A Kinetic Study of the Reaction of *tert*-Butyl Hydroperoxide with Iron(III) 5,10,15,20-tetra(4-sulfonatophenyl)porphyrin† and Related Compounds in Aqueous Solution

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The kinetics of the reaction of *tert*-butyl hydroperoxide with three iron(III) tetra(4-X-phenyl)-porphyrins [X = SO_3^- (Fe^{III}TSPP); CO_2^- (Fe^{III}TCPP); and N^+Me_3 (Fe^{III}TMAPP)] in aqueous solution have been investigated using an excess of 2,2'-azinobis(3-ethyl-2,3-dihydrobenzothiazole-6-sulfonate) as a one-electron oxidant trap. The reaction with Fe^{III}TSPP is first order in [Bu^tO_2H] and in [Fe^{III}TSPP] at all pH values studied (3.8–9.8). At pH ≥ 6.0 the concentration of Fe^{III}TSPP has to be lowered to eliminate the problem of μ-oxo dimer formation and allow the kinetics of the monomer to be studied. The measured second order rate constant shows a complex dependence on pH that is very similar to those reported previously for sterically hindered iron(III) tetra-(sulfonatophenyl)porphyrins. Attempts to measure the rate of reaction of the μ-oxo dimer of Fe^{III}TSPP, at pH 9.2, suggest that it is unreactive towards Bu^tO_2H.

The reactivity of Fe^{III}TCPP towards Bu^tO_2H at pH 9.2 is essentially the same as that of Fe^{III}TSPP. However, Fe^{III}TMAPP reacts significantly more slowly both at pH 9.2 and at 4.8. This is attributed to the greater tendency of this iron(III) porphyrin to form μ-oxo dimers.

The study of the mechanisms of peroxidases and their chemical models continues to be an active area of interest.[1] The research is aimed at identifying the key factors that control the reactivity of the catalysts and that lead to the preference of one pathway over another in the reactions between hydroperoxides (including H_2O_2) and haem enzymes or iron(III) porphyrins. This has revealed the importance of acid/base catalysis,[1d,e,f,2] axial ligation to[1c,d,3] and the steric accessibility of the iron atom,[1b,g] polarity of the medium, the nature of the porphyrin macrocycles[1e,4] and porphyrin aggregation.[1e]

As part of the above studies, Bruice and his coworkers[1e] have carried out detailed investigations of the pH dependence of the kinetics of the reaction of Bu^tO_2H with the sterically hindered iron(III) tetra(2,6-dimethyl-3-sulfonatophenyl)porphyrin (Fe^{III}TDMSPP)‡ and iron(III) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin (Fe^{III}TDCSPP) using the one-electron active oxidant trap 2,2'-azinobis(3-ethyl-2,3-dihydrobenzothiazole-6-sulfonate) (ABTS). They accounted for the complex pH–rate profile that they obtained in terms of pH dependent equilibria between hydroxy and aqua iron porphyrin complexes and related Bu^tO_2H species and a mechanism involving homolytic cleavage of the peroxide bond. In analogous studies, we have shown that this mechanistic interpretation also applies to the reaction of Bu^tO_2H with the unhindered cationic Fe^{III}T4MPyP and that bulky substituents and the charge on the porphyrin macrocycle have a relatively small effect on the reactivity of the iron(III) porphyrin towards Bu^tO_2H in aqueous buffer.[4]

In this paper we report the results of our studies on the pH dependence of the rate of reaction of Bu^tO_2H with three unhindered ionic iron(III) tetra(4-X-phenyl)porphyrins (X = SO_3^-, CO_2^- and N^+Me_3) using the one-electron trap ABTS. The iron(III) porphyrins in the present study show a greater tendency to form μ-oxo dimers than those used previously and this has allowed the behaviour of the monomeric and dimeric species to be examined.

Results

Kinetics of the Reaction between tert-*Butyl Hydroperoxide and Iron*(III) 5,10,15,20-*Tetra*(4-*sulfonatophenyl*)*porphyrin Tetrasodium Salt in Aqueous Acetate Buffer*.—The reaction between Bu^tO_2H and Fe^{III}TSPP has been studied at 30 °C in aqueous solution at ionic strength 0.2 mol dm^{-3} (maintained with $NaNO_3$), by using the efficient one-electron oxidation traps diammonium and disodium 2,2'-azinobis(3-ethyl-2,3-dihydrobenzothiazole-6-sulfonate) [$(NH_4)_2$ABTS and Na_2ABTS, respectively].[5] Both the traps are oxidized to the relatively stable blue–green radical cation $ABTS^{\cdot +}$ (λ_{max} 660 nm, ε_{660} 1200 m^2 mol^{-1}).[6]

The initial experiments in 0.1 mol dm^{-3} acetic acid–acetate buffer (pH 5.2–5.5) were used to characterize the kinetics of the system. Under these conditions no reaction occurs between $(NH_4)_2$ABTS and Bu^tO_2H in the absence of Fe^{III}TSPP. Kinetic studies were carried out using 6.1×10^{-5} mol dm^{-3} Bu^tO_2H with $(0.53–10.5) \times 10^{-6}$ mol dm^{-3} Fe^{III}TSPP and 9.40×10^{-3} mol dm^{-3} $(NH_4)_2$ABTS. Under these conditions, the formation of $ABTS^{\cdot +}$ follows first order kinetics for over three half-lives and the observed pseudo-first order rate constants, k_{obs}, vary linearly with [Fe^{III}TSPP] (Fig. 1).

Decreasing the large excess of $(NH_4)_2$ABTS over Bu^tO_2H by a factor of six produces a small increase (24%) in k_{obs} (Table 1). However, changing the initial concentration of Bu^tO_2H while maintaining constant Fe^{III}TSPP and $(NH_4)_2$ABTS concentrations (1.05×10^{-6} and 9.4×10^{-3} mol dm^{-3}, respectively) gives significant changes in the rate of reaction and final yield of $ABTS^{\cdot +}$. The final absorbance at 660 nm was found to be linearly dependent on the initial [Bu^tO_2H] (Fig. 2). Since two $ABTS^{\cdot +}$ should be produced from every Bu^tO_2H reacted, the slope of Fig. 2 corresponds to a 79% yield of $ABTS^{\cdot +}$ based on Bu^tO_2H.

The initial rates of $ABTS^{\cdot +}$ formation (derived from the $\Delta A_{660\ nm}$ *vs.* *t* traces) were linearly dependent on $[Bu^tO_2H]_i$

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† 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrinato iron(III).

