fe^{III}T2MPyP$, 1×10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}. [b] ±10%.

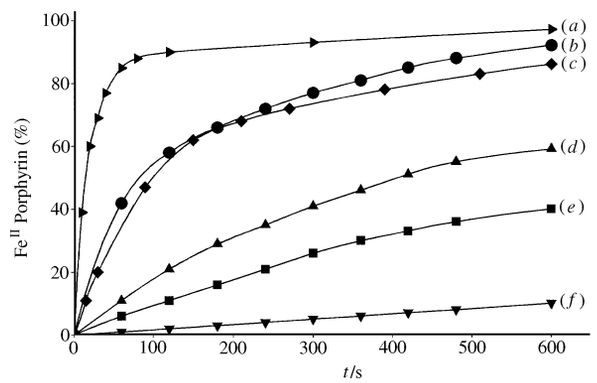


Fig. 2 The formation of iron(II) porphyrin as a function of time in the photoreactions of $Fe^{III}T2MPyP$ (10^{-5} mol dm^{-3}) in the presence of (*a*) *N*-acetylglycine, (*b*) propionic acid, (*c*) 4-acetamidobutyric acid, (*d*) 6-aminohexanoic acid, (*e*) 4-aminobutyric acid and (*f*) glycine (0.1 mol dm^{-3}) in anaerobic aqueous acid (pH 3.1)

complex, typically 90 s to achieve 50% conversion (Table 1). We next explored the effect on the rate of iron(II) formation of increasing the separation between the amino and carboxy groups and of *N*-acylation of the amino acids (Table 1). The former revealed that the rate of photoreduction increases in the order glycine < 4-aminobutyric acid < 6-aminohexanoic acid. However, a much more significant rate increase was observed following *N*-acylation with *N*-acetyl–glycine having the fastest rate of all. These differences in rates of photoreduction are clearly seen in Fig. 2.

Examination of the UV–VIS spectra of $Fe^{III}T2MPyP$ in the presence of the above carboxylic acids, at pH 3.1, reveals that iron(III) carboxylate complex formation is relatively unfavourable for the amino acids and for betaine in comparison with the amido acids or propionic acid.

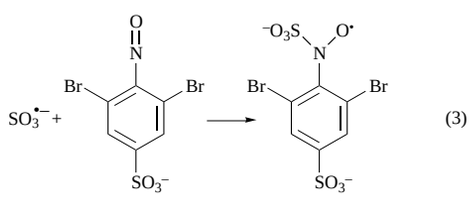
In parallel experiments, EPR spectroscopy was employed to detect and identify the radicals formed. Thus, photolysis of an anaerobic aqueous solution of $Fe^{III}T2MPyP$ (2×10^{-4} mol dm^{-3}) and glycine (0.2 mol dm^{-3}), in the presence of the nitrone spin-trap DMPO (5×10^{-2} mol dm^{-3}), gave a very weak signal with EPR parameters (Table 2) which characterise it as a nitroxide radical spin-adduct from a carbon-centred radical; this is attributed to $^+NH_3CH_2^{\bullet}$ [reaction (1)] (see below). The signal increased in intensity over a period of 30 min continuous photolysis. Also present initially was a signal from the hydroxyl radical spin-adduct (DMPO–OH) which disappeared on continuous photolysis. Similar results were observed with the analogous reactions of L-alanine although the signals obtained were more intense.

In an attempt to identify the radicals formed, the photolyses were repeated in the presence of the nitroso trap, DBNBS (5×10^{-3} mol dm^{-3}). At pH 3.1 glycine gave a spectrum showing a triplet of triplets ($a_N = 1.246$, $a_H = 0.055$ mT), attributed

Table 2 EPR parameters of radical-adducts formed in the photoreactions of Fe^{III}T2MPyP complexes of selected monobasic amino acids and derivatives in the presence of DMPO or DBNBS[a]

Carboxylic acid	Spin trap[a]	pH	Hyperfine splittings/mT[b] a_N	a_H	Assignment of trapped radical[c]
Glycine	DMPO	6.3	1.58(t)	2.30(d)	$R^{\bullet}$ ($H_3\overset{+}{N}CH_2^{\bullet}$)
N-Acetylglycine	DMPO	6.1	1.56(t)	2.22(d)	$R^{\bullet}$ ($AcNHCH_2^{\bullet}$)
	DBNBS	3.1	1.39(t) 0.25(t)	0.83(t)	$AcNHCH_2^{\bullet}$
L-Alanine	DMPO	6.2	1.53(t)	2.32(d)	$R^{\bullet}$ ($CH_3\dot{C}H\overset{+}{N}H_3$)
	DBNBS	3.1 and 6.3	1.31(t)	0.77(d)	$CH_3\dot{C}H\overset{+}{N}H_3$
4-Aminobutyric acid	DBNBS	3.1	1.40(t)	1.18(t)	$H_3\overset{+}{N}(CH_2)_2CH_2^{\bullet}$
			1.31(t)	0.60(t)	*d* $H_3\overset{+}{N}(CH_2)_2\dot{C}HCO_2H$ / $H_3\overset{+}{N}CH_2\dot{C}HCH_2CO_2H$
4-Acetamidobutyric acid	DBNBS	3.1	1.40(t)	1.18(t)	$AcNH(CH_2)_2CH_2^{\bullet}$
			1.31(t)	0.60(d)	*d* $AcNH(CH_2)_2\dot{C}HCO_2H$ / $AcNHCH_2\dot{C}HCH_2CO_2H$

[a] Fe^{III}T2MPyP, 2×10^{-4} mol dm^{-3}; carboxylic acid, 0.2 mol dm^{-3}; DMPO, 5×10^{-2} mol dm^{-3} and DBNBS, 5×10^{-3} mol dm^{-3}. [b] Hyperfine splittings (±0.1 mT) with DMPO and DBNBS are characteristic of carbon-centred radicals derived from amino acids, see refs. 14 and 15. [c] Carbon-centred radical believed to be the same as that trapped by DBNBS. [d] Minor radicals detected in the reaction.



