PERKIN 2

The mechanism of the photo-decarboxylation of alkyl- and arylmethyl-carboxylates using visible light and iron(III) tetra-(2-*N*-methylpyridyl)porphyrin pentachloride in aqueous solution

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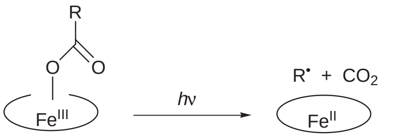
The photo-decarboxylations of a selection of alkyl-, arylmethyl- and cycloalkyl-carboxylate complexes of iron(III) tetra(2-*N*-methylpyridyl)porphyrin pentachloride in aqueous solution have been studied. An analysis of the influence of substituent electronic effects, σ^* for alkyl- and σ for arylmethyl-carboxylic acids, and α,α-deuteration on the rates of reaction indicates that the reactions involve the discrete formation of a carboxyl radical. Thus after the initial photo-excitation, there is a rate-determining homolytic cleavage of the iron–carboxylate bond followed by rapid decarboxylation of the resultant carboxyl radical. Support for this two-step mechanism, over an alternative synchronous process, comes from a study of the influence of ring size on the reactions of five cycloalkylcarboxylic acids.

Introduction

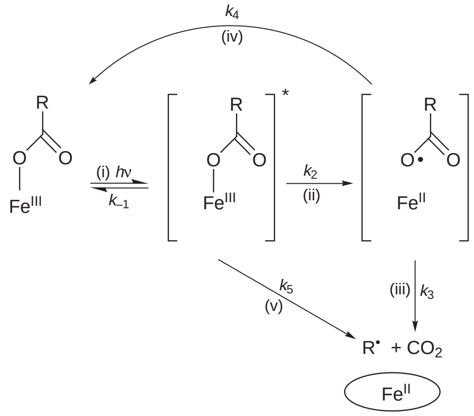
The photo-redox cleavage of the metal–axial ligand bond in iron(III) porphyrins has been the subject of many studies in recent years.[1–11] By selective choice of the axial ligand, the reaction can be used to generate a wide range of carbon, nitrogen, oxygen and halogen radicals [reaction (1)]. Our interest in this chemistry has been to develop new routes to carbon centred radicals by photo-decarboxylation of carboxylate complexes of iron(III) porphyrins in aqueous solution [reaction (2)].[12–16] These studies have shown that the reaction is generally applicable to alkyl-, substituted alkyl-, aralkyl- and aryl-carboxylates. The rates of the reactions under anaerobic conditions can be readily followed, by UV–VIS spectroscopy, by monitoring the appearance of the iron(II) porphyrin and the carbon radicals can be identified by EPR spectroscopy using spin traps.

(1)

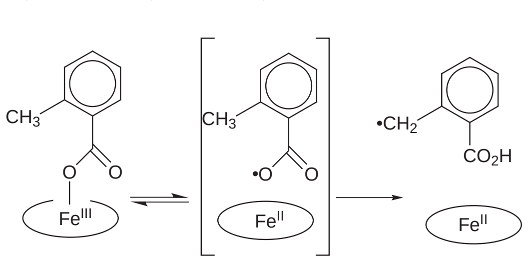


(2)

The mechanism we have proposed for this photo-reaction involves a light initiated electron-transfer from the carboxylate ligand to the iron(III) porphyrin to give a solvent-caged iron(II) porphyrin and carboxyl radical [Scheme 1, step (ii)]. In further reactions, these species either undergo geminate pair recombination to regenerate the starting complex [step (iv)] or, following decarboxylation, give the carbon radical and iron(II) porphyrin [step (iii)] which can be detected as described above. This mechanism, which requires the carboxyl radical to be formed as a discrete intermediate with the iron(II) porphyrin in the solvent cage, accounts for the structure-dependence of the rates of the photo-reduction of the individual carboxylate complexes in terms of how effectively decarboxylation [step (iii)] competes with the back reaction [step (iv)]. An alternative mechanism, which involves the direct generation of the carbon radical and carbon dioxide from the photo-excited iron porphyrin–carboxylate complex without the intermediacy of the carboxyl radical {Scheme 1, [step (v)]}, was considered unlikely and this was supported by the reactions of 2-methylbenzoic and 3,3-dimethylacrylic acids.[13] These substrates form the 2-carboxybenzyl and 2-methyl-3-carboxyprop-2-enyl radicals, respectively, by intramolecular hydrogen abstraction by the initially formed carboxyl radical, in preference to the substituted phenyl and vinyl radicals by decarboxylation (Scheme 2 illustrates the reaction of 2-methylbenzoic acid). However, it could be argued that because the rates of decarboxylation of the latter substrates are relatively slow (*ca.* 2–6 × 10^6 s^{-1})[17] this could favour the discrete formation of the carboxyl radical in their reactions,



Scheme 1



Scheme 2

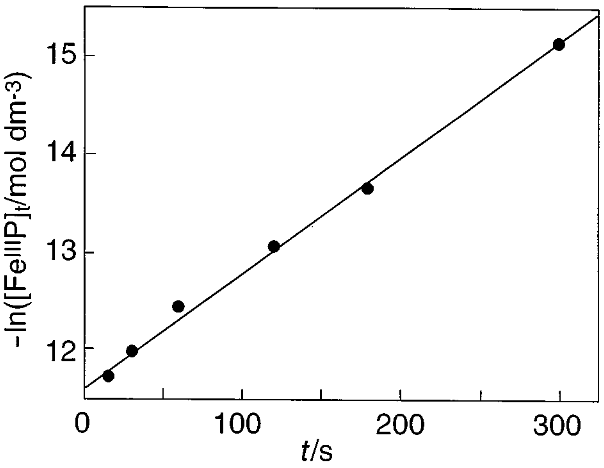


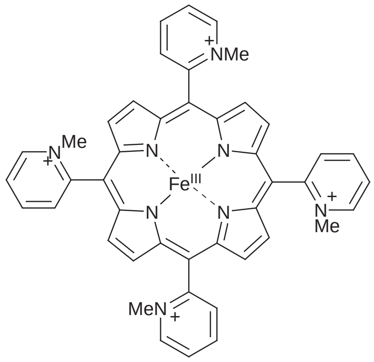
Fig. 1 A first-order plot of $-\ln([\mathrm{Fe^{III}T2MPyP}]_t/\mathrm{mol\ dm^{-3}})$ *vs.* time for the photo-reaction of the isobutyric acid–Fe^{III}T2MPyP complex in aqueous solution.

consequently the question remains as to whether or not the mechanism also holds for the reactions of substrates where decarboxylation occurs much more readily. This paper addresses this problem and shows that the carboxyl radical is a required intermediate in these photo-initiated decarboxylations.

Results and discussion

The photosystem and kinetic analysis

The photo-reactions (using visible light, $\lambda > 390$ nm) in this study were carried out with iron(III) tetra(2-*N*-methylpyridyl)porphyrin pentachloride (**1**) (Fe^{III}T2MPyP) and the carboxylic acid in aqueous solution (pH 4–5) and were followed as described previously by monitoring, with UV–VIS spectroscopy, the formation of the iron(II) porphyrin. To ensure the complete exclusion of dioxygen, the reaction solutions were thoroughly degassed by repeated freeze–thaw cycles and then back filled to atmospheric pressure with argon before illumination. Using this procedure the rates of the photo-reactions of a selection of alkyl-, aralkyl- and cycloalkyl-carboxylic acids were measured. To overcome problems from the decay of the lamp output over long periods of time, the reactions of each group of related substrates were carried out consecutively and repeatability was checked by rerunning the reaction of the first substrate at the end of the series.



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All the reactions showed good linear plots of −ln(concentration of iron(III) porphyrin), ($-\ln[\mathrm{Fe^{III}P}]_t$), against time for >3 three half-lives (for example, the reaction of isobutyric acid, Fig. 1). As pointed out very recently by Logan,[18] it is important to note that although these photo-reactions follow first-order kinetics they are not true first-order reactions. However, the k_{obs} values obtained (Tables 1–4) provide data to compare the rates of the different photo-decarboxylations. Another potential problem in measuring k_{obs} as described above arises from the selective filtration of the light by the product iron(II) porphyrin. To investigate this further the reactions were also monitored using initial rate measurements, as described previously.[15] Analysing the data by both methods gave almost identical results (*vide infra*).

Kinetic analyses of the alternative reaction mechanisms in Scheme 1 show that each of them leads to the "first-order" formation of iron(II) porphyrin or, since the total iron porphyrin concentration remains constant, the first order disappearance of iron(III) porphyrin. Thus, following photo-excitation, assuming that the solvent-caged carboxyl radical and iron(II) porphyrin can be treated as a single species, the sequence of reactions beginning with step (ii) gives the rate equation (1) and that beginning with step (v) gives rate equation (2).

$$-\mathrm{d}[\mathrm{Fe^{III}P}]/\mathrm{d}t = k_{\mathrm{obs}}I_{\mathrm{abs}},$$

$$\text{where } k_{\mathrm{obs}} = k_2k_3/(k_{-1} + k_2)(k_3 + k_4) \qquad (1)$$

$$\text{where } k_{\mathrm{obs}} = k_5/(k_5 + k_{-1}) \qquad (2)$$

For a specific iron(III) porphyrin, k_{-1} should be approximately constant for all the complexes and k_4 should also be effectively constant for all the complexes. Thus assuming $k_{-1} \gg k_2$ or k_5, eqn. (1) and (2) become eqn. (3) and (4), respectively.

$$-\mathrm{d}[\mathrm{Fe^{III}P}]/\mathrm{d}t = k_2k_3I_{\mathrm{abs}}/k_{-1}(k_3 + k_4) \qquad (3)$$

$$-\mathrm{d}[\mathrm{Fe^{III}P}]/\mathrm{d}t = k_5I_{\mathrm{abs}}/k_{-1} \qquad (4)$$

Eqn. (3) can be simplified further since primary and secondary geminate pair recombination of photodissociated species are both extremely fast processes, typically occurring in less than a pico- or a nano-second respectively ($k_4 = 10^9$–10^{12} s^{-1}).[19,20] The rate constants for decarboxylation of aliphatic carboxylic acids are in the range 10^9–10^{10} s^{-1}.[21] Thus k_4 is either $\gg k_3$ or $\approx k_3$ giving eqn. (5) and (6), respectively.

$$-\mathrm{d}[\mathrm{Fe^{III}P}]/\mathrm{d}t = k_2k_3I_{\mathrm{abs}}/k_{-1}k_4 \qquad (5)$$

$$-\mathrm{d}[\mathrm{Fe^{III}P}]/\mathrm{d}t = k_2I_{\mathrm{abs}}/2k_{-1} \qquad (6)$$

From eqn. (4), it is clear that if the photo-reaction involves a concerted cleavage of the Fe–carboxylate bond and decarboxylation [Scheme 1, step (v)], the rate will depend on k_5. Alternatively if the reaction is a stepwise process [Scheme 1, steps (ii) and (iii)], the rate will either depend on k_2k_3 [eqn. (5)] or k_2 [eqn. (6)]. The influence of substituent and structural effects in R (Scheme 1) on the rates of the photo-reductions shows conclusively that the reactions do not proceed *via* step (v) (*vide infra*).

Alkylcarboxylic acids

The rates of the photo-reactions of the alkylcarboxylic acids, as noted previously,[12,15] parallel the rates of decarboxylation of the corresponding carboxyl radicals, increasing as the alkyl group is changed in the order methyl, ethyl, 2-methylprop-1-yl, prop-2-yl and 2-methylprop-2-yl (Table 1). We argued previously that the increase in the rate of photo-reduction arises from the increase in the rate of decarboxylation of the carboxyl radicals, since whether the reaction proceeds by step (ii) or step (v), the faster the decarboxylation occurs the more effectively it can compete with the back reaction [steps (iv) and (−i) respectively], regenerating the starting complex, leading to a faster overall rate of formation of the iron(II) porphyrin. Altern-

Table 1 The measured first-order rate constants (k_{obs}) for the photo-reduction of Fe^{III}T2MPyP–alkylcarboxylate complexes in aqueous solution[a]

R in RCO_2H	$k_{obs}/10^{-3}\ s^{-1}$	σ^{*} [b]	E_s [c]
CH_3	0.5 ± 0.016	0	0.0
CH_3CH_2	4.5 ± 0.102	−0.1	−0.07
$(CH_3)_2CHCH_2$	6.5 ± 0.544	−0.125	−0.93
$(CH_3)_2CH$	11.8 ± 0.30	−0.19	−0.47
$(CH_3)_3C$	48 ± 2.11	−0.3	−1.54

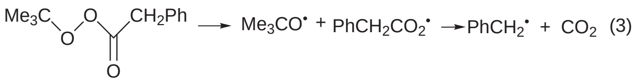
[a] Fe^{III}T2MPyP, 1×10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}. [b] σ^{*} values from ref. 22. [c] E_s values from ref. 23.

Table 2 The measured first-order rate constants (k_{obs}) for the photo-reduction of Fe^{III}T2MPyP complexes of propionic and phenylacetic acids and their α-deuterated analogues[a]

Carboxylic acid	Solvent	$k_{obs}/10^{-3}\ s^{-1}$
Propionic acid	Water	6.1 ± 0.14
α[$^2H_2$]-Propionic acid	Water	6.2 ± 0.15
Phenylacetic acid	Aqueous acetone	21.6 ± 0.9
α[$^2H_2$]-Phenylacetic acid	Aqueous acetone	21.8 ± 0.9

[a] Fe^{III}T2MPyP, 1×10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}; the output of the lamp for these experiments was reduced in order to lower the rates of the reactions.

atively, if the reaction proceeds by step (ii), the rate of reaction could simply depend on the rate of cleavage of the iron–oxygen bond following photo-excitation and the rate would be controlled by the influence of the alkyl group on the effective change from a complexed carboxylate anion to a carboxyl radical. We attempted to distinguish between these mechanisms by comparing the rates of reaction of propionic and 2,2-[$^2H_2$]propionic acids. We argued that if the decarboxylation [step (iii) or (v)] is involved in determining the rate of formation of the iron(II) porphyrin, α-deuteration should, through an α-secondary kinetic isotope effect, slow down the loss of carbon dioxide. A significant and readily detectable α-secondary isotope effect is expected for the rehybridisation of the carbon α to the carboxyl group in going from the substrate (sp^3) to the alkyl radical (sp^2) in steps (iii) or (v) of Scheme 1.[24] If, however, decarboxylation is not involved in the rate-determining step the isotope effect should be ~1.0. Our results (Table 2) show that within experimental error (±3%) the two propionic acids react at the same rate (k_H/k_D ~ 1.0), suggesting that the rate of iron(II) porphyrin formation depends on the rate of homolytic cleavage of the iron–ligand bond [step (ii)] and not decarboxylation to give the alkyl radical. In agreement with this conclusion Koenig and Wolff[25] have shown that in the thermal decomposition of *tert*-butyl α[$^2H_2$]-phenylperoxyacetate [reaction (3)], a reaction that is known to give a carboxyl radical intermediate, α-deuteration results in a very small α-secondary kinetic isotope effect, k_H/k_D = 1.06.



$$Me_3COOC(=O)CH_2Ph \longrightarrow Me_3CO^{\bullet} + PhCH_2CO_2^{\bullet} \longrightarrow PhCH_2^{\bullet} + CO_2 \quad (3)$$

Further support for the photo-reaction proceeding *via* step (ii) rather than step (v) comes from a plot of the log k_{obs} values for the alkylcarboxylic acid reactions against the Taft σ^{*} constant of the alkyl group which gives a good linear correlation (r = 0.980) with a ρ^{*} value of −6.35 ± 0.735 (Fig. 2). Using initial rate measurements a ρ^{*} value of −6.87 ± 0.666 (r = 0.986) was obtained. This large negative ρ^{*} value is in agreement with a rate-determining step in which the carboxylic acid ligand donates an electron to the metal (k_2) and effectively changes from RCO_2^- to $RCO_2^{\bullet}$. Plotting the log k_{obs} values against the steric parameter E_s gave a relatively poor linear correlation (r = 0.829) and using a dual parameter (σ^{*}, E_s) approach gave a negligible contribution from E_s and no significant improvement in the linear correlation (r = 0.981) over that using σ^{*}, from which we conclude that steric effects are unimportant in these reactions.

Table 3 The measured first-order rate constants (k_{obs}) for the photo-reduction of Fe^{III}T2MPyP–arylacetate complexes in water–acetone (1 : 1 v/v) solution[a]

X in $XC_6H_4CH_2COOH$	$k_{obs}/10^{-1}\ s^{-1}$	σ [b]	$\sigma^{\bullet}$ [c]
4-MeO	2.38 ± 0.001	−0.27	0.018
4-Me	2.05 ± 0.002	−0.17	0.015
H	1.88 ± 0.009	0	0
4-Cl	1.39 ± 0.070	0.23	0.011
3-CF_3	1.34 ± 0.060	0.43	−0.017
4-CF_3	0.89 ± 0.052	0.54	−0.009
3-NO_2	0.68 ± 0.069	0.71	
4-NO_2	0.58 ± 0.030	0.78	

[a] Fe^{III}T2MPyP, 1×10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}. [b] σ values from ref. 26. [c] $\sigma^{\bullet}$ values from ref. 27.

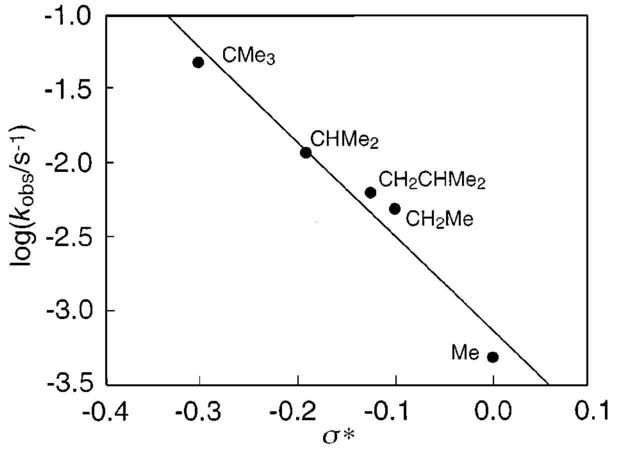


Fig. 2 The Taft plot of log(k_{obs}/s^{-1}) *vs.* σ^{*} for the photo-reaction of alkylcarboxylic acids with Fe^{III}T2MPyP in water.

Substituted phenylacetic acids

The photo-reactions of Fe^{III}T2MPyP with phenylacetic acid and with seven of its 3- or 4-substituted derivatives, in aqueous acetone (1 : 1, v/v), have been investigated. A mixed solvent system was used for this study to ensure complete dissolution of all the phenylacetic acids. Although this makes the direct comparison of the k_{obs} values for the alkyl- and aralkyl-carboxylates less meaningful, the results from the latter group of substrates are self-consistent. The first-order rate constants (Table 3) show that the rates of the reactions are increased by electron-donating groups. Thus 4-methoxyphenylacetic acid reacts approximately four times faster than the 4-nitro-analogue and a Hammett plot of log k_{obs} against σ gives a good linear correlation (r = 0.978) with ρ = −0.56 ± 0.049 (Fig. 3). As discussed above, the Taft plot suggests that step (ii) in Scheme 1, where there is significant electron-donation from the carboxylate ligand to the iron(III), is the rate-determining step, *i.e.* a complexed carboxylate anion is converted to a neutral carboxyl radical. The sign and absolute magnitude of the ρ value from the Hammett study on the phenylacetic acids supports this mechanism. A good comparative model for this reaction is the ionisation of phenylacetic acids which has a ρ of a very similar magnitude (0.471);[28] although predictably the sign is reversed because the latter reaction involves formation of a carboxylate ion from a neutral carboxylic acid (effectively a charge reversal of the photochemical process).

Table 4 The measured first-order rate constants (k_{obs}) for the photo-reduction of Fe^{III}T2MPyP–cycloalkylcarboxylate complexes in aqueous solution[a] and ^{13}C–H coupling constants of the corresponding cycloalkane

Ring size	$k_{obs}/10^{-2}$ s^{-1}	Cycloalkane, J ^{13}C–H/Hz[b]
3	0.12 ± 0.005	161
4	2.0 ± 0.045	134
5	4.7 ± 0.464	128
6	9.4 ± 0.617	124
7	11.5 ± 0.396	123

[a] Fe^{III}T2MPyP, 1 × 10^{-5} mol dm^{-3}; carboxylic acid, 0.1 mol dm^{-3}. [b] J ^{13}C–H values from ref. 34.

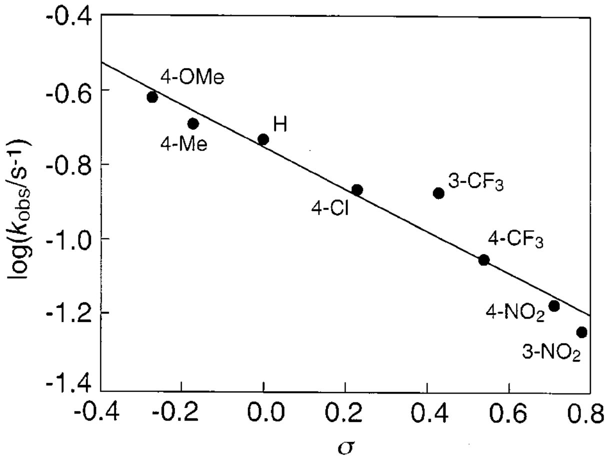


Fig. 3 The Hammett plot of log(k_{obs}/s^{-1}) *vs.* σ for the photo-reaction of arylmethylcarboxylic acids with Fe^{III}T2MPyP in water–acetone (1 : 1 v/v).

In contrast, when the log k_{obs}values are plotted against $\sigma^{\bullet}$ constants the correlation of the data is very poor ($r = 0.737$ for the six substituents for which $\sigma^{\bullet}$ constants are available). This indicates that, although the rate of decarboxylation of a phenylacetoxyl radical is very fast (~1 × 10^{9} s^{-1}),[29] the loss of carbon dioxide does not occur synchronously with cleavage of the carboxylate–iron bond [step (v) in Scheme 1]. Such a process would generate benzyl radicals and might be expected to correlate with $\sigma^{\bullet}$, particularly because the $\sigma^{\bullet}$ scale for substituent effects in radical reactions was itself devised using benzyl radicals.[27] Further evidence for the non-participation of benzyl radicals in the rate-determining step was obtained from the identical reactivity of phenylacetic and 2,2-[$^{2}H_2$]-phenylacetic acids (Table 2). As discussed above, a rate-determining step involving the formation of a benzyl radical would be expected to show a significant α-secondary kinetic isotope effect.

Cycloalkylcarboxylic acids

The photo-reactions of five cycloalkylcarboxylic acids (cyclopropane- to cycloheptane-carboxylic acid) with Fe^{III}T2MPyP have been investigated by UV–VIS spectroscopy to measure the rate of formation of the iron(II) porphyrin. These studies reveal that the rate of photo-reduction of the iron(III) porphyrin increases with ring size; the difference in reactivity between cyclopropyl- and cycloheptyl-carboxylic acids is almost 100-fold (Table 4 and Fig. 4). Comparison of these kinetic data with the results from other reactions of cycloalkyl compounds provides definitive evidence that the rate-determining step in the photo-reactions is cleavage of the iron–axial ligand bond [step (ii)] and does not involve the formation of the cycloalkyl radical [step (iii) or (v)].

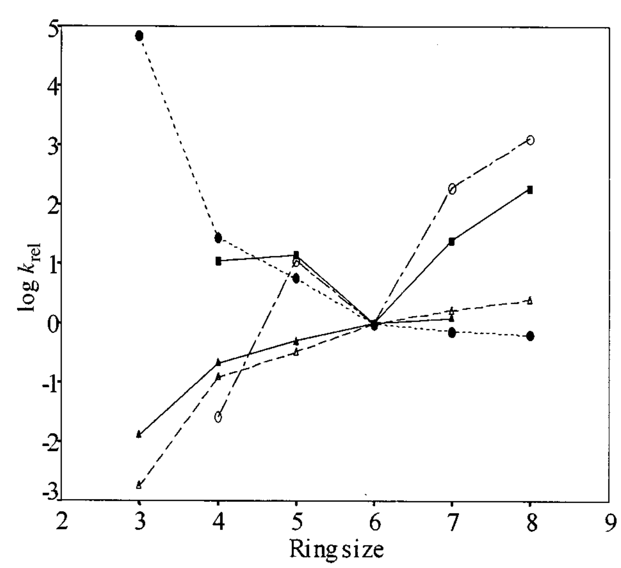
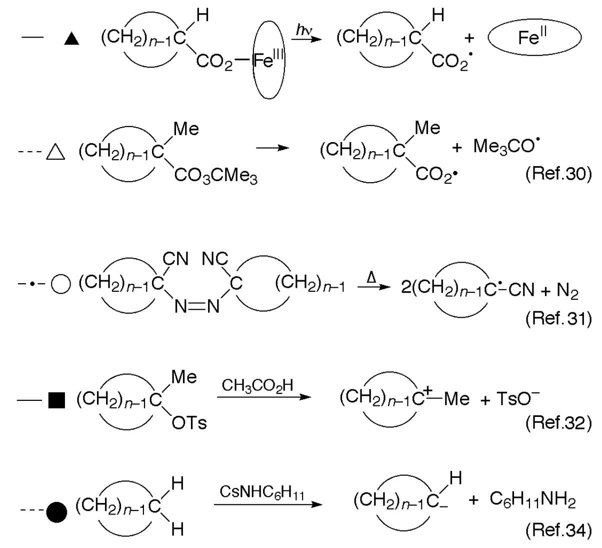


Fig. 4 Plots of log (rate constants relative to cyclohexyl standard) *vs.* ring size for the photo-reactions of cycloalkylcarboxylate–Fe^{III}T2MPyP complexes and for other reactions involving carbocations, carbanions and radicals.



The influence of ring size on the rate of formation of carbon anions, cations and radicals in saturated carbon rings has been extensively studied and can be accounted for in terms of two effects, the electronegativity of the ring carbon atoms and the hybridisation of the carbon in the transient intermediate.[35] These effects, for different reactions, are most readily compared by plotting log (rate constant) *vs.* ring size profiles standardised relative to that of a given ring size (by convention the six membered ring). For the formation of carbanions, there is no change in the hybridisation of the reaction centre and the rate is determined by its electronegativity so that the reaction is fastest with the smallest rings (the most electronegative carbons) (Fig. 4).[33,34] In contrast, for carbocation and radical forming reactions the reaction centre becomes sp^{2} hybridised and the rate *vs.* ring size profile shows a very characteristic minimum for the cyclohexyl system (Fig. 4).[31,32,35] For both these reactions the relative rates of reaction are controlled by the change in hybridisation from sp^{3} to sp^{2} which gives rise to a marked increase in conformational strain for the six membered ring compared with those of the pentyl, heptyl and octyl systems. The results from the present study do not show the minimum in rate for the cyclohexylcarboxylic acid that would be expected if the cycloalkyl radical were formed in the rate-determining step [step (iii) or (v)], instead they show a good linear dependence (gradient, -0.051 ± 0.0028; $r = 0.995$; the initial rate method gave the values -0.043 ± 0.0026 and 0.995, respectively) on the electronegativity of the ring carbons as measured by the ^{13}C–H

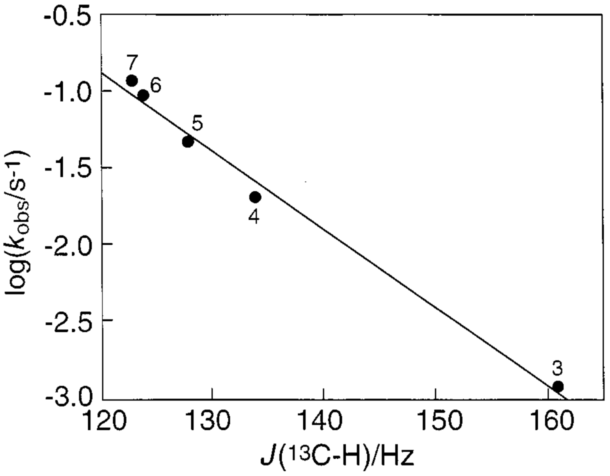


Fig. 5 Plot of log(k_{obs}/s^{-1}) for photo-reaction of cycloalkylcarboxylate–Fe^{III}T2MPyP complexes in aqueous solution *vs.* ^{13}C–H coupling constant of analogous cycloalkane.[34]

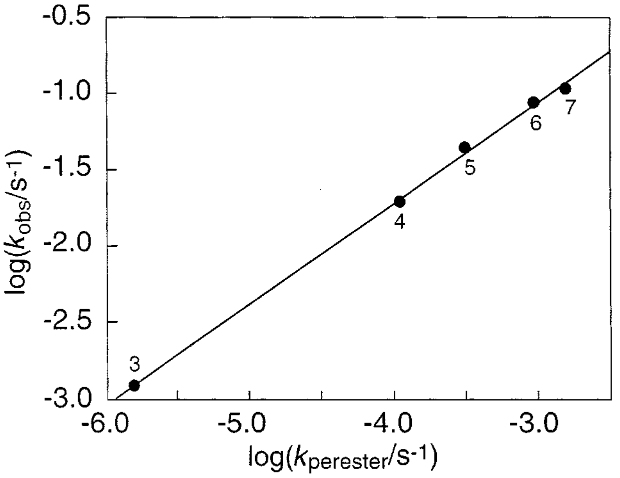
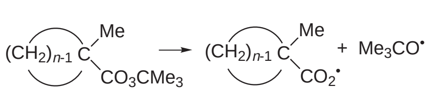


Fig. 6 Plot of log(k_{obs}/s^{-1}) for photo-reaction of cycloalkylcarboxylate–Fe^{III}T2MPyP complexes in aqueous solution *vs.* log(first-order rate constant) for thermolysis of analogous *tert*-butyl 1-methylcycloalkylperoxycarboxylates.[30]

coupling constants of the corresponding cycloalkanes (Fig. 5).[34] In this respect the photo-reactions resemble the thermolyses of the *tert*-butyl cycloalkylperoxycarboxy esters where the rate-determining step involves cleavage of the O–O bond without concomitant loss of carbon dioxide [reaction (4)].[30] The close similarity of the ring size effects on these two reactions is confirmed by the excellent linear correlation ($r = 0.999$) when log(k_{obs} for Fe^{II}T2MPyP formation) is plotted against log(k for thermolysis of *tert*-butyl 1-methylcycloalkylperoxycarboxylate)[30] (Fig. 6). It is noteworthy that the linearity of the plots in Fig. 5 and 6 shows that all five cycloalkylcarboxylic acids react by the same mechanism.



(4)

Conclusions

The influence of substituent electronic effects (σ^* and σ), kinetic isotope effects and ring size on the photo-decarboxylation of alkyl- and arylmethyl-carboxylic acid complexes of Fe^{III}-T2MPyP in aqueous solution show that, following excitation, the reaction involves two discrete steps, cleavage of the iron–carboxylate bond to form the carboxyl radical, followed by loss of carbon dioxide to give the alkyl or arylmethyl radical.

Experimental

Materials

All the carboxylic acids employed in this study were commercially available and were used without further purification. The preparation of iron(III) 5,10,15,20-tetra(2-*N*-methylpyridyl)porphyrin pentachloride has been reported previously.[36]

Instrumentation

UV–VIS spectra were recorded on Hewlett-Packard 8452A and 8453 diode array spectrometers.

Photolyses

All the photolyses were carried out as described previously, at 25 °C, using an ILC302 UV Xenon high intensity light source (300 W; $\lambda > 390$ nm) directed by a liquid light guide (Laser Lines Ltd.).[16] The solution of the iron(III) porphyrin (1×10^{-5} mol dm^{-3}) and carboxylic acid (0.1 mol dm^{-3}) in water or aqueous acetone (3 cm^3) was degassed on a vacuum line using four freeze–thaw cycles, transferred to a quartz cuvette (1 cm path length) and back filled to atmospheric pressure with argon.

The rates and initial rates of iron(II) porphyrin formation in the photolyses were obtained by monitoring the absorbance at 430 nm, the λ_{max} value for Fe^{II}T2MPyP.

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References

1 A. Tohara and M. Sato, *Chem. Lett.*, 1989, 153.
2 C. Bartocci, A. Maldotti, G. Varani, V. Carassiti, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1989, 964.
3 Y. Ito, *J. Chem. Soc., Chem. Commun.*, 1991, 622.
4 A. Maldotti, C. Bartocci, R. Armadelli, E. Polo, P. Battioni and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1991, 1487.
5 C. Bartocci, A. Maldotti, G. Varani, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1991, **30**, 1255.
6 Y. Ito, K. Kuriputo, S. Miyachi and T. Kako, *Tetrahedron Lett.*, 1991, **32**, 4007.
7 K. S. Suslik and R. A. Watson, *New J. Chem.*, 1992, **16**, 623.
8 M. Hashino, K. Veda, M. Takahashi, M. Yaraji and Y. Hamon, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 405.
9 A. Maldotti, R. Amadelli, C. Bartocci, V. Carassite, E. Polo and G. Varani, *Coord. Chem. Rev.*, 1993, **125**, 143.
10 A. Maldotti, C. Bartocci, G. Varani, A. Molinari, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1996, **35**, 1126.
11 A. Maldotti, A. Molinari, L. Andreotti, M. Fogannolo and R. Amadelli, *Chem. Commun.*, 1998, 507.
12 B. C. Gilbert, J. R. Lindsay Smith, P. MacFaul and P. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2033.
13 B. C. Gilbert, J. R. Lindsay Smith, P. MacFaul and P. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1996, 511.
14 B. C. Gilbert, G. R. Hodges, J. R. Lindsay Smith, P. MacFaul and P. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1996, 519.
15 B. C. Gilbert, G. R. Hodges, J. R. Lindsay Smith, P. MacFaul and P. Taylor, *J. Mol. Catal. A: Chem.*, 1997, **117**, 249.
16 B. C. Gilbert, J. R. Lindsay Smith, A. F. Parsons and P. K. Setchell, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1065.
17 J. Wang, M. Tsuchiya, H. Sakuragi, K. Tokumaru and I. Itoh, *Tetrahedron Lett.*, 1994, **35**, 6321.
18 S. R. Logan, *J. Chem. Educ.*, 1997, **74**, 1303.
19 B. J. Schwartz, J. C. King and C. B. Harris, in *Ultrafast dynamics of chemical systems*, ed. J. D. Simon, Kluwer, Dordrecht, 1994, p. 235.
20 T. G. Traylor, D. Magde, J. Luo, K. N. Walda, D. Bandyopadhyay, G.-Z. Wu and V. S. Shama, *J. Am. Chem. Soc.*, 1992, **114**, 904.
21 J. W. Hilbon and J. A. Pincock, *J. Am. Chem. Soc.*, 1991, **113**, 2683.
22 R. W. Taft, *J. Am. Chem. Soc.*, 1952, **74**, 2729.
23 J. Shorter, in *Correlation analysis in organic chemistry: an introduction to linear-free energy relationships*, Clarendon, Oxford, 1973, p. 35.

24 A. Streitweiser, R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, 1958, **80**, 2326; E. Halevi, *Prog. Phys. Org. Chem.*, 1963, **1**, 109.
25 T. Koenig and W. Wolff, *J. Am. Chem. Soc.*, 1969, **91**, 2574.
26 D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
27 D. R. Arnold, in *Substituent effects in radical chemistry*, ed. H. G. Viehe, Z. Janousek and R. Merenyi, Reidel, Dordrecht, 1986, p. 171.
28 L. P. Hammett, *J. Am. Chem. Soc.*, 1937, **59**, 96.
29 T. M. Bockman, S. M. Hubig and J. A. Kochi, *J. Org. Chem.*, 1997, **62**, 2210.
30 P. Lorenz, C. Rüchardt and E. Schacht, *Tetrahedron Lett.*, 1969, 2787.
31 C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilkerand and J. Herbert, *J. Am. Chem. Soc.*, 1953, **75**, 2078.
32 H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, 1956, **78**, 2753; R. Heck and V. Prelog, *Helv. Chim. Acta*, 1955, **38**, 1541.
33 A. Streitweiser, W. R. Young and R. A. Caldwell, *J. Am. Chem. Soc.*, 1969, **91**, 527.
34 A. Streitweiser, R. A. Caldwell and W. R. Young, *J. Am. Chem. Soc.*, 1969, **91**, 529.
35 C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 830.
36 D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1917.

Paper 8/06410E