Mechamism of oxidation of azo dyes by a sterically hindered anionic oxoiron(IV) porphyrin in aqueous solution

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The oxidation of 1-(substituted phenylazo)-2-hydroxynaphthalene-6-sulfonate dyes by oxoiron(IV) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin (OFe^{IV}TDCSPP) in aqueous solution is first-order in the concentration of the dye and of the oxoiron(IV) species over the pH range 6.93–12.68. The pH dependence of the second-order rate constant, k_{obs}, which shows a minimum between pH 8.5 and 9.5, can be simulated using two pH-dependent equilibria [OFe^{IV}TDCSPP(OH$_2$)/OFe^{IV}TDCSPP(OH) and dye/dye anion] and the rate constants for three oxidations, dye by OFe^{IV}TDCSPP(OH$_2$) and OFe^{IV}TDCSPP(OH) and dye anion by OFe^{IV}TDCSPP(OH). The fourth combination, the oxidation of the dye anion by OFe^{IV}TDCSPP(OH$_2$), makes an insignificant contribution to the overall rate of reaction. The mechanisms of the three oxidation processes have been studied using Hammett correlations of substituent effects and by comparisons with the oxidations of isomeric 1-aryl-4-hydroxynaphthalenesulfonate dyes, of an *O*-methylated dye and of a deuterated 1-phenylazo-2-hydroxynaphthalene-6-sulfonate dye, bearing in mind that the dyes in aqueous solution exist as an equilibrium between azo and hydrazone tautomers.

In strongly basic solution the dominant reaction is an electron-transfer oxidation between the dye anion and OFe^{IV}TDCSPP(OH) whereas at neutral pH the major reaction is hydrogen atom-abstraction by OFe^{IV}TDCSPP(OH$_2$) from the azo tautomer of the dye. The mechanism at the pH–rate minimum, between OFe^{IV}TDCSPP(OH) and dye, is less clear and alternatives are discussed.

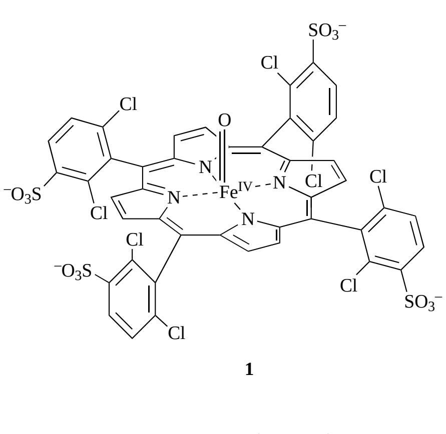
Introduction

Since their original discovery by Perkin in 1856,[1] azo dyes have been extensively developed and now have major commercial applications as colouring agents.[2] Consequently there is considerable interest in the factors that control their stability and colour fastness, particularly with respect to oxidation. On the one hand there is a need to be able to oxidise dyes in industrial effluent[3] and on the other is the requirement that dyed fabrics do not fade through oxidation in washing processes[4] or through photo-oxidation in sunlight.[5]

There have been many studies on azo dye oxidation[4,6] and from these it is possible to conclude that the key factors which control oxidative stability arise from substituents adjacent to the azo linkage. These can, through steric blocking, protect the azo group from attack and also by hydrogen-bonding and bulk effects influence the planarity and consequently the extent of conjugation in the dye molecule.[4] Note that twisting of the azo linkage which influences the extent of conjugation in the dye molecule not only affects the dye's oxidative stability but also its colour and there is a fine balance between the two effects.[6a]

Enzyme-catalysed oxidations of azo dyes are of particular importance since these provide potential clean and selective routes to treating dye effluent and for bleaching fugitive dyes in washing processes.[7] In this respect the peroxidase-catalysed oxidations of horseradish peroxidase (HRP) † and lignin peroxidases have been most thoroughly studied.[8–10] The generally accepted initial step in these reactions involves electron-abstraction from the dye coupled with loss of a proton.[10] Subsequent reactions of the dye radical result in the loss of conjugation (loss of colour) and cleavage of the azo linkage, although there is some disagreement about the precise mechanism of these steps.[10d]

The oxidations of peroxidases have been modelled using synthetic iron and manganese porphyrin catalysts and these simplified systems have been employed to obtain mechanistic information relevant to the enzymic processes.[11] At York we have investigated the oxidation of phenols by oxoiron(IV) and oxomanganese(IV) porphyrins (models for HRP compound II) in aqueous solution (pH 7.6) and shown that the first step in the reaction is hydrogen-abstraction from the phenol rather than electron-abstraction from the phenol or its anion.[12] In this paper we report the results of our kinetic and mechanistic investigations on the oxidation of 1-arylazohydroxynaphthalene-6-sulfonate dyes by the sterically hindered anionic oxoiron(IV) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin (**1**) in aqueous solution.