‡ The following abbreviations are used: 5,10,15,20-tetraarylporphyrins. TSPP, tetra(4-sulfonatophenyl)porphyrin; TCPP, tetra(4-carboxyphenyl)porphyrin; TMAPP, tetra(4-trimethylammoniophenyl)porphyrin; TDMSPP, tetra(2,6-dimethyl-3-sulfonatophenyl)porphyrin; TDCSPP, tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin; T4MPyP, tetra(4-*N*-methylpyridyl)porphyrin. $(NH_4)_2$ABTS and Na_2ABTS, diammonium and disodium 2,2'-azinobis(3-ethyl-2,3-dihydrobenzothiazole-6-sulfonate). $ABTS^{\cdot +}$ and $ABTS^{2+}$ the one- and two-electron oxidation products of ABTS, respectively.

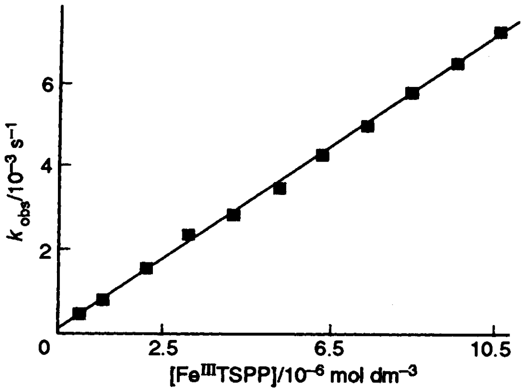


Fig. 1 Dependence of pseudo-first order rate constant for formation of $ABTS^{\cdot+}$ on the concentration of $Fe^{III}TSPP$. Bu^tO_2H, 6.1×10^{-5} mol dm^{-3}, $(NH_4)_2ABTS$, 9.4×10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} (with $NaNO_3$); pH 5.2 at 30 °C.

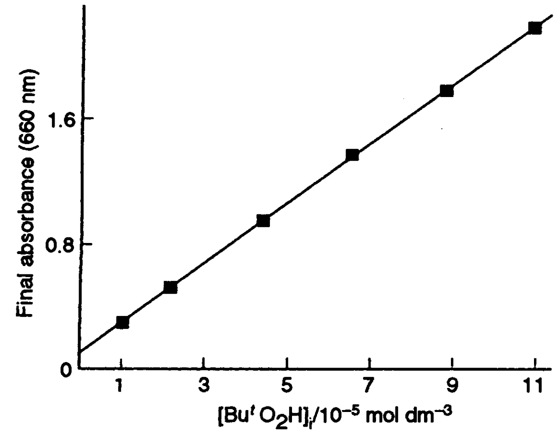


Fig. 2 Dependence of the final absorbance at 660 nm on the initial concentration of Bu^tO_2H. $Fe^{III}TSPP$, 1.05×10^{-6} mol dm^{-3}; $(NH_4)_2$ ABTS, 9.4×10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} (with $NaNO_3$); pH 5.5 at 30 °C.

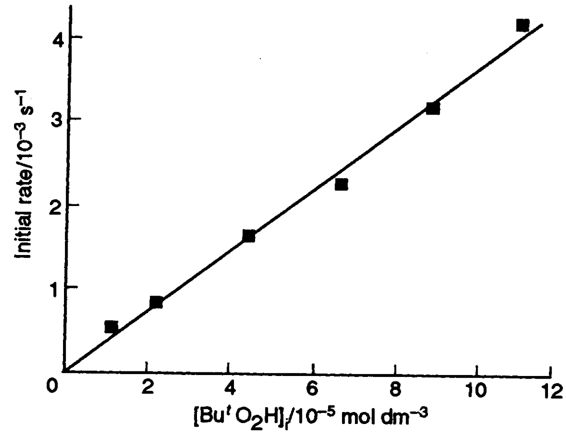


Fig. 3 Dependence of the initial rate of reaction on the concentration of Bu^tO_2H. $Fe^{III}TSPP$, 1.05×10^{-6} mol dm^{-3}; $(NH_4)_2ABTS$, 9.4×10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} (with $NaNO_3$); pH 5.5 at 30 °C.

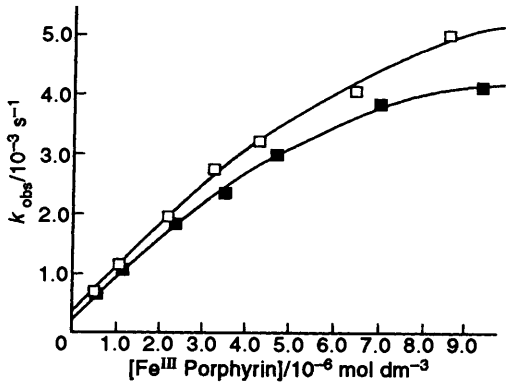


Fig. 4 Dependence of the pseudo-first order rate constant for formation of $ABTS^{\cdot+}$ on the concentration of $Fe^{III}TSPP$ (□) and of $Fe^{III}TCPP$ (■) at pH 9.2. Bu^tO_2H, 6.1×10^{-5} mol dm^{-3}; $(NH_4)_2ABTS$, 9.4×10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} (with $NaNO_3$) at 30 °C.

Table 1 Dependence of the pseudo-first order rate constant, k_{obs}, for $ABTS^{\cdot+}$ formation on $[(NH_4)_2ABTS]$ in the reaction of Bu^tO_2H with $Fe^{III}TSPP$ at pH 5.5[a]

$[(NH_4)_2ABTS]/10^{-2}$ mol dm^{-3}	$k_{obs}/10^{-3}\ s^{-1}$
1.61	1.34
1.34	1.38
1.07	1.43
0.81	1.49
0.54	1.56
0.27	1.67

[a] $[Bu^tO_2H]$, 6.1×10^{-5} mol dm^{-3}; $[Fe^{III}TSPP]$, 1.05×10^{-6} mol dm^{-3}; μ, 0.20 mol dm^{-3}; 30 °C.

with a gradient of 3.09×10^{-3} s^{-1} (Fig. 3). Allowing for the oxidation stoichiometry and the 79% yield of $ABTS^{\cdot+}$, this gradient gives a pseudo-first order rate constant of 1.96×10^{-3} s^{-1}. This value compares well with the average value of k_{obs} (1.49×10^{-3} s^{-1}) determined from the first order analysis of the rate data.

These results show that the reaction follows the rate law eqn. (A), where $k_{obs} = k_2[Fe^{III}TSPP]$.

$$d[ABTS^{\cdot+}]/dt = k_{obs}[Bu^tO_2H] \qquad (A)$$

pH Dependence of the Second Order Rate Constant, k_2.—The kinetics of the reaction between Bu^tO_2H and $Fe^{III}TSPP$ were studied over the pH range 3.8–9.8. The reaction was not investigated outside this pH range since, as noted previously,[4] the kinetics are complicated by other reactions of ABTS and $ABTS^{\cdot+}$. The buffers employed for this study were acetic acid–acetate (pH 3.8–5.6), dihydrogen phosphate–monohydrogen phosphate (5.9–7.6) and trihydrogen borate–dihydrogen borate (7.9–9.8).

At all the pH values studied, $ABTS^{\cdot+}$ formation follows first order kinetics. In acetic acid–acetate buffers plots of k_{obs} *vs.* $[Fe^{III}TSPP]$ [(0.5–10) $\times 10^{-6}$ mol dm^{-3}] are linear. However, with solutions of pH $\geq$ 6, using similar concentration ranges of $Fe^{III}TSPP$, these plots display curvature (see, *e.g.* Fig. 4). The extent of this curvature increases with pH.

Linear plots of k_{obs} *vs.* $[Fe^{III}TSPP]$ are obtained using lower concentrations of $Fe^{III}TSPP$ than those used in the acetate buffer study (Fig. 5). These plots were used to obtain second order rate constants, k_2, over the complete pH range and the log k_2 *vs.* pH profile for the reaction of Bu^tO_2H with $Fe^{III}TSPP$ (Fig. 6).

Dependence of the Reaction Rate on $[Fe^{III}TSPP]$ *at* pH 9.18 *using More Concentrated Solutions of Iron Porphyrin*.—The reaction of 6.1×10^{-5} mol dm^{-3} Bu^tO_2H with (0.79–83.2) $\times 10^{-4}$ mol dm^{-3} $Fe^{III}TSPP$ in the presence of 9.4×10^{-3} mol dm^{-3} Na_2ABTS at pH 9.18 gives first order kinetics for the formation of $ABTS^{\cdot+}$. A plot of k_{obs} *vs.* $[Fe^{III}TSPP]$ shows very marked curvature (Fig. 7). Concentrations of $Fe^{III}TSPP$ > 8.32×10^{-3} mol dm^{-3} could not be used since the strong

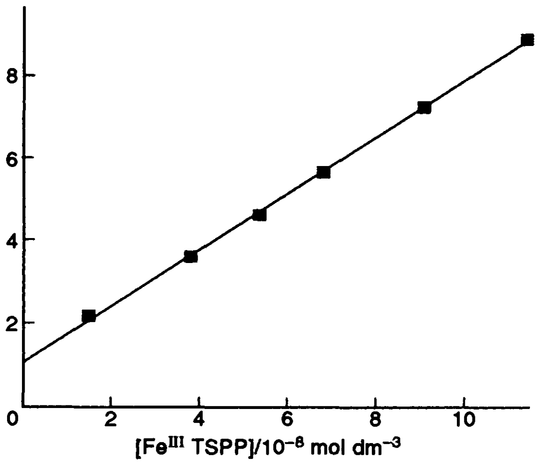


Fig. 5 Dependence of the pseudo-first order rate constant for formation of ABTS$^{•+}$ on the concentration of Fe^{III}TSPP at pH 8.29 at low [Fe^{III}TSPP]. Bu^{t}O$_2$H, 6.1 × 10^{-5} mol dm^{-3}; (NH$_4$)$_2$ABTS, 9.4 × 10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} (with NaNO$_3$) at 30 °C.

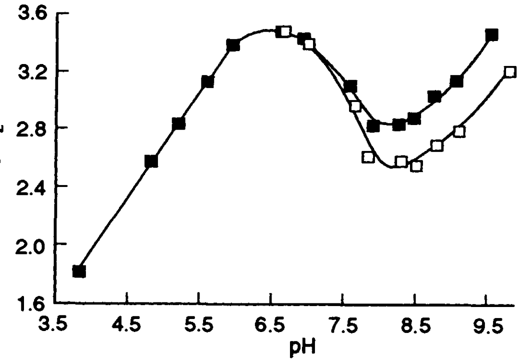


Fig. 6 log k_2 *vs.* pH profile for the reaction of monomeric Fe^{III}TSPP with Bu^{t}O$_2$H using (NH$_4$)$_2$ABTS (■) and Na$_2$ABTS (□) traps. μ, 0.20 mol dm^{-3} at 30 °C.

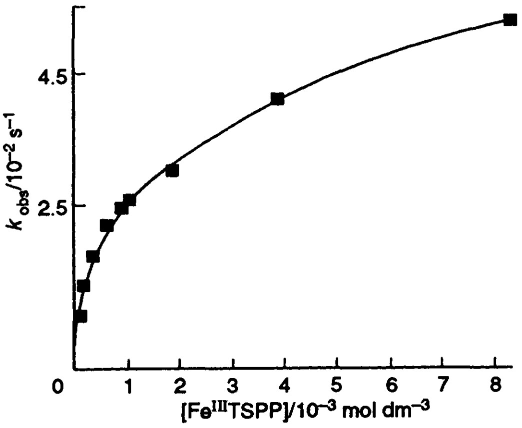


Fig. 7 Dependence of the pseudo-first order rate constant for formation of ABTS$^{•+}$ on the concentration of Fe^{III}TSPP at pH 9.18. Bu^{t}O$_2$H, 6.1 × 10^{-5} mol dm^{-3}; (NH$_4$)$_2$ABTS, 9.4 × 10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} at 30 °C.

absorbance of these solutions prevents the passage of light through the cuvette.

Comparison of Rates Measured with (NH$_4$)$_2$ABTS *and* Na$_2$ABTS *as Oxidant Traps*.—Disodium ABTS was used in place of (NH$_4$)$_2$ABTS in the pH range 6.65–9.73 to overcome complications arising from the presence of ammonia with the latter trap [pK_a(NH$_4^+$) = 9.09 at 30 °C].[7] Second order rate constants were obtained, with the more dilute Fe^{III}TSPP solutions as described above and used to plot a log k_2 *vs.* pH profile (Fig. 6). This study shows that at pH values ≥7 (NH$_4$)$_2$ABTS has a significant rate accelerating effect on the reaction of Fe^{III}TSPP with Bu^{t}O$_2$H.

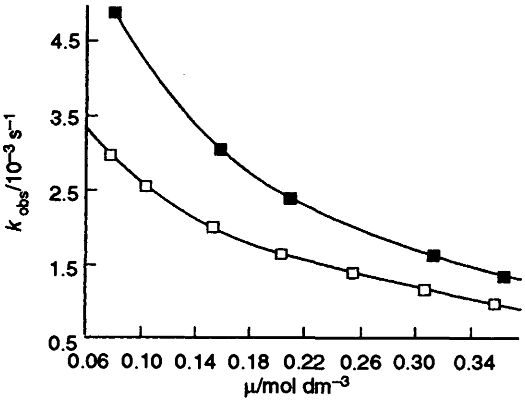


Fig. 8 Dependence of the pseudo-first order rate constant for formation of ABTS$^{•+}$ on the ionic strength of the medium (■) Fe^{III}TSPP, 2.52 × 10^{-6} mol dm^{-3} and (□) Fe^{III}TCPP, 2.55 × 10^{-6} mol dm^{-3}; Bu^{t}O$_2$H, 6.1 × 10^{-5} mol dm^{-3}; (NH$_4$)$_2$ABTS, 9.4 × 10^{-3} mol dm^{-3}; μ, 0.20 mol dm^{-3} pH 9.2 at 30 °C.

Dependence of the Reaction Rate on the Ionic Strength of the Medium.—This was investigated at pH 3.8 and 9.2 (acetic acid–acetate and trihydrogen borate–dihydrogen borate buffers, respectively) by varying the sodium nitrate concentration. At pH 3.8, k_{obs} (and hence k_2) gives a small increase (25%) when the ionic strength is increased from 0.1 to 0.46 mol dm^{-3}. By contrast, at pH 9.2 k_{obs} shows a marked decrease as the ionic strength is raised (Fig. 8).

Dependence of the Second-order Rate Constant on the Buffer Concentration.—This was examined for all the buffers used in this study with a constant ionic strength (0.2 mol dm^{-3}) and (NH$_4$)$_2$ABTS as the oxidant trap. A ten-fold increase in the [acetate buffer] at pH 4.8 has no effect on k_{obs} whilst a similar increase in the [phosphate buffer] at pH 6.6 results in an increase in k_{obs} of *ca.* 25%. At pH 9.1 a five-fold increase in the [borate buffer] gives 36% increase in k_{obs}.

Kinetics of the Reaction of Bu^{t}O$_2$H *with* Fe^{III}TCPP.—This reaction was investigated less extensively than that of Fe^{III}TSPP. The formation of ABTS$^{•+}$, from 6.1 × 10^{-5} mol dm^{-3} Bu^{t}O$_2$H, (0.58–9.28) × 10^{-6} mol dm^{-3} Fe^{III}TCPP and 9.40 × 10^{-3} mol dm^{-3} (NH$_4$)$_2$ABTS at pH 9.2, at ionic strength 0.20 mol dm^{-3} and 30 °C, is first order. Analogous to the corresponding reactions of Fe^{III}TSPP, the plot of k_{obs} values against [Fe^{III}TCPP] is non-linear (Fig. 4) and increasing the ionic strength produced a decrease in k_{obs} (Fig. 8).

Kinetics of the Reaction of Bu^{t}O$_2$H *with* Fe^{III}TMAPP.—This reaction was investigated at pH 9.2 and 4.8. At the former pH using 9.9 × 10^{-7} mol dm^{-3} Fe^{III}TMAPP and the conditions described above for Fe^{III}TCPP, the formation of ABTS$^{•+}$ does not follow first order kinetics and is very slow, taking *ca.* 42 h to go to completion. This should be compared with 2 h for the corresponding reaction times of Fe^{III}TCPP and Fe^{III}TSPP and Fe^{III}T4MPyP. In addition, the final yield of ABTS$^{•+}$ based on Bu^{t}O$_2$H is only 23% [*cf.* the equivalent values for the other ionic iron(III) porphyrins at this pH are 70–75%].

ABTS$^{•+}$ formation from 6.1 × 10^{-5} mol dm^{-3} Bu^{t}O$_2$H, (0.54–8.64) × 10^{-6} mol dm^{-3} Fe^{III}TMAPP and 9.4 × 10^{-3} mol dm^{-3} (NH$_4$)$_2$ABTS, at pH 4.8 is faster than that at pH 9.2, follows first order kinetics and gives a final 80% yield of

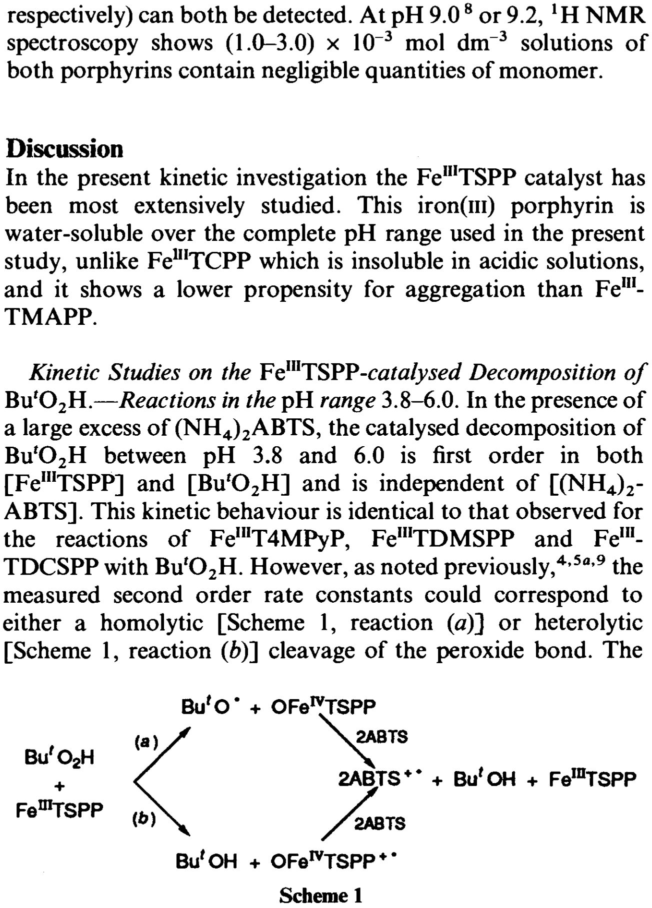
$ABTS^{\cdot +}$. The plot of k_{obs} *vs.* [Fe^{III}TMAPP], however, is non-linear unlike that from the analogous reaction of Fe^{III}TSPP at this pH. In addition the k_{obs} values from Fe^{III}TMAPP are 5–18 times smaller than those from Fe^{III}TSPP for the same porphyrin concentrations.

^{1}H *NMR Study of* Fe^{III}TMAPP *and* Fe^{III}TSPP.—The ^{1}H NMR spectrum of 1.05×10^{-3} mol dm^{-3} Fe^{III}TMAPP at pH 4.8 and ionic strength 0.2 mol dm^{-3} reveals that the dominant species is the μ-oxo dimer. Particularly noticeable is the broad peak at δ 12.7 from the β-pyrrole hydrogens, whereas the corresponding signal from the monomer, shifted downfield by the paramagnetic iron atom, could not be detected. Increasing the concentration of the metalloporphyrin to 4.15×10^{-3} mol dm^{-3} results in the virtual disappearance of all the monomer signals and a relative increase in those from the dimer. In contrast, with 9.44×10^{-4} mol dm^{-3} Fe^{III}TSPP at pH 4.8 the monomer is the dominant species although β-pyrrole hydrogen peaks from the monomer and the dimer (δ 54.8 and 13.0, respectively) can both be detected. At pH 9.0[8] or 9.2, ^{1}H NMR spectroscopy shows $(1.0\text{–}3.0) \times 10^{-3}$ mol dm^{-3} solutions of both porphyrins contain negligible quantities of monomer.

Discussion

In the present kinetic investigation the Fe^{III}TSPP catalyst has been most extensively studied. This iron(III) porphyrin is water-soluble over the complete pH range used in the present study, unlike Fe^{III}TCPP which is insoluble in acidic solutions, and it shows a lower propensity for aggregation than Fe^{III}-TMAPP.

Kinetic Studies on the Fe^{III}TSPP-*catalysed Decomposition of* Bu^tO_2H.—*Reactions in the* pH *range* 3.8–6.0. In the presence of a large excess of $(NH_4)_2$ABTS, the catalysed decomposition of Bu^tO_2H between pH 3.8 and 6.0 is first order in both [Fe^{III}TSPP] and [Bu^tO_2H] and is independent of [$(NH_4)_2$-ABTS]. This kinetic behaviour is identical to that observed for the reactions of Fe^{III}T4MPyP, Fe^{III}TDMSPP and Fe^{III}-TDCSPP with Bu^tO_2H. However, as noted previously,[4,5a,9] the measured second order rate constants could correspond to either a homolytic [Scheme 1, reaction (*a*)] or heterolytic [Scheme 1, reaction (*b*)] cleavage of the peroxide bond. The results from the present study cannot distinguish between these alternative pathways although they are more consistent with the former.



Scheme 1

Reactions in the pH *range* 6.0–9.8. Reactions carried out at all pH values ≥ 6.0 are first order in [Bu^tO_2H] but the pseudo-first order rate constants, k_{obs}, show non-linear dependence on [Fe^{III}TSPP] (Fig. 4). This behaviour becomes more pronounced the higher the pH of the reaction medium. The most likely cause of the curvature of these plots is the tendency of Fe^{III}TSPP to form μ-oxo dimers in basic solution.[8,10] μ-Oxo dimers are known to be less reactive than their respective monomers[11] and their formation is concentration dependent.[10a,d,e] Consequently as [Fe^{III}TSPP] increases the proportion of μ-oxo dimers to monomers also increases, resulting in k_{obs} being smaller than expected and a curved k_{obs} *vs.* [Fe^{III}TSPP] plot.

There have been several studies on the pH dependent equilibria of Fe^{III}TSPP in aqueous solution.[10a,d,e,12] These indicate that within the pH range of the present study, monomeric Fe^{III}TSPP exists in two forms (1) and (2) with a pK_a of 7.0 [reaction (1)].[10d] All combinations of these species can

$$\underset{\mathbf{1}}{H_2O + H_2O\text{–}Fe^{III}\text{–}OH_2} \xrightleftharpoons{pK_a\,=\,7.0} H_3O^+ + \underset{\mathbf{2}}{HO\text{–}Fe^{III}\text{–}OH_2} \qquad (1)$$

dimerize [reactions (2)–(4)],[10d,e] however, the reported

$$\mathbf{1} + \mathbf{1} \xrightleftharpoons{K_2\,=\,4.5\,\times\,10^{-9}\ \text{mol dm}^{-3}} \underset{\mathbf{3}}{Fe^{III}\text{–}O\text{–}Fe^{III}} + H_2O + 2H_3O^+ \qquad (2)$$

$$\mathbf{1} + \mathbf{2} \xrightleftharpoons{K_3\,=\,8\,\times\,10^{-2}} \mathbf{3} + 2H_2O + H_3O^+ \qquad (3)$$

$$\mathbf{2} + \mathbf{2} \xrightleftharpoons{K_4\,=\,8\,\times\,10^{5}\ \text{dm}^3\ \text{mol}^{-1}} \mathbf{3} + 3H_2O \qquad (4)$$

equilibrium constants show that only reaction (4), the self-reaction of the monohydroxy species, will be significant in the present study.[10d] Furthermore, since the relative amount of monohydroxy- to diaqua-Fe^{III}TSPP monomer increases with pH, with the former species dominating at pH values above 7.0, so dimerization also becomes increasingly favoured. In agreement with this conclusion in acetate buffer (pH 3.8–5.6), where dimerization will be minimal, k_{obs} *vs.* [Fe^{III}TSPP] plots are linear.

To obtain second order rate constants for the reaction of Bu^tO_2H with monomeric Fe^{III}TSPP at pH ≥ 6.0 a lower concentration range of the iron(III) porphyrin than that used in acetate buffer, had to be employed. This had the effect of reducing the amount of the dimer relative to the monomer such that the former was kinetically insignificant. That this was successful is borne out by the linear k_{obs} *vs.* [Fe^{III}TSPP] plots from reactions carried out under these conditions (Fig. 5). The k_2 values measured in this way have been used to obtain the log k_2–pH profile of the reaction of monomer Fe^{III}TSPP (Fig. 6).

A further kinetic complication at high pH values arises from the ammonium ions from $(NH_4)_2$ABTS which have a pK_a value of 9.09 at 30 °C.[7] Bruice and coworkers[13] have noted previously that ammonia catalyses the reaction of Fe^{III}TDMSPP with Bu^tO_2H. Following a detailed kinetic analysis of this reaction in the presence of a variety of nitrogen bases, they interpreted the effect in terms of monoligation of NH_3 to the iron atom of the metalloporphyrin. At high concentrations ammonia has an inhibiting effect, under these conditions the Fe^{III}TDMSPP forms an unreactive bis-ligated amine complex.

When the $(NH_4)_2$ABTS was replaced by Na_2ABTS in this study the expected reduction in k_{obs} (and k_2), analogous to that observed by Bruice and coworkers for Fe^{III}TDMSPP, was observed. The log k_2–pH profiles of the monomeric Fe^{III}TSPP/Bu^tO_2H reaction for the two traps are compared in Fig. 6.

Comparison of the log k_2 *vs.* pH profiles for Fe^{III}TSPP, Fe^{III}TDMSPP,[5b,14] and Fe^{III}TDCSPP[9] (Fig. 9) reveals the close similarity of the pH dependencies of the reactions of all three tetra-anionic iron(III) porphyrins with Bu^tO_2H. Indeed the reaction of the tetra-cationic Fe^{III}T4MPyP also shows a very comparable behaviour.[4]

Bruice and coworkers[5b,9] have analysed the complex pH dependence of the second order rate constants for Fe^{III}TDMSPP and Fe^{III}TDCSPP in terms of the formation of three key intermediates (**4**, **5** and **6**), from diaqua, mono-hydroxy-aqua, monohydroxy and dihydroxy iron(III) porphyrin precursors and their subsequent further reaction by homolytic

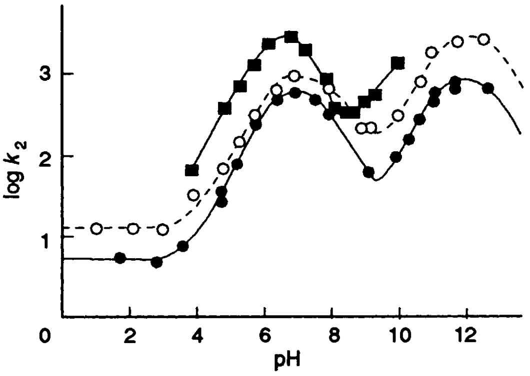
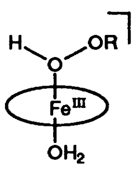


Fig. 9 Log k_2 *vs.* pH profiles for the reaction of $\mathrm{Bu^tO_2H}$ with Fe$^{\mathrm{III}}$TSPP (■), Fe$^{\mathrm{III}}$TDMSPP[5b,14] (●) and Fe$^{\mathrm{III}}$TDCSPP[9] (○) at 30 °C, μ, 0.20 mol dm^{-3}. $\mathrm{Na_2ABTS}$ was the trap for all reactions except those of Fe$^{\mathrm{III}}$TSPP at pHs ≤ 5.96 where $\mathrm{(NH_4)_2ABTS}$ was used.



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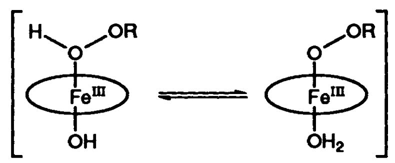

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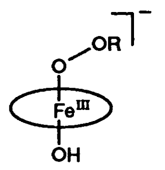

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cleavage of the peroxide bond. Using the pH dependent equilibria of the precursors, intermediates and the oxidant ($\mathrm{Bu^tO_2H + OH^- \rightleftharpoons H_2O + Bu^tO_2^-}$) they have provided a rational account of the log k_2–pH profiles. Given the very similar shape of the log k_2–pH profile of monomeric Fe$^{\mathrm{III}}$TSPP to those of Fe$^{\mathrm{III}}$TDMSPP and Fe$^{\mathrm{III}}$TDCSPP, we propose that the unhindered iron(III) porphyrin also follows the same reaction scheme. The small shift in the rate minimum from approximately 8.5 for Fe$^{\mathrm{III}}$TDMSPP and Fe$^{\mathrm{III}}$TDCSPP to 8.0 for Fe$^{\mathrm{III}}$TSPP must reflect small differences in the acid dissociation constants of intermediates **5** and **6** or their precursors. The generally greater reactivity of Fe$^{\mathrm{III}}$TSPP may arise from the absence of sterically hindering substituents on the aryl groups of the porphyrins.

Overall, as noted previously,[4] charge and steric effects of the aryl groups on the iron(III) porphyrins have remarkably little influence on the log k_2 *vs.* pH profiles. This supports Bruice's hypothesis that the reaction involves homolysis rather than heterolysis of the peroxide bond, since the latter process would generate an oxoiron(IV) porphyrin radical cation [rather than an oxoiron(IV) porphyrin]. Such a process might be expected to show significant substituent effects, for even though there is little conjugation between the porphyrin ring and the almost orthogonal aryl groups inductive effects from the substituents will be present.

Reaction of the μ-*Oxo Dimer of* Fe$^{\mathrm{III}}$TSPP *with* $\mathrm{Bu^tO_2H}$.—As described above, in basic solutions of Fe$^{\mathrm{III}}$TSPP there is a concentration dependent equilibrium between monomers **1** and **2** and μ-oxo dimer **3** [reactions (2)–(4)]. Therefore an attempt was made to study the rate of reaction of the μ-oxo dimer of Fe$^{\mathrm{III}}$TSPP with $\mathrm{Bu^tO_2H}$ at pH 9.18. This required using more concentrated solutions of the catalyst ≤ 8.32 × 10^{-3} mol dm^{-3}. ^{1}H NMR[8,10e,15] and magnetic moment studies[10b] have shown that in the concentration range (3.0–10) × 10^{-3} mol dm^{-3} the predominant species is the dimer. Unfortunately the nonlinear plots of k_{obs} *vs.* [Fe$^{\mathrm{III}}$TSPP] (Fig. 7) show that monomeric Fe$^{\mathrm{III}}$TSPP is present in kinetically significant amounts throughout the porphyrin concentrations employed. More concentrated Fe$^{\mathrm{III}}$TSPP could not be used because the optical density of the solutions was too great for accurate analyses.

Since the second order rate constant for the μ-oxo dimer could not be obtained directly from the k_{obs} *vs.* [Fe$^{\mathrm{III}}$TSPP] plot we have attempted to calculate it using the monomer–dimer equilibrium constants of Wilkins and coworkers.[10d] Assuming that both monomers and dimers react with $\mathrm{Bu^tO_2H}$ the observed first order reaction kinetics will be described by eqns. A–C, where k_2^{mon} and k_2^{dim} are the second order rate constants of the monomer species **1** and **2** and the μ-oxo dimer respectively and $k_{\mathrm{obs}}^{\mathrm{mon}}$ and $k_{\mathrm{obs}}^{\mathrm{dim}}$ are the pseudo-first order rate constants of both monomer species and the μ-oxo dimer respectively and $[\mathrm{mon}]_{\mathrm{T}}$ is the sum of the concentrations of both monomers.

$$k_{\mathrm{obs}} = k_{\mathrm{obs}}^{\mathrm{mon}} + k_{\mathrm{obs}}^{\mathrm{dim}} \quad \text{(B)}$$

$$= k_2^{\mathrm{mon}}[\mathrm{mon}]_{\mathrm{T}} + k_2^{\mathrm{dim}}[\mathrm{dimer}] \quad \text{(C)}$$

The favoured dimerization route will be the reaction of two monohydroxy-aqua species **2** [reaction (4)] since this has the largest equilibrium constant and at pH 9.18 **2** is the dominant monomer species. This allows the concentration of monomeric ($[\mathrm{mon}]_{\mathrm{T}}$) and dimeric ([dimer]) Fe$^{\mathrm{III}}$TSPP to be calculated for each porphyrin concentration studied (Table 2) and consequently, using the measured k_2 for the monomer Fe$^{\mathrm{III}}$TSPP, $k_{\mathrm{obs}}^{\mathrm{mon}}$ and $k_{\mathrm{obs}}^{\mathrm{dim}}$ can be obtained.

Table 2 reveals that the measured k_{obs} and calculated $k_{\mathrm{obs}}^{\mathrm{mon}}$, although not identical are very similar in size. Furthermore, despite a 130-fold change in the concentration of the dimer concentration $k_{\mathrm{obs}}^{\mathrm{dim}}$ values remain essentially constant. These observations suggest that the μ-oxo dimer is unreactive towards $\mathrm{Bu^tO_2H}$ and that the measured k_{obs} values arise solely from the reaction of residual monomer Fe$^{\mathrm{III}}$TSPP. The discrepancy between k_{obs} and $k_{\mathrm{obs}}^{\mathrm{mon}}$ is likely to arise from the choice of the dimerization and dissociation constants as well as from small errors in the measured $k_{\mathrm{obs}}^{\mathrm{mon}}$ value.§ It is noteworthy that the dimerization and dissociation constants used for the calculations[10d] were obtained at 25 °C and an ionic strength of 0.1 mol dm^{-3} and therefore small adjustments to allow for the conditions used in the present study are required. (Higher ionic strength will favour the dimer,[10b,d,e] whilst higher temperature will lead to more monomer.[10b])

Structure studies on the Fe$^{\mathrm{III}}$TSPP μ-oxo dimer suggest that both iron atoms are five-coordinated and displaced from the porphyrin plane towards the oxygen bridge by approximately 0.5 Å.[8,16] An X-ray crystal structure for the μ-oxo dimer of Fe$^{\mathrm{III}}$T4MPyP agrees with this conclusion.[10e] In contrast ^{1}H NMR studies suggest that monomeric Fe$^{\mathrm{III}}$TSPP is six-coordinated. The lack of reactivity of dimeric Fe$^{\mathrm{III}}$TSPP could arise from the reduced accessibility of the iron atoms or because ligation of $\mathrm{Bu^tO_2H}$ to the iron would be accompanied by the movement of the iron atoms into the porphyrin plane. Such movement would lead to an unfavourable reduction in the inter-porphyrin distance. In the context of this study it is

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§ W. R. Scheidt and coworkers[10e] quote values $K_4 = 1 \times 10^{3.8}$ and $K_{\mathrm{a}} = 1 \times 10^{-6.7}$ mol dm^{-3}. However, using these values for the calculations leads to $k_{\mathrm{obs}}^{\mathrm{mon}}$ values that are much greater than the measured k_{obs} values.

Table 2 Pseudo-first order rate constants, k_{obs}, for the reaction of monomeric and μ-oxo dimeric $\mathrm{Fe^{III}}$TSPP with $\mathrm{Bu^tO_2H}$ at pH 9.18

[$\mathrm{Fe^{III}}$TSPP]/ 10^{-4} mol dm^{-3}	[mon]$_T$/ 10^{-5} mol dm^{-3} [a]	[dimer]/ 10^{-4} mol dm^{-3} [a]	Measured k_{obs}/ 10^{-2} s^{-1}	Calc. k_{obs}^{mon}/ 10^{-2} s^{-1} [b]	Calc. k_{obs}^{dim}/ 10^{-2} s^{-1} [c]
0.79	0.675	0.361	0.84	0.45	0.39
1.70	1.01	0.800	1.26	0.67	0.59
3.50	1.46	1.68	1.72	0.96	0.76
6.00	1.92	2.90	2.21	1.27	0.93
9.05	2.36	4.41	2.46	1.56	0.90
10.4	2.53	5.07	2.55	1.67	0.88
18.5	3.39	9.08	3.00	2.24	0.76
38.6	4.91	19.1	4.13	3.24	0.84
83.2	7.22	46.2	5.35	4.77	0.58

[a] Calculated using the dimerization and acid dissociation constants of Wilkins and coworkers.[10d] [b] Using $k_2^{mon} = 660$ mol^{-1} dm^3 s^{-1} derived from Fig. 6 at pH 9.18. [c] $k_{obs}^{dim} = k_{obs} - k_{obs}^{mon}$.

noteworthy that dimeric iron(III) deuteriohaem, haematohaem, coprohaem and deuteriohaemdisulfonate have been shown to be unreactive towards H_2O_2 and dimeric iron(III) protohaem and mesohaem exhibit small rate constants (k_2 *ca.* 100 mol^{-1} dm^3 s^{-1}).[11b]

Dependence of the Reaction Rate on Ionic Strength and Buffer Concentration.—Previous studies have shown that increasing the ionic strength of $\mathrm{Fe^{III}}$TSPP solutions favours μ-oxo dimer formation.[10a,d,e] This has been accounted for in terms of the increasing concentration of cations which improve the screening of the negative charges on $\mathrm{Fe^{III}}$TSPP thereby reducing porphyrin–porphyrin repulsive forces. Consistent with this explanation, in the present study at pH 9.2 increase in ionic strength (and consequent increase in unreactive [μ-oxo dimer]) leads to a reduction in the rate of reaction (Fig. 8). In contrast, at pH 4.8, where dimerization is not favoured, this decrease in rate with increased ionic strength is not observed.

The studies of Bruice and coworkers[5a,9] reveal that the rates of $\mathrm{Bu^tO_2H}$ with $\mathrm{Fe^{III}}$TDMSPP and $\mathrm{Fe^{III}}$TDCSPP are independent (within 10%) of the oxy acid–oxy acid anion buffer concentrations. This was used as evidence for the reactions involving homolysis rather than heterolysis of the peroxide bond since it was argued that the latter would be favoured by acid–base catalysis. The results from the present study are essentially the same although significant small rate increases were observed with the borate buffer (pH 9.1).

Comparison of the Reactions of $\mathrm{Bu^tO_2H}$ *with* $\mathrm{Fe^{III}}$TSPP, $\mathrm{Fe^{III}}$TCPP *and* $\mathrm{Fe^{III}}$TMAPP.—The reaction of $\mathrm{Fe^{III}}$TMAPP was examined at pH 9.2 and 4.8, whereas $\mathrm{Fe^{III}}$TCPP, which is not soluble in acidic aqueous solution, was investigated at pH 9.2 only. Perhaps not surprisingly the two anionic iron(III) porphyrins show remarkably similar kinetic behaviour and reactivity (Figs. 4 and 8). Thus $\mathrm{Fe^{III}}$TCPP, like $\mathrm{Fe^{III}}$TSPP, showed curved k_{obs} *vs.* [$\mathrm{Fe^{III}}$TCPP] plots and a decrease in k_{obs} with increasing ionic strength suggesting that kinetically significant quantities of μ-oxo dimer were also present in the $\mathrm{Fe^{III}}$TCPP reactions at the similar porphyrin concentrations used. In contrast, the cationic $\mathrm{Fe^{III}}$TMAPP, at pH 9.2 is dramatically less reactive than $\mathrm{Fe^{III}}$TSPP, the reaction does not follow pseudo-first order kinetics and gives much smaller yields of $\mathrm{ABTS^{\bullet +}}$. We interpret this in terms of $\mathrm{Fe^{III}}$TMAPP existing mainly as the μ-oxo dimer which leads to a very low rate of reaction with $\mathrm{Bu^tO_2H}$ such that the further reaction of $\mathrm{ABTS^{\bullet +}}$ to colourless $\mathrm{ABTS^{2+}}$ becomes significant.[5b] We argued that at pH 4.8, where dimerization would be expected to be less favourable, these problems should not arise. Indeed at this pH the reaction of $\mathrm{Fe^{III}}$TMAPP is faster, follows pseudo-first order kinetics and gives a high yield of $\mathrm{ABTS^{\bullet +}}$. However, the plot of k_{obs} *vs.* [$\mathrm{Fe^{III}}$TMAPP] is not linear, suggesting that although the majority of $\mathrm{Fe^{III}}$TMAPP is monomeric a significant amount of dimer is also present at the concentrations used in this study. ^{1}H NMR spectra of solutions of $\mathrm{Fe^{III}}$TMAPP at pH 4.8 reveals that, at the higher concentrations needed for the NMR study, the dimer is the dominant species.

We conclude that the tendency to form μ-oxo dimers increases in the series $\mathrm{Fe^{III}}$TSPP ≈ $\mathrm{Fe^{III}}$TCPP < $\mathrm{Fe^{III}}$TMAPP. $\mathrm{Fe^{III}}$T4MPyP, which we used previously, is known to dimerize less readily than any of the iron(III) porphyrins used in this study.[4,17] The tendency for ionic iron(III) tetraarylporphyrins to form μ-oxo dimers in aqueous solution has been reported to depend on the extent of delocalization of the charge on the ionic aryl groups.[8,18] This accounts for the above trend since with $\mathrm{Fe^{III}}$TMAPP the positive charge is localized on the 4-position, with $\mathrm{Fe^{III}}$TSPP and $\mathrm{Fe^{III}}$TCPP the negative charge is more dispersed and with $\mathrm{Fe^{III}}$T4MPyP the positive charge is delocalized on the aromatic rings.

Experimental

Materials.—All materials were commercially available unless otherwise stated. The aqueous *tert*-butyl hydroperoxide was 56–60% w/v by iodometric titration.

The disodium salt of ABTS was prepared from the diammonium salt by the method of Gopinath and Bruice.[5b] $\mathrm{Fe^{III}}$TCPP was prepared from commercially available TCPP and iron(II) chloride following the method of Goff and Morgan.[15]

Methods.—UV–VIS spectra and kinetic studies were carried out on a Hewlett Packard 8452A diode array spectrometer. For the study of rapid reactions a Photophysics RX 1000 stopped-flow apparatus equipped with 2.5 cm^3 drive syringes and a dual pathlength cuvette (10/2 mm) was attached to the spectrometer.

^{1}H NMR spectra of D_2O solutions were recorded on a Bruker MSL 300 (300 MHz) spectrometer using DSS [3-(trimethylsilyl)propane-1-sulfonic acid, sodium salt] as the reference.

pH Measurements were made with a Philips PW 9410 or Corning Delta 220 pH meter equipped with a Russells CE7L combined pH/reference electrode.

Kinetic Procedures.—The kinetic procedures used for the reactions of all three ionic iron(III) porphyrins were the same and are illustrated using $\mathrm{Fe^{III}}$TSPP. The reactions of $\mathrm{Bu^tO_2H}$ with $\mathrm{Fe^{III}}$TSPP, with all but the more concentrated solutions of catalyst, were studied in 1 cm pathlength cuvettes at 30 °C. Buffered solutions containing $\mathrm{Fe^{III}}$TSPP, $\mathrm{(NH_4)_2ABTS}$ or $\mathrm{Na_2ABTS}$ and $\mathrm{NaNO_3}$ (to give ionic strength 0.20 mol dm^{-3}) were thermally equilibrated prior to initiation of reaction by the addition of aqueous Bu^tO_2H. The total volume of each reaction was 3 cm^3. The pH of each reaction mixture was measured at the end of the kinetic run.

The kinetics were followed by monitoring the increase in absorbance of $ABTS^{\bullet +}$ at 660 nm. The data were analysed on a Hewlett Packard Chem Station computer HP 9500, interfaced to the spectrometer, using kinetic software package HP 89512A.

The fast reactions between Bu^tO_2H and the higher concentrations of $Fe^{III}TSPP$ used a stopped-flow apparatus linked to the spectrometer. In a typical experiment one of the drive syringes was filled with a buffered solution of $Fe^{III}TSPP$ and ABTS salt whilst the second contained a buffered solution of Bu^tO_2H and $NaNO_3$. The reaction was initiated by rapid mixing of equal volumes of solutions from each syringe and followed by monitoring the increase in absorbance at 660 nm. The volume of each reaction was 0.30 cm^3. Five reactions were followed in this way using the same drive syringe solutions and the resulting kinetic data were averaged. At the highest $Fe^{III}TSPP$ concentrations the pathlength of the cuvette was reduced from 10 to 2 mm. pH Measurements were made of the combined reaction mixtures of identical kinetic runs.

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