(3)

DBNBS

to the adduct of DBNBS and $SO_3^{\bullet-}$ [reaction (3)]:[16] the most likely source of this is the photodecomposition of the spin trap. No signals from carbon-centred radical adducts [reaction (2)] were detected. A tenfold increase in the concentration of the spin trap (5×10^{-2} mol dm^{-3}) only served to increase the signal from the $SO_3^{\bullet-}$ adduct. Betaine showed similar behaviour. In contrast, an analogous experiment with L-alanine gave a weak signal with DBNBS with characteristic splittings ($a_N = 1.31$ and $a_H = 0.77$ mT from a single β-proton) which we interpret as arising from the expected $^+NH_3\dot{C}HCH_3$ radical-adduct [reaction (2) and Table 2]. Over 30 min of continuous photolysis, the signal from this spin-adduct increased in intensity but remained relatively weak compared with the dominant signal from the $SO_3^{\bullet-}$ adduct. Increasing the pH to 6.3 increased the rate of formation of, and the intensity of the signal, from the carbon-centred radical adduct so that after 10 min continuous photolysis a relatively strong signal was observed.

Photolysis of an anaerobic aqueous solution of Fe^{III}-T2MPyP, 4-aminobutyric acid and DBNBS at pH 3.1 gave an EPR spectrum immediately of an adduct recognised, from its parameters, as arising from a primary carbon radical, $RCH_2^{\bullet}$, evidently derived by decarboxylation of the carboxyl radical [Fig. 3(*a*), Table 2]. Repeating the reaction with the *N*-acetyl derivative, 4-acetamidobutyric acid, gave a much more intense EPR signal from a primary carbon radical adduct with the same hyperfine splittings. In both cases after 40 min of continuous photolysis a very weak signal, assigned to a secondary carbon radical adduct, appeared in the spectra (Table 2). The enhanced signal intensity following *N*-acylation was also observed with the glycine analogue in the presence of DMPO. In addition, a very strong EPR spectrum from a primary radical adduct was observed immediately on photolysis when the spin trap was changed to DBNBS [Table 2, Fig. 3(*b*)].

Discussion. The relative rates of photoreduction of iron(III) porphyrins by simple alkyl carboxylic acids have been explained in terms of the relative rates of decarboxylation of the resulting

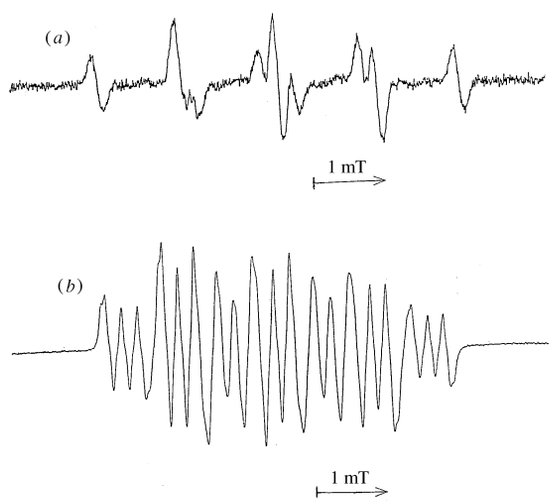
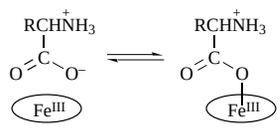


Fig. 3 EPR spectra of the adduct of (*a*) $^{\bullet}CH_2(CH_2)_3NH_3^+$ and (*b*) $^{\bullet}CH_2NHAc$ to DBNBS, obtained from the photoreaction of Fe^{III}-T2MPyP (2×10^{-4} mol dm^{-3}) with 4-aminobutyric acid and *N*-acetylglycine (0.2 mol dm^{-3}) in the presence of DBNBS (5×10^{-3} mol dm^{-3}) in anaerobic aqueous acid (pH 3.1)

acyloxyl radicals (Scheme 1).[11–13] Thus a faster rate of decarboxylation is able to compete more successfully with recombination with Fe^{II}T2MPyP to give the starting complex (the back reaction). This explanation is based on the concentration of the initial iron(III) porphyrin carboxylate complex being approximately the same for all the carboxylic acids: UV–VIS spectroscopy supports this conclusion for complexes of the type **3**, where R is uncharged, but not for the amino acid ligands or betaine where R is positively charged. We conclude that charge repulsion between the positively charged porphyrin ligand and the positive charge on the nitrogen of the amino acid ensures that the position of the equilibrium shown in Scheme 3 lies well



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Scheme 3

to the left-hand side. We believe that, as a result, the low concentration of the iron(III) porphyrin–carboxylate complex leads to a low rate of photoreduction, and that detailed considerations (below) support this conclusion.

Comparing the photoreactions of glycine, 4-aminobutyric acid and 6-aminohexanoic acid shows that increasing the separation between the NH_3^+ and CO_2H groups results in an increased rate of reaction. However, all three amino acids react more slowly than propionic acid where R in **3** is neutral. This difference in reactivity cannot arise from an inductive effect of the NH_3^+ group since this would be too attenuated in 6-aminohexanoic acid to influence the formation of the acyloxyl radical or the alkyl radical, following decarboxylation.

The main cause for the rate changes must be the charge repulsion between the cationic porphyrin and cationic amino acid ligands, described above, which directly influences the concentration of the photoactive iron(III) porphyrin–carboxylate complex. Thus, moving the positively charged NH_3^+ group further from the carboxy group makes complex formation more favourable and results in an increased rate of photoreaction. Support for this conclusion comes from the rate of iron(II) formation in the photoreaction of the *N*-acylated species, 4-acetamidobutyric acid, which does not have a formal positive charge on the nitrogen. The porphyrin is extensively complexed to this acid (UV–VIS spectroscopy) and the rate of reaction is comparable to that of propionic acid (Table 1 and Fig. 2).

The photoreduction of Fe^{III}T2MPyP by *N*-acetylglycine is, perhaps surprisingly, the fastest of the reactions measured at pH 3.1. This acid, like propionic acid, provides a neutral ligand in the iron(III) carboxylate complex, however, its reaction is six times faster than that of propionic acid. We believe that this arises from the more rapid decarboxylation of the α-amidoacyloxyl radical to give the resonance stabilised amidomethyl radical.

The EPR spin-trapping experiments confirm that decarboxylation takes place with all the amino acids and that the expected radicals are produced (Table 2). Furthermore, the signal intensities of the EPR spectra of the spin-adducts increases in the order glycine < L-alanine < 4-aminobutyric acid < 4-acetamidobutyric acid. This supports UV–VIS studies since the increase in EPR signal intensities parallels the increase in the rate of iron(II) formation. The difference in rates of reaction of the two α-amino acids is as expected since L-alanine gives a secondary carbon radical, the rate of formation of which would be expected to be faster than the reaction of glycine which forms a primary radical.[11] The reactions of the two 4-substituted butyric acids give primary carbon spin-adducts of DBNBS with the same hyperfine splitting constants; however, the *N*-acylated compound reacts faster because, as can be seen by UV–VIS spectroscopy, the neutral ligand complexes significantly better with the iron(III) porphyrin.

In the photoreactions of Fe^{III}T2MPyP with the two 4-substituted butyric acids, EPR spectroscopy revealed a small background signal from secondary carbon-radical adducts which increased in intensity on prolonged photolysis. This suggests that a minor side reaction involving hydrogen atom abstraction from the amino acid was also occurring. Confirmation for this conclusion came from the photolysis (UV light) of a solution of 4-aminobutyric acid and hydrogen peroxide in the presence of DBNBS which generated a mixture of spin-adducts from hydroxyl radical mediated hydrogen abstraction from the C–H bonds. The hyperfine splittings of these spin-adducts are identical to the weak background signals from the photoreaction of 4-aminobutyric acid and Fe^{III}T2MPyP. 4-Acetamidobutyric when used in place of 4-aminobutyric acid behaved similarly. The structures of the trapped radicals are not known but it is likely that they have the radical centres α and β (but not γ) to the carboxyl group (Table 2). It is noteworthy that photolysis of H_2O_2 in the presence of L-glutamic acid has been reported to result in hydrogen abstraction α to the carboxyl group in the side chain (a_N 1.35; a_H 0.56 mT).[15] The species that gives rise to the secondary carbon radicals in the present study is unclear; however, it could be the hydroxyl radical from a competing photolysis of complex **5** present in the aqueous solutions. In agreement with the latter conclusion, the oxidation of alkanes, initiated by hydroxyl radicals, generated by the photocleavage of the iron–hydroxyl bond in hydroxyiron(III) porphyrins analogous to **5**, has been reported in a very recent study by Maldotti *et al.*[9]

Table 3 Times taken to reduce half the iron(III) porphyrin ($t_{\frac{1}{2}}$) in the photolysis of Fe^{III}T2MPyP complexes of dibasic amino acids and derivatives in aqueous solution at pH 3.1[a]

Acid	Major species at pH 3.1	$t_{\frac{1}{2}}$, time for 50% reduction/s[b]
L-Aspartic acid	$H_3\overset{+}{N}CH(CO_2^-)CH_2CO_2H$	150
N-Boc-L-aspartic acid	$BocNHCH(CO_2^-)CH_2CO_2H$	13
L-Glutamic acid	$H_3\overset{+}{N}CH(CO_2^-)CH_2CH_2CO_2H$	150
N-Acetyl-L-glutamic acid	$AcNHCH(CO_2H)CH_2CH_2CO_2H$	25
N-Boc-L-glutamic acid	$BocNHCH(CO_2H)CH_2CH_2CO_2H$	9
L-Glutamic acid 5-methyl ester	$H_3\overset{+}{N}CH(CO_2^-)CH_2CH_2CO_2Me$	720
Succinic acid	$HO_2CCH_2CH_2CO_2H$	120

[a] Fe^{III}T2MPyP, 1×10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}. [b] ±10%.

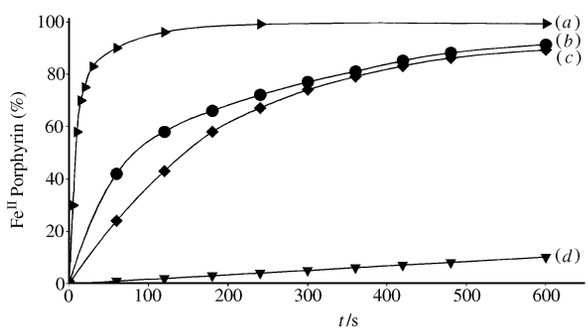

Fig. 4 The formation of iron(II) porphyrin as a function of time in the photoreactions of Fe^{III}T2MPyP (10^{-5} mol dm^{-3}) in the presence of (*a*) *N*-Boc-L-glutamic acid, (*b*) propionic acid, (*c*) L-glutamic acid and (*d*) glycine (0.1 mol dm^{-3}) in anaerobic aqueous acid (pH 3.1)

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The photoreactions of dibasic amino acids in aqueous acid (pH 3–6)

Results. Photolysis of an anaerobic, aqueous solution of Fe^{III}T2MPyP (1×10^{-5} mol dm^{-3}) and L-aspartic or L-glutamic acid (0.1 mol dm^{-3}) (pH 3.1) leads to the rapid reduction of the iron(III) (Soret band λ_{max} 396 nm) to iron(II) porphyrin (Soret band, λ_{max} 430 nm). These UV–VIS spectral changes are the same as those observed with the monobasic amino acids. The L-aspartic and L-glutamic acid reactions each took 150 s for 50% conversion of iron(III) to iron(II) porphyrin and the comparator, succinic acid, was slightly quicker (120 s). *N*-Acylated analogues of L-glutamic and L-aspartic acid reacted extremely fast whilst the reaction of the 5-methyl ester of L-glutamic acid was extremely slow (Table 3). UV–VIS spectroscopy shows that the two dibasic amino acids have a greater binding affinity for Fe^{III}T2MPyP than the monobasic amino acids described above.

Fig. 4 shows a comparison of the rates of iron(II) formation

Table 4 EPR parameters of the radical adducts formed in the photoreactions of Fe^{III}T2MPyP complexes of selected dibasic amino acids and derivatives in the presence of DBNBS[a]

	Hyperfine splittings[b]/mT		
Dibasic acid	a_N	a_H	Assignment of trapped radical
L-Glutamic acid	1.39(t)	1.17(t)	$H_3\overset{+}{N}CH(CO_2^-)CH_2\dot{C}H_2$
N-Acetyl-L-glutamic acid	1.40(t)	1.19(t)	$AcNC\dot{H}(CO_2H)CH_2CH_2$
	1.39(t)	0.65(d)	$AcNH\dot{C}HCH_2CH_2CO_2H$
	0.28(t)		
N-Boc-L-glutamic acid	1.39(t)	1.18(t)	$BocNHCH(CO_2H)CH_2\dot{C}H_2$
L-Glutamic acid 5-Methyl ester	1.31(t)	0.77(d)	$H_3\overset{+}{N}\dot{C}HCH_2CH_2CO_2Me$
N-Boc-L-aspartic acid	1.36(t)	0.94(t)	$BocNHCH(CO_2H)\dot{C}H_2$
Succinic acid	1.38(t)	1.19(t)	$HO_2CCH_2\dot{C}H_2$

[a] Fe^{III}T2MPyP, 2×10^{-4} mol dm^{-3}; dibasic acid, 0.2 mol dm^{-3}; DBNBS, 5×10^{-3} mol dm^{-3}; pH 3.1. [b] ±0.01 mT.

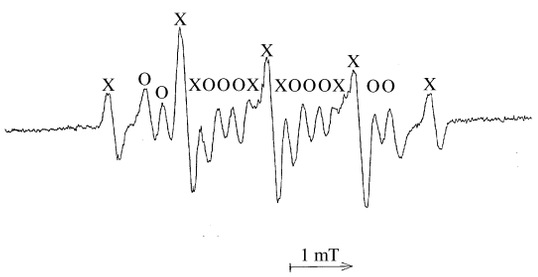
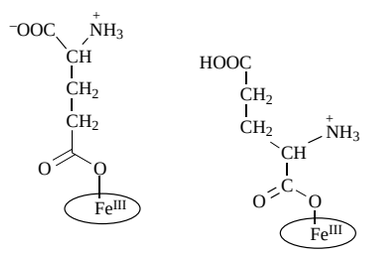


Fig. 5 EPR spectra of the adducts of $^{\bullet}CH_2CH_2(CO_2H)NHAc$ (t of t, X) and $^{\bullet}CH(NHAc)CH_2CH_2CO_2H$ (t of d of t, 10 of 18 lines identified, O) to DBNBS, obtained from the photoreaction of Fe^{III}T2MPyP (2×10^{-4} mol dm^{-3}) with *N*-acetyl-L-glutamic acid (0.2 mol dm^{-3}) in the presence of DBNBS (5×10^{-3} mol dm^{-3}) in anaerobic aqueous acid (pH 3.1)

for the slowest reaction monitored (glycine), a typical alkyl carboxylic acid (propionic acid), a dibasic and an *N*-acylated-dibasic amino acid (L-glutamic and *N*-Boc-L-glutamic acid). It is clear that the L-glutamic acid complex (and that of L-aspartic acid, not shown) which has a rate of reaction approaching that of propionic acid, is much faster than that of glycine. The rate of reaction of *N*-Boc -L-glutamic acid, the fastest rate observed, is >400 times that of glycine.

Spin-trapping experiments showed that the photolysis of an anaerobic aqueous solution of Fe^{III}T2MPyP (2×10^{-4} mol dm^{-3}) and L-glutamic acid (0.2 mol dm^{-3}) in the presence of DBNBS (5×10^{-3} mol dm^{-3}) at pH 3.1 gave an immediate strong signal from a primary radical adduct: this is more intense than that from 4-aminobutyric acid (Fig. 3) but with almost identical hyperfine splittings (Table 4). Photolysis of solutions of Fe^{III}T2MPyP with succinic acid or *N*-acetyl-L-glutamic acid at pH 3.1 also gave very strong signals from a primary radical adduct to DBNBS. However, the latter photolysis also generated a radical adduct we assign to a secondary radical (Fig. 5); confirmation for this interpretation of the spectrum was obtained using computer simulation which indicates that the secondary and primary radical adducts were in the ratio 2:1 after 4 min of photolysis. Replacing the *N*-acetyl group with *N*-Boc gave an intense signal from a primary radical together with a signal from an adduct too weak to assign, which may be from the secondary radical from loss of the carboxy group α to the amino group. In contrast the EPR spectrum obtained from *N*-Boc-L-aspartic acid in the presence of DBNBS was a mixture of at least three species; the dominant signal, a triplet of triplets, we tentatively assign to the adduct of the primary radical shown in Table 4. Photolysis of the 5-methyl ester of L-glutamic acid, where complexation with the side-chain carboxyl group is effectively blocked, with Fe^{III}T2MPyP in the presence of DBNBS, (pH 3.1) gave an EPR spectrum of a secondary radical adduct with very similar hyperfine constants to that obtained from L-alanine.

Discussion. UV–VIS spectroscopy shows that both L-aspartic and L-glutamic acids complex with Fe^{III}T2MPyP significantly better than the monobasic amino acids. Consequently, their rates of iron(II) porphyrin formation during photolysis are faster and approach that of propionic acid. This suggests that the dicarboxylic acids bind through the side-chain carboxy (**6**) rather than the α carboxy group (**7**) and the zwitterionic amino–



6 **7**

carboxylate ligand is then effectively a neutral entity. Binding at the α carboxy group would generate a positively charged ligand and a weaker complex. EPR spectroscopy supports complexation through the γ- rather than the α-carboxylic acid group. Photolysis of L-glutamic acid and Fe^{III}T2MPyP in the presence of DBNBS gave a primary radical spin-adduct, consistent with decarboxylation on the side-chain. Further support comes from the reaction of the 5-methyl ester of L-glutamic acid (where side chain complexation is blocked); the rate of iron(II) porphyrin formation was very slow and comparable to that of L-alanine. The former, which is a monobasic acid, forms a positively charged ligand and is forced to react *via* the carboxy group α to the NH_3^+. Likewise the EPR spectrum obtained in the presence of DBNBS is that of a secondary radical adduct similar to that obtained from L-alanine.

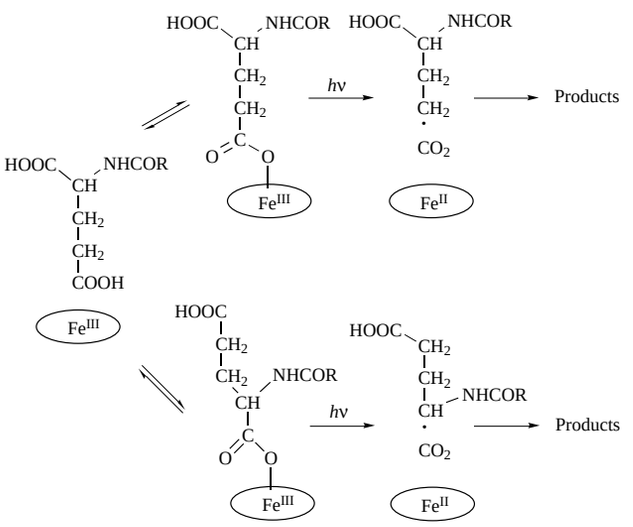
Interestingly, the rates of Fe^{II}T2MPyP formation in the photoreactions of *N*-acyl-L-glutamic and *N*-Boc-L-aspartic acids (Table 3 and Fig. 4) are much faster than those of succinic acid and the corresponding amino acids. One inference is that the binding of the dibasic *N*-acylamino acids is not restricted to the side-chain carboxy group since the rates of reaction are faster than that expected for the formation of a primary radical. Furthermore binding to the α-carboxy group should favour the reaction since, as discussed above for *N*-acetylglycine, it results after decarboxylation in the formation of the stabilised α-amido radical (Scheme 4). That the photoreaction of *N*-Boc-L-glutamic acid is faster than that of *N*-acetyl-L-glutamic acid may be a consequence of the bulk of the Boc group which discourages recombination of Fe^{II}T2MPyP and the acyloxyl radical (the back reaction) following photolysis.

Since *N*-acetyl-L-glutamic acid can complex with Fe^{III}-T2MPyP *via* either of its carboxy groups, its photodecarboxylation, unlike that of L-glutamic acid, is relatively unselective and gives a mixture of primary and secondary radicals, as seen in the EPR spectra of the DBNBS adducts (Fig. 5). Interest-

Table 5 Time taken to reduce half of the iron(III) porphyrin ($t_{\frac{1}{2}}$) in the photolysis of Fe^{III}T2MPyP complexes of selected amino acids and their derivatives in aqueous solution at pH 9.0 [a]

Carboxylic acid	$t_{\frac{1}{2}}$, time for 50% reduction/s [b]
Glycine	180
N-Acetylglycine	Unreactive [c]
L-Alanine	180
4-Aminobutyric acid	720
4-Aminobutyric acid [d]	360
4-Acetamidobutyric acid	Unreactive [c]
L-Aspartic acid	25
L-Glutamic acid	30
N-Acetyl-L-glutamic acid	210
Propionic acid	Unreactive [c]

[a] Fe^{III}T2MPyP, 1×10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}. [b] ±10%. [c] No significant change in absorbance. [d] Reaction carried out at pH 10.0.



Scheme 4

ingly, only the primary-radical adduct with DBNBS was detected in the photoreaction of *N*-Boc-L-glutamic acid. We suggest that this probably arises from steric hindrance of the Boc group which hinders trapping of the secondary radical.

The photoreactions of mono- and di-basic amino acids in aqueous base (pH 9.0 and 10.0)

Results. Photolysis of an aqueous solution of glycine or L-alanine with Fe^{III}T2MPyP at pH 9.0, using the same reagent concentrations as described above for reactions at pH 3.1, resulted in the rapid reduction of the iron(III) to iron(II) porphyrin with a shift of the Soret band from 420 to 430 nm and a change of the broad α, β band at 540 nm into two distinct bands at 532 and 564 nm. The time for glycine and L-alanine to bring about 50% reduction of Fe^{III}T2MPyP (*ca.* 3 min) is markedly less than those for reaction at pH 3.1 (65 and 20 min, respectively). The reactions are also dramatically different from that of propionic acid which at pH 9.0 is unreactive (Fig. 6).