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Results and discussion

Azo dye substrates

The azo dyes used in these oxidation studies with OFe^{IV}-TDCSPP were the eight 1-arylazo-2-hydroxynaphthalene-6-

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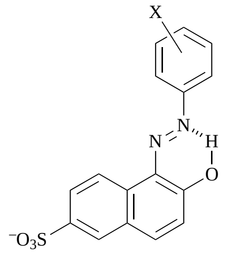
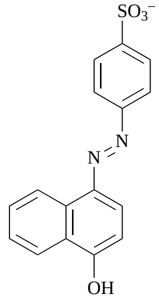
† The following abbreviations are used: HRP for horseradish peroxidase; TDCSPP for tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin ligand; DMSPP for tetra(2,6-dimethyl-3-sulfonatophenyl)porphyrin ligand; TMP for tetramesitylporphyrin ligand; P, as in Fe^{III}P, for porphyrin ligand in general; 3-CPBA for 3-chloroperoxybenzoic acid.



2 4-NO_2
3 4-COMe
4 3-CF_3
5 4-Cl
6 H
7 4-$CHMe_2$
8 4-Me
9 4-OMe



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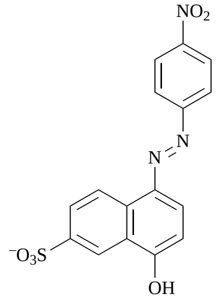

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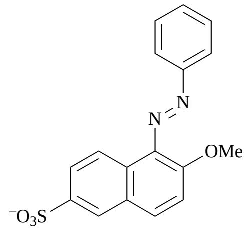

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sulfonates (**2**–**9**), 1-(4-sulfonatophenylazo)-4-naphthol (**10**), 1-(4-nitrophenyl)-4-hydroxynaphthalene-6-sulfonate (**11**) and the *O*-methylated derivative of 1-phenylazo-2-hydroxynaphthalene-6-sulfonate (**12**). The 2-hydroxynaphthalenesulfonate azo dyes were selected to carry out a systematic investigation of the substituent electronic effects on the azo dye oxidation and the 4-naphthol compounds were included for comparison to examine the influence of intramolecular effects between the naphthol and azo functional groups in the dyes.

It is important to note that although azo dyes are conventionally shown as azo compounds, in solution they exist in a rapid dynamic equilibrium of azo (**13**) and hydrazone (**14**) tautomers with the latter isomer being the dominant species (illustrated for 2-naphthol dyes in Scheme 1). Furthermore, in aqueous solution these species are in a pH dependent equilibrium with a common anion (**15**) (Scheme 1). Table 1 records the pK_a values of all the dyes used in this study and, from these data, it is clear that the internal H-bonding in the 2-naphthol compounds stabilises the dyes relative to their anions making them weaker acids than their 4-naphthol analogues. The strong H-bonding is also indicated by the downfield shift of the ^{1}H NMR peak of the tautomeric hydrogen (Table 1).

Generation of the oxoiron(IV) porphyrin oxidant

In previous studies we have used cationic oxometal(IV) porphyrins.[12] However, for this investigation, to avoid problems from precipitation of anionic dye/cationic porphyrin complexes from the aqueous media, we selected the anionic tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin ligand. We showed in an earlier study on anionic iron porphyrins that this ligand gave the most stable oxoiron(IV) species.[13] A further advantage in using this porphyrin is that steric hindrance from the chlorine substituents prevents the formation of potentially unreactive μ-oxodimers.[14] Note also that the analogous unsulfonated iron(III) porphyrin is an excellent oxidation catalyst in organic solution.[15]

Table 1 pK_a values and ^{1}H NMR chemical shifts of tautomeric hydrogens of substituted 1-arylazonaphthol dyes

Dye (**2**–**9**) (substituent)	pK_a [a]	δ_H value of tautomeric hