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Axial ligand exchange of iron(III) tetramesitylporphyrin phenolate complexes

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The axial ligand of a series of iron(III) 5,10,15,20-tetramesitylporphyrin phenolate complexes was found to exchange with added carboxylic acids and alcohols. The rates of axial ligand exchange with carboxylic acids were found to be dependent on acidity of the carboxylic acid, basicity of the phenolate, and the steric bulk of both the carboxylic acid and the phenolate axial ligand. The rates of axial ligand exchange with alcohols were found to be dependent on the nucleophilicity of the alcohol, leaving group ability of the phenolate, and the steric bulk of both the alcohol and the phenolate axial ligand. Different mechanisms for ligand exchange are proposed for carboxylic acids and alcohols.

Introduction

Iron porphyrins play central roles in a number of enzymes and proteins. These heme proteins serve a wide range of functions and the nature of the axial ligand on the iron is thought to play a key role in controlling the properties of the heme proteins. Of particular interest are the oxidizing enzymes peroxidases, cytochrome P-450s, and catalases for which high-valent oxoiron(IV) porphyrin π-cation radical species are thought to be active oxidation intermediates.[1–3] In the case of peroxidases and heme catalases the well characterized oxoiron(IV) porphyrin π-cation radical is called compound I. While the active intermediate in cytochrome P-450s has not directly been observed, a compound I species also has been proposed.[4] Despite the involvement of similar active intermediates, these three classes of heme enzymes catalyse different reactions. Peroxidases catalyse the oxidation of organic and inorganic compounds by peroxides, cytochrome P-450s the transfer of a single oxygen atom from dioxygen to organic substrates and catalases the disproportionation of hydrogen peroxide to water and dioxygen. The diverse functions of these classes of enzymes are thought to be in part related to the different proximal ligands on the heme prosthetic group in the active site of these enzymes. Peroxidases have a proximal imidazole from a histidine, cytochrome P-450s have a thiolate ligand from a cysteine and heme catalases have a phenolate from a tyrosine.

Synthetic iron porphyrins have proved useful as chemical models for the above heme proteins. However, most of these studies have used iron porphyrins with axial ligands which could dissociate from the metal centre, consequently the role and identity of the axial ligand on the catalysts is often subject to question. Groves *et al*. reported the characterization of the active species generated from iron(III) 5,10,15,20-tetramesitylporphyrin chloride [Fe(TMP)Cl] and 3-chloroperoxybenzoic acid (mCPBA) as an oxoiron(IV) porphyrin π-cation radical[5] and assumed that the axial chloride ligand of Fe(TMP)Cl was replaced by the carboxylate anion of the reduced peroxyacid in a dichloromethane–methanol mixture.[6] There, however, are conflicting views on the nature of the axial ligand *trans* to the oxo group and even whether there is a *trans* ligand. Trautwein *et al.*,[7] based on Mössbauer evidence, concluded that there is no ligand *trans* to the oxo group. Kitagawa and co-workers[8] proposed methanol coordinates in place of the chloride ion based on resonance Raman studies. Gross and co-workers[9] generated the oxoiron(IV) porphyrin π-cation radical, in non-co-ordinating solvents with different ligands *trans* to the oxo group, by treating Fe(TMP)X with ozone, an oxidant whose reduced form, dioxygen, is a poor ligand. Paeng *et al*.[10] reported resonance Raman evidence for the presence of *trans* halide ligands even in the presence of mCPBA and methanol.

As part of a study in our laboratories on the structure and chemistry of oxoiron(IV) 5,10,15,20-tetramesitylporphyrin π-cation radical species, generated from a series of iron(III) tetramesitylporphyrin phenolates [Fe(TMP)(OAr)], the fate of the phenolate axial ligand was brought into question and it was important to determine whether the phenolate ligand was replaced on the iron(III) porphyrin prior to formation of the oxoiron(IV) porphyrin π-cation radical. The question of ligand exchange in iron(IV) porphyrins is more difficult to study. Axial ligand exchange studies of iron porphyrins have focused primarily on neutral nitrogen ligands such as imidazoles. To our knowledge, only one study on the kinetics of anionic ligand exchange of iron(III) porphyrins has been reported. Uno *et al*.[11] studied the reaction of iron(III) 2,3,7,8,12,13,17,18-octaethylporphyrin methoxide [Fe(OEP)(OMe)] with a series of phenols, carboxylic acids, and thiols. Equilibrium constants were measured for the reaction of phenols and carboxylic acids with [Fe(OEP)(OMe)], while thiols were found to react irreversibly. In the present study we have investigated the ligand exchange reaction of a series of iron(III) tetramesitylporphyrin phenolate complexes with carboxylic acids and alcohols and report on the mechanism of this exchange.

Results and discussion

Iron(III) 5,10,15,20-tetramesitylporphyrin phenolate complexes undergo axial ligand exchange with added carboxylic acids or alcohols. As was observed with the reaction of carboxylic acids and phenols with [Fe(OEP)(OMe)],[11] there is an equilibrium between the phenolate complexes and the carboxylate or alkoxide complexes.

Carboxylic acids

The addition of carboxylic acids to solutions of all of the phenolate complexes in CH_2Cl_2 at 25 °C results in an equilibrium being established between the iron(III) tetramesitylporphyrin carboxylate and the iron(III) tetramesitylporphyrin phenolate complexes. The equilibrium favours the carboxylate complex with all [Fe(TMP)(OAr)] complexes except that of the 4-nitrophenolate. However, the reaction of the iron(III) tetramesitylporphyrin 4-trifluoromethylphenolate complex with 160

Table 1 Pseudo-first order rate constants (s^{-1}) for axial ligand exchange of [Fe(TMP)(OAr)] with carboxylic acids in dichloromethane at 25.0 °C

	Phenolate ligand substituent(s) (phenol pK_a)			
Acid (pK_a)	2,4,6-Me_3 (10.9)	4-CH_3O (10.2)	H (10.0)	4-CF_3 (8.7)
$BrCH_2CO_2H$ (2.7)	2.1×10^{-3}	$>2 \times 10^{-1}$	$>2 \times 10^{-1}$	1.4×10^{-1}
$CH_3CH(Br)CO_2H$ (2.9)	9.0×10^{-4}	1.8×10^{-1}	1.7×10^{-1}	5.0×10^{-2}
2,6-$(CH_3)_2C_6H_3CO_2H$ (3.2)	3.5×10^{-3}	1.6×10^{-1}	1.7×10^{-1}	6.6×10^{-2}
3-$ClC_6H_4CO_2H$ (3.8)	7.5×10^{-4}	2.2×10^{-1}	2.3×10^{-1}	5.4×10^{-2}
4-$NO_2C_6H_4CH_2CO_2H$ (3.8)	6.9×10^{-4}	1.9×10^{-1}	1.3×10^{-1}	4.0×10^{-2}
$C_6H_5CH_2CO_2H$ (4.3)	1.6×10^{-4}	8.2×10^{-2}	5.6×10^{-2}	2.2×10^{-2}
CH_3CO_2H (4.8)	2.7×10^{-4}	6.4×10^{-2}	6.0×10^{-2}	1.9×10^{-2}
$CH_3CH_2CO_2H$ (4.9)	2.6×10^{-4}	4.1×10^{-2}	2.8×10^{-2}	1.2×10^{-2}
$(CH_3)_2CHCO_2H$ (4.8)		1.9×10^{-2}	1.6×10^{-2}	7.2×10^{-3}
$(CH_3)_3CCO_2H$ (5.0)		4.0×10^{-3}	2.9×10^{-3}	9.7×10^{-4}

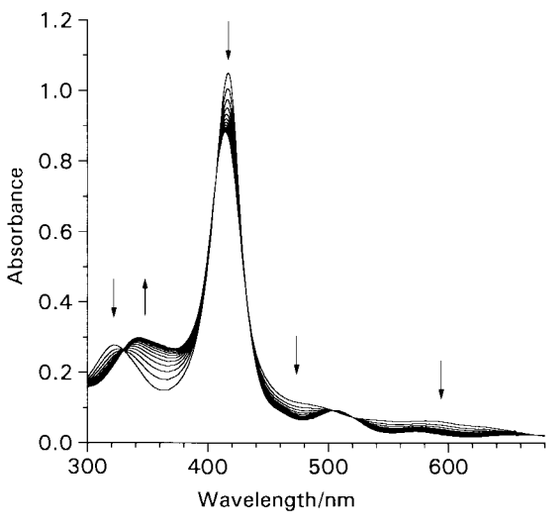


Fig. 1 The UV-visible changes for the reaction of [Fe(TMP)($OC_6H_2Me_3$-2,4,6)], 7.6×10^{-6} M, and 2-bromopropanoic acid, 1.3×10^{-3} M, in CH_2Cl_2 at 25 °C. Spectra recorded every 300 s.

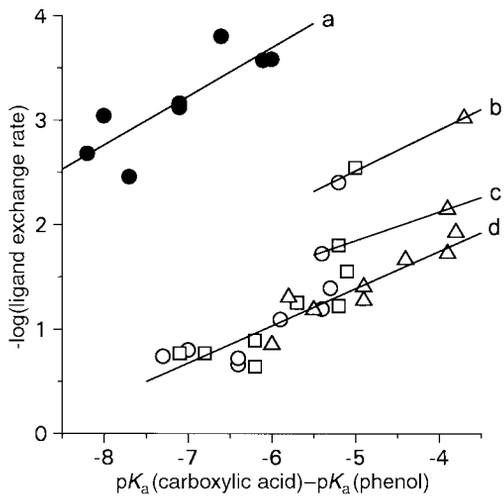


Fig. 2 Plots of −log(ligand exchange rate in CH_2Cl_2 at 25 °C) *versus* the difference in the pK_a of the carboxylic acid and the pK_a of the conjugate acid of the phenolate ligand. ●, [Fe(TMP)($OC_6H_2Me_3$-2,4,6)]; ○, [Fe(TMP)(OC_6H_4OMe-4)]; □, [Fe(TMP)(OPh)]; and △, [Fe(TMP)($OC_6H_4CF_3$-4)]. The lines represent least squares fits of each data set: (a) sterically unhindered carboxylic acids and 2,4,6-trimethylphenolate, (b) 2,2-dimethylpropanoic acid with unhindered phenolate ligands, (c) 2-methylpropanoic acid with unhindered phenolate ligands, and (d) sterically unhindered carboxylic acids with unhindered phenolate ligands.

equivalents of propanoic acid is effectively stopped by the addition of 140 equivalents of 4-trifluoromethylphenol. When a strong carboxylic acid, such as 2-bromopropanoic acid, and a complex with a relatively basic phenolate ligand, such as the 4-methoxyphenolate complex, are combined in a 1:1 molar ratio, the 2-bromopropanoate complex is formed essentially quantitatively. The equilibria and kinetics were measured by UV-visible spectroscopy by monitoring the spectral changes between 300 and 800 nm with time. The spectral changes observed for a typical kinetic run, the reaction of iron(III) tetramesitylporphyrin 2,4,6-trimethylphenolate and 2-bromopropanoic acid, are shown in Fig. 1.

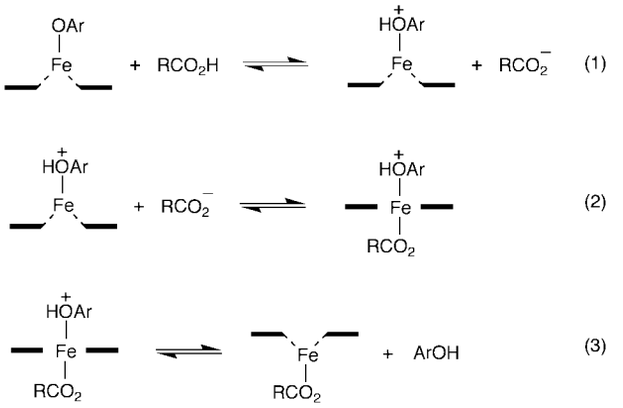
The kinetics of the exchange of phenolate ligand by carboxylate was studied with a large excess (160-fold) of carboxylic acid. Under these conditions the reverse reaction should be unimportant and as expected the reactions show pseudo-first order kinetics. As confirmation for this conclusion the addition of 10 equivalents of 4-trifluoromethylphenol to the reaction of the iron(III) tetramesitylporphyrin 4-trifluoromethylphenolate complex and 2-bromoethanoic acid has no effect on the rate of formation of the carboxylate complex. The pseudo-first order rates of axial ligand exchange for the complexes of four phenolate ligands, 2,4,6-trimethylphenolate, 4-methoxyphenolate, phenolate and 4-trifluoromethylphenolate, with a series of carboxylic acids were measured in dichloromethane at 478 nm and are listed in Table 1. Kinetics measurements at other wavelengths gave comparable rates.

A plot of −log(rate constant) in dichloromethane *versus* the difference in the pK_a of the carboxylic acid and of the conjugate acid of the phenolate ligand is shown in Fig. 2. The results fall into four main sets: the reaction of (a) sterically unhindered carboxylic acids and the sterically hindered phenolate ligand, 2,4,6-trimethylphenolate; (b) the sterically hindered carboxylic acid, 2,2-dimethylpropanoic acid, with unhindered phenolate ligands; (c) the sterically hindered carboxylic acid, 2-methylpropanoic acid, with unhindered phenolate ligands; and (d) sterically unhindered carboxylic acids with unhindered phenolate ligands. The slopes from the least-squares fit for each set are approximately the same, suggesting that there is a general trend where the more acidic the carboxylic acid or the more basic the phenolate ion, the faster is the rate of the exchange. Overlayed on this acidity effect is a steric effect, either bulky carboxylic acids or phenolate ligands, which results in the differentiation of the carboxylic acid/phenolate ligand sets. Thus the iron(III) tetramesitylporphyrin 2,4,6-trimethylphenolate undergoes exchange about 100 times slower than the other three phenolate complexes and the exchange with 2,2-dimethylpropanoic acid is about 10 times slower than with less bulky carboxylic acids. Close inspection of the results from the "unhindered" carboxylic acids and phenolate ligands reveals that the reactions of 2-methylpropanoic acid are slightly slower than those of the remainder of the less bulky carboxylic acids.

It is interesting that 2,6-dimethylbenzoic acid, which might be expected to exchange at a slower rate than its pK_a predicts, actually exchanges at a rate which suggests that the methyl groups do not hinder the exchange. Molecular modelling indicates that the carboxylic acid group of 2,6-dimethylbenzoic acid

is slightly twisted out of the plane of the aromatic ring whilst in 2,2-dimethylpropanoic acid methyl groups extend above and below the plane of the carboxylic group, suggesting that steric effects on the ligand exchange are most pronounced for groups out of the plane of the carboxylic group.

These kinetic results are consistent with a mechanism where there is a fast pre-equilibrium protonation step, followed by the formation of a six-co-ordinate complex, and the loss of the protonated phenolate ligand (Scheme 1). The difference in acid-



Scheme 1 Mechanism for the exchange of axial phenolate ligands with carboxylic acids.

ity between the carboxylic acid and the phenol affects the first equilibrium, the protonation step. Bulky phenolate ligands or carboxylic acids affect the second equilibrium, the formation of a six-co-ordinate complex. In the five-co-ordinate iron porphyrin complex the metal is out of the plane of the porphyrin ring and therefore the steric effects between the axial ligand and the porphyrin ring are minimized. However, the six-co-ordinate iron porphyrin complex has the metal in the same plane as the porphyrin ring and the distance between the porphyrin ring and both of the axial ligands is less than in the five-co-ordinate complex. Therefore bulky phenolate ligands or carboxylic acids will disfavour formation of the six-co-ordinate complex.

In contrast to the phenolate complexes described above, the 4-nitrophenolate complex, even with a 160-fold excess of carboxylic acid, is not completely converted into the corresponding carboxylate complex, except with the most acidic carboxylic acids.

In the exchange reaction with different oxygen ligands the forward rate of exchange is dependent (in part) on the acidity of the oxygen acid, RCO_2H, and the basicity of the oxygen axial ligand on the porphyrin, OAr, eqn. (i). Conversely, the rate

$$[Fe(TMP)(OAr)] + RCO_2H \overset{K}{\rightleftharpoons} [Fe(TMP)(O_2CR)] + ArOH \quad (i)$$

of the reverse exchange is dependent on the acidity of ArOH and the basicity of RCO_2^-. If we assume that the Fe–O bond is ionic, then $pK \approx pK_a(RCO_2H) - pK_a(ArOH)$. Based on the aqueous acidities of the species involved, it would be expected that the equilibrium constant should favour the carboxylate complex for all combinations of carboxylic acids and phenolates, including 4-nitrophenolate. Since this is not the case it is likely that the aqueous acidities are not good estimates of the relative acidities of carboxylic acids and phenols in a non-polar solvent such as dichloromethane. Gas phase acidities may provide a better measure of the relative acidities in non-polar solvents.

Kebarle and co-workers have measured the gas phase acidities of a series of substituted phenols and benzoic acids[12] and aliphatic carboxylic acids.[13] Bartmess *et al.*[14] measured the gas phase acidities of a range of oxygen, nitrogen, carbon, sulfur and phosphorus acids, including alcohols and some phenols. Table 2 lists the gas phase acidities of most of the carboxylic acids, phenols and alcohols used in this study. They were reported on different scales, however there were at least several common acids allowing the acidities to be compared on a common scale (the values are probably only accurate to ±5 kJ mol^{-1}). The value for 4-nitrophenol was not measured directly because the sample decomposed under the measurement conditions. However, because of the good linear correlation between the gas phase and aqueous phase acidities of other substituted phenols, the gas phase acidity of 4-nitrophenol was estimated by Kebarle to be greater than that of any of the carboxylic acids used in this study. In a similar manner, we have estimated the gas phase acidity of 4-trifluoromethylphenol from its aqueous acidity.

Table 2 Gas phase acidities

Acid	D − EA[a]/kJ mol^{-1}
4-Nitrophenol	31[b]
2-Bromoethanoic acid	75
3-Chlorobenzoic acid	77
2-Bromopropanoic acid	84
4-Trifluoromethylphenyl	88[b]
2-Phenylethanoic acid	104
2,2-Dimethylpropanoic acid	117
2-Methylpropanoic acid	122
Propanoic acid	128
Ethanoic acid	133
Phenol	139
4-Methoxyphenyl	143
2,2,2-Trifluoroethanol	191
2-Methyl-2-propanol	232
2-Propanol	236
Ethanol	244
Methanol	256

[a] Difference between the bond dissociation energy D(A–H) and the electron affinity EA(A). [b] Estimated value, see text.

It is clear that the acidity of phenols is greatly enhanced in the gas phase relative to carboxylic acids and that in the gas phase phenols have comparable acidities to carboxylic acids. It is a reasonable assumption that the acidities of carboxylic acids and phenols in dichloromethane will be closer to the gas phase rather than the aqueous phase values. Furthermore the data predict that for most of the carboxylic acids the equilibrium between the 4-nitrophenolate complex and the carboxylate complexes will favour the former species.

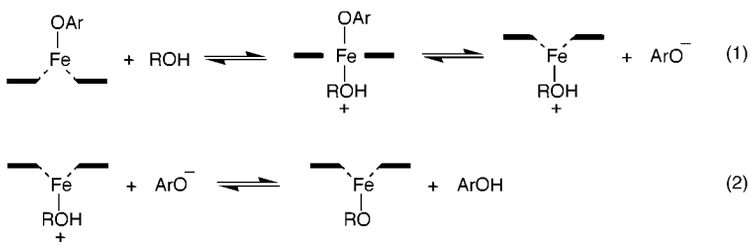
Alcohols

The reactions of alcohols with the iron(III) tetramesitylporphyrin phenolates are much slower than those with carboxylic acids and required elevated temperatures (60 °C in toluene) and a large excess of alcohol [$(2–6) \times 10^4$-fold] to obtain rates comparable to those of the acids. The reactions were followed by monitoring the decrease in the Soret band absorbance (417 nm) of the phenolate complexes and the rate constants are given in Table 3.

The alcohol exchange reactions show two major differences from those of the carboxylic acids. First, for a given alcohol the order of ease of ligand exchange with a series of phenolate complexes is 4-nitrophenolate > 4-trifluoromethylphenolate > phenolate ≈ 4-methoxyphenolate ⩾ 2,4,6-trimethylphenolate. This order is different from that observed with carboxylic acids; indeed for unhindered phenolates the order of reactivity is reversed. Secondly, the order of reactivity of a series of alcohols with a given phenolate complex (4-nitrophenolate) is $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > CF_3CH_2OH > (CH_3)_3COH$. This is not unexpected since the gas phase acidities suggest that the alcohols are not strong enough acids to protonate the phenolate ligands. These results are consistent

Table 3 Pseudo-first order rate constants (s^{-1}) for ligand exchange rates of alcohols with [Fe(TMP)(OAr)] in dichloromethane at 60.0 °C

	Phenolate ligand substituent(s) (phenol pK_a)				
Alcohol	2,4,6-Me_3 (10.9)	4-CH_3O (10.2)	H (10.0)	4-CF_3 (8.7)	4-NO_2 (7.2)
CH_3OH	3×10^{-4}	2×10^{-3}	2×10^{-3}	3×10^{-3}	8×10^{-3}
CH_3CH_2OH					5×10^{-3}
$(CH_3)_2CHOH$					2×10^{-3}
CF_3CH_2OH					8×10^{-4}
$(CH_3)_3COH$					1×10^{-4}



Scheme 2 Mechanism for the exchange of axial phenolate ligands with alcohols.

with a mechanism where the phenolates are displaced by a direct nucleophilic attack by the alcohol (Scheme 2) where the rate depends on the nucleophilicities and the bulk of the alcohol and the leaving group ability of the phenolate.

Experimental

Materials

Dichloromethane and toluene were refluxed over calcium hydride then distilled. Methanol and ethanol were refluxed over the corresponding magnesium alkoxide then distilled. Tetrahydrofuran was refluxed over sodium and distilled from the ketyl of benzophenone. Benzene was refluxed over sodium and distilled. 5,10,15,20-Tetramesitylporphyrin (H_2TMP) was prepared by the method of Lindsey and coworkers.[15] Iron(III) tetramesitylporphyrin chloride [Fe(TMP)Cl] was prepared by refluxing H_2TMP in acetic acid containing iron(III) chloride.[16]

Iron(III) tetramesitylporphyrin 2,4,6-trimethylphenolate [Fe(TMP)($OC_6H_2Me_3$-2,4,6)]. To a solution of 2,4,6-trimethylphenol (0.0689 g, 5.06×10^{-4} mol) in dry THF (10 cm^3) was added sodium (0.0112 g, 4.87×10^{-4} mol) and the mixture allowed to react until all of the sodium had been consumed. A portion of the phenolate solution (5 cm^3) was then added to a solution of [Fe(TMP)Cl] (0.0942 g, 1.08×10^{-4} mol) in dry benzene. The mixture was refluxed for 2 h and the progress of the reaction monitored by UV-Vis spectroscopy. At the end of the reaction the solvent was removed under vacuum and the resulting residue redissolved in dichloromethane, washed with water, dried (Na_2SO_4), and evaporated to dryness. The crude product was recrystallized from hot cyclohexane to give purple crystals of [Fe(TMP)($OC_6H_2Me_3$-2,4,6)] (0.0945 g, 90%) (Found: C, 79.90; H, 6.82. $C_{65}H_{63}FeN_4O$ requires C, 80.31; H, 6.53%).

Other iron(III) tetramesitylporphyrin phenolate complexes were prepared in a similar manner: iron(III) tetramesitylporphyrin 4-methoxyphenolate [Fe(TMP)(OC_6H_4OMe-4)] (Found: C, 78.80; H, 6.56. $C_{63}H_{59}FeN_4O_2$ requires C, 78.82; H, 6.19%); iron(III) tetramesitylporphyrin phenolate [Fe(TMP)(OPh)] (Found: C, 80.07; H, 6.18. $C_{62}H_{57}FeN_4O$ requires C, 80.07; H, 6.18%); iron(III) tetramesitylporphyrin 4-trifluoromethylphenolate [Fe(TMP)($OC_6H_4CF_3$-4)] (Found: C, 76.09; H, 6.19. $C_{69}H_{68}F_3FeN_4O$ requires C, 76.58; H, 6.33%); iron(III) tetramesitylporphyrin 4-nitrophenolate [Fe(TMP)($OC_6H_4NO_2$-4)] (Found: C, 76.47; H, 5.81. $C_{62}H_{56}FeN_5O_3$ requires C, 76.38; H, 5.79%).

Ultraviolet-visible spectroscopy

The UV-vis spectra and kinetics were measured on a Hewlett-Packard 8453 Diode Array spectrophotometer equipped with a thermostatted cell holder. The kinetics with carboxylic acids were studied at 25.0 °C with [Fe(TMP)(OAr)] = 7.7×10^{-6} M and [carboxylic acid] = 1.3×10^{-3} M, and with alcohols at 60.0 °C in toluene with [Fe(TMP)(OAr)] = 7.7×10^{-6} M and [alcohol] = 0.17–0.40 M.

The iron(III) tetramesitylporphyrin carboxylate complexes were found to undergo slow photochemical decomposition in dichloromethane to form [Fe(TMP)Cl], probably by photochemically induced homolytic cleavage of the iron–oxygen bond to give iron(II) tetramesitylporphyrin and a carboxyl radical.[17] The latter can then undergo unimolecular decomposition to a carbon radical and carbon dioxide. Chloride ion must then be formed by a reaction of the carbon radical with dichloromethane and subsequent decomposition of the dichloromethyl radical. The diode array light source initiates this photochemical decomposition. Use of a 300 nm cut-off filter significantly reduces the rate of photochemical decomposition of the carboxylate complex. Reactions in toluene do not undergo this decomposition presumably because the toluene absorbs strongly below 280 nm.

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