The times for 50% conversion of iron(III) to iron(II) porphyrin in the photoreactions of a selection of mono- and di-basic amino acids and their *N*-acetyl analogues at pH 9.0 reveal that the dibasic amino acids react fastest (Table 5). Furthermore, in contrast to the reactions at pH 3.1, acylating the nitrogen atom decreases the rate of reaction of both mono- and di-basic acids considerably. Thus *N*-acetylglycine is inert at pH 9.0. The photoreaction of 4-aminobutyric acid is four times slower than that of glycine. Interestingly, increasing the pH of the reaction to 10.0 increases the rate of the former reaction. 4-Acetamidobutyric acid is, however, unreactive even at pH 10.0. These differences in reaction rates are illustrated in Fig. 6.

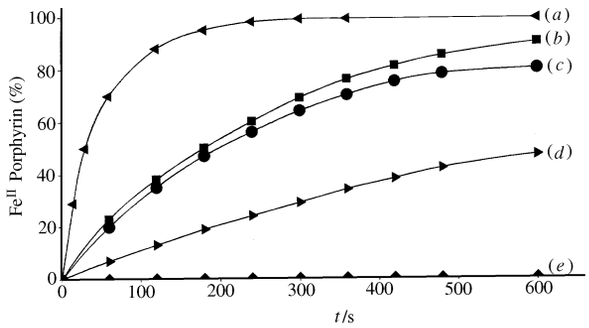


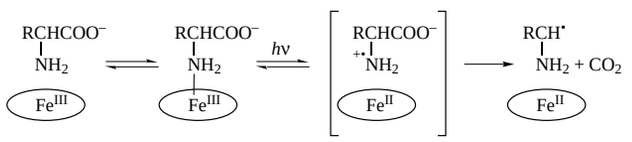
Fig. 6 The formation of iron(II) porphyrin as a function of time in the photoreactions of Fe^{III}T2MPyP (10^{-5} mol dm^{-3}) in the presence of (*a*) L-glutamic acid, (*b*) glycine, (*c*) *N*-acetyl-L-glutamic acid, (*d*) 4-aminobutyric acid and (*e*) propionic acid (0.1 mol dm^{-3}) in anaerobic aqueous base (pH 9.0)

EPR studies show that the photoreactions of all the α-amino acids and of 4-aminobutyric acid, in the presence of DMPO, give adducts of carbon-centred free radicals. Furthermore, in parallel with the increase in rate of iron(II) formation, noted above, the EPR signal intensities increase on changing the pH from 3.1 to 9.0. DBNBS, however, could not be used as a spin trap for the photoreactions of amino acids at pH 9 since UV–VIS studies showed that Fe^{III}T2MPyP in these reactions was completely reduced to Fe^{II}T2MPyP prior to photolysis. Control reactions showed that no reduction occurred in the absence of an α-amino acid, or at pH 3.1.

In basic solution the photoreactions of the *N*-acetylated derivatives of glycine and L-glutamic acid with DBNBS and Fe^{III}T2MPyP gave EPR spectra from secondary-radical adducts (Table 6).

UV–VIS spectra of the reaction mixtures at pH 9.0 show that whereas the α-amino acids form distinct complexes with Fe^{III}-T2MPyP there is no evidence of complexation of propionic acid or 4-aminobutyric acid. However, increasing the pH to 10.0 leads to complexation with 4-aminobutyric acid although propionic acid remains uncomplexed.

Discussion. The nature of Fe^{III}T2MPyP in aqueous solution over a range of pH values has been well documented;[17–21] at pH < 6 a diaquo species is prevalent, which on increasing the pH to 11 is replaced by the hydroxyiron species (**5**).[20,21] Both species are high-spin.[17–19] At pH > 11 a further change occurs to give a low-spin bis-ligated hydroxy species,[19–21] and possibly a high-spin hydroxyiron(II) species.[19] In the presence of a carboxylic acid, as discussed earlier,[11] the diaquo species is replaced by the carboxylate ligated iron porphyrin at pH 2–6, (**3**). However, in the pH range 6–11, the hydroxy complex still dominates since the carboxylate anion cannot compete successfully with the hydroxide anion as a ligand for the iron porphyrin. The UV–VIS spectra of Fe^{III}T2MPyP at pH 9.0 in the presence and absence of propionic acid are very similar, confirming that the amount of carboxylate complex present at this pH is very small. In contrast UV–VIS spectroscopy shows that L-alanine under the same conditions clearly ligates to the iron(III) porphyrin. This suggests that the amino acid binds through the nitrogen atom, an option not open to propionic acid, to form complex (**8**) (see Scheme 5).



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Scheme 5 The sixth ligand on the iron porphyrin is omitted for clarity

It is well documented that the addition of nitrogen bases to iron(III) tetraphenylporphyrins in non-polar solvents generally

Table 6 The EPR parameters of the radical adducts formed in the photoreactions of Fe^{III}T2MPyP complexes of selected amino acids and their derivatives in the presence of DMPO and DBNBS in basic solution[a]

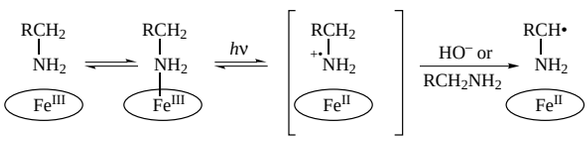
Carboxylic acid	Spin trap[a]	pH	Hyperfine splittings/mT[b] a_N	a_H	Assignment of trapped radical
Glycine	DMPO	9.0	1.56(t)	2.32(d)	$R^{\bullet}$ ($NH_2CH_2^{\bullet}$)
N-Acetylglycine	DBNBS	9.0	1.39(t) 0.25(t)	0.83(t)	$AcNHCH_2^{\bullet}$
L-Alanine	DMPO	9.0	1.58(t)	2.32(d)	$R^{\bullet}$ ($NH_2\dot{C}HCH_3$)
4-Aminobutyric acid	DMPO	10.0	1.58(t)	2.27(d)	$R^{\bullet}$ [$NH_2\dot{C}H(CH_2)_2CO_2^-$]
L-Aspartic acid	DMPO	9.0	1.57(t)	2.24(d)	$R^{\bullet}$ ($NH_2\dot{C}HCH_2CO_2^-$)
L-Glutamic acid	DMPO	9.0	1.58(t)	2.27(d)	$R^{\bullet}$ [$NH_2\dot{C}H(CH_2)_2CO_2^-$]
N-Acetyl-L-glutamic acid	DBNBS	10.0	1.39(t) 0.28(t)	0.65(t)	$AcNH\dot{C}HCH_2CH_2CO_2^-$

[a] Fe^{III}T2MPyP, 2×10^{-4} mol dm^{-3}; carboxylic acid, 0.2 mol dm^{-3}; DMPO, 5×10^{-2} mol dm^{-3} and DBNBS, 5×10^{-3} mol dm^{-3}. [b] ±10% (±0.01 mT).

leads to a bis-ligated, low-spin iron(III) complex.[22–28] The equilibria involved are such that the second equilibrium constant for formation of the bis-complex is larger than that of the first for mono-ligation and consequently iron(III) porphyrins prefer to be bis-ligated. For this reason it is probable that the amino acid complexes in this study are also bis-ligated (not shown in Scheme 5) and low spin. The formation of such complexes leads to the replacement of the bands in the visible spectrum of Fe^{III}-T2MPyP, between 500 and 700 nm [high-spin iron(III) complex], by a single band at *ca.* 550 nm, characteristic of a low-spin bis-ligated iron(III) species.[23] In agreement with this, the latter absorption band is present in the UV–VIS spectra of Fe^{III}T2MPyP in the presence of the amino acids glycine, L-alanine, L-aspartic acid and L-glutamic acid at pH 9.0 but not in the corresponding spectra of Fe^{III}T2MPyP in the presence of propionic acid and the α-amido acids. In addition the UV–VIS spectra of the iron(II) species, formed in the photoreactions with the amino acids are typical of bis-ligated low-spin iron(II) porphyrins.[29–31] These usually show two characteristic bands in the region 500–600 nm. For the photoreactions of glycine, L-alanine, L-aspartic acid and L-glutamic acid these are observed at 532 and 564 nm.

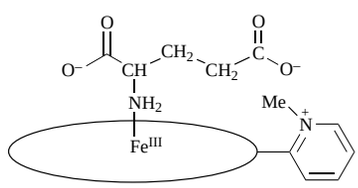
The photoreactions of the α-amino acid complexes at pH 9.0 are very fast compared with the equivalent reactions under acidic conditions (pH 3.1) and compared with that of propionic acid at pH 9.0. These differences can also be accounted for assuming that at pH 9.0 the amino acids ligate through the nitrogen atom. Irradiation of the resulting complex (**8**) brings about a ligand-to-metal electron transfer to form the aminium radical cation and the iron(II) porphyrin in a solvent cage (Scheme 5). The radical cation can either recombine with the iron(II) porphyrin to regenerate the starting complex or decarboxylate to form the α-aminoalkyl radical. The decarboxylation of α-amino acid radical cations, which is very rapid, has been thoroughly discussed in a recent paper by Armstrong *et al.*[32] Following decarboxylation, the iron(II) porphyrin is stabilised by bis-ligation with unreacted amino acid. Support for this mechanism comes from the lower rates of reaction of the *N*-acetylated amino acids. Amido groups by comparison with amines are poor ligands for the iron(III) porphyrins. Thus the photoreactions of *N*-acetyl-L-glutamic acid and *N*-acetylglycine are much slower than those of their parent amino acids.

The rate of reaction of 4-aminobutyric acid at pH 9.0 is significantly less than those of the α-amino acids glycine and L-alanine. In part this is due to the higher pK_a of the former (pK_a 10.5) which results in a relatively low concentration of complex with Fe^{III}T2MPyP. Increasing the pH of the reaction mixture to 10.0 results in more of the complex and a faster rate of reaction. However, even at pH 10.0 the rate of the photoreaction of 4-aminobutyric acid is lower than those of the α-amino acids at pH 9.0. We interpret this in terms of the alternative reactions of the solvent-caged aminium radical cations. For the α-amino acids the forward reaction involves the ready loss of CO_2 whereas with 4-aminobutyric acid a base is required to remove an α-proton; the latter process is less effective at competing with the back reaction to regenerate the initial complex (Scheme 6).



Scheme 6 The sixth ligand on the iron porphyrin is omitted for clarity

The significantly faster photoreactions of the dibasic acids, L-glutamic and L-aspartic acid, compared with the monobasic compounds we attribute to an electrostatic interaction between the negative charge on the side chain carboxylate groups of the former with the positively charged *N*-methylpyridinium groups (**9**). This favours ligation and leads to a faster reaction.



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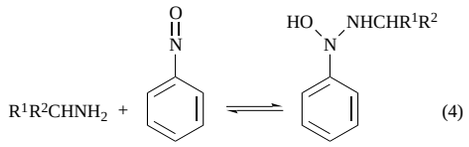
The EPR spin-trapping experiments with DMPO show that the photoreactions of the α-amino acids and Fe^{III}T2MPyP at pH 9.0 generate carbon-centred radicals (Table 6). We believe these are α-aminoalkyl radicals, arising from decarboxylation of the amino acid radical cations (Scheme 5), even though such radicals are easily oxidised and can be difficult to detect in a redox system. It is noteworthy that they have been observed previously by EPR spectroscopy as adducts of the spin trap 2-methyl-2-nitrosopropane.[33]

It was not possible to confirm the identity of the radicals by spin-trapping with DBNBS since, in basic solution, DBNBS and α-amino acids bring about the rapid reduction of the iron(III) porphyrin prior to illumination. Nucleophilic addition of amines to nitrosobenzenes is well known[34] [reaction (4)]; consequently DBNBS may be prone to nucleophilic attack by amino acids in basic solution to give the corresponding hydroxyhydrazine [reaction (5)]; this latter species could bring about the reduction of the iron(III) porphyrin. Alternatively, amino acids have been reported[35] to give signals from spin-adducts on mixing with DBNBS at room temperature (pH 7.5). The mechanism of this reaction is far from clear but it is thought to involve, as a first step, the formation of a hydroxyl-



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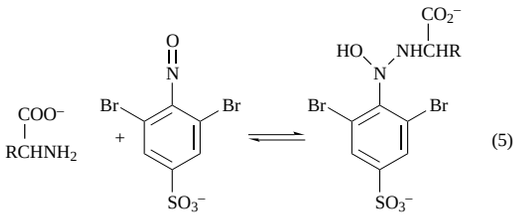

(5)

DBNBS

amine, which could again reduce the iron(III) porphyrin. The reduction of Fe^{III}T2MPyP does not occur at pH 3.1 since protonation of the amino acid in acidic solution makes it unreactive towards DBNBS. Consequently, the spin trap can be used to identify the carbon-centred radicals formed in acidic photoreactions.

Support for the formation of α-aminoalkyl radicals in the photoreactions of α-amino acids in basic solution comes from the corresponding reactions of *N*-acetylglycine and *N*-acetyl-L-glutamic acid. DBNBS with these amido acids does not bring about the reduction of Fe^{III}T2MPyP prior to illumination, consequently it can be successfully used as a spin trap. *N*-Acetylglycine and *N*-acetyl-L-glutamic acids give adducts which we assign to the primary and secondary α-amidoalkyl radicals, *N*-$AcNHCH_2^{\bullet}$ and *N*-$AcNH\dot{C}HCH_2CH_2CO_2^-$, respectively. It is noteworthy that at pH 10.0 the photodecarboxylation of *N*-acetyl-L-glutamic acid is selective for the α-carboxy group whereas at pH 3.1 reaction occurs at both the α and γ positions. These observations and the lack of reactivity of alkyl carboxylic acids at 10.0 suggest that the photoreaction of α-amido acids, like those of amino acids in basic solution, involves ligation of the amide nitrogens rather than the carboxyl group followed by electron-transfer to the iron(III) porphyrin.

Conclusions

(*i*) In aqueous acid, monobasic amino acids form weak complexes with the cationic iron(III) tetrakis(2-*N*-methylpyridyl)-porphyrin, compared with alkylcarboxylic acids, due to unfavourable charge interactions. Consequently, photolysis of the former solutions leads to a relatively slow overall rate of photofragmentation to give the iron(II) porphyrin.

(*ii*) Increasing the separation between the NH_3^+ and carboxy group in the amino acid results in an increase in the rate of the photoreduction.

(*iii*) Removal of the positive charge on the carboxylate ligand by *N*-acylation of the amino acid leads to a large increase in the rate of the photoreaction.

(*iv*) Dibasic amino acids in acidic solution ligate to Fe^{III}-T2MPyP through the side-chain carboxy group; the resulting zwitterionic ligand is effectively neutral which favours initial complex formation. The photoreactions of these complexes are rapid and selectively lead to side-chain decarboxylation.

(*v*) *N*-Acylation of the dibasic acids enhances the rate of reaction but removes the side chain selectivity since both carboxylic acid groups compete in complexation with Fe^{III}T2MPyP.

(*vi*) In basic aqueous solution, α-amino acids complex to Fe^{III}T2MPyP *via* their amino groups and irradiation brings about electron transfer to the iron followed by decarboxylation of the resulting aminium radical. *N*-Acylation inhibits complexation and reduces the rate of the photoreaction.

Experimental

Materials

The amino and carboxylic acids were commercially available and used without further purification. The preparation of iron(III) tetrakis(2-*N*-methylpyridyl)porphyrin has been reported previously.[36] DMPO (Sigma) was purified with activated charcoal, and DBNBS was prepared and purified according to the method described by Kaur *et al.*[37]

Methods

Instrumentation

EPR spectra were recorded using a JEOL JES-RE1X spectrometer equipped with 100 kHz modulation. UV–VIS spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. As reported previously, the 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.).[11]

Photolyses

For the EPR studies, the photolyses were carried out *in situ* in an aqueous sample cell at room temp. The solutions were deoxygenated, prior to photolysis, using a stream of dioxygen free nitrogen. Hyperfine splittings were determined directly from the field scan. Spectral simulations were carried out using a program written originally by Dr M. F. Chiu and later adapted by Dr A. C. Whitwood (both of Department of Chemistry, University of York) to run on an IBM compatible 486 PC. This program allows the simulation of complex isotropic spectra of multiple radicals and takes into account the relative concentrations of each species, variations in linewidth, *g* values, multiplicity of splittings and, where necessary, second-order effects and exchange processes. In all cases, simulations were carried out with a range of parameters until the best visual fit between the experimental and simulated spectra was obtained. For the UV–VIS studies, the photolyses were carried out in a sealed 1 cm pathlength quartz cuvette. The sample was degassed by repeated freeze–slow cycles on a vacuum line and then restored to atmospheric pressure with argon. The pH of the solutions was adjusted by addition of small amounts of aqueous NaOH or HCl as required.

The percentages of iron(III) and iron(II) prophyrin in the photolysed reaction mixtures were obtained, using standard spectra of the iron(III) and iron(II) porphyrins, by simultaneously monitoring the absorbances at 412 and 430 nm.

Acknowledgements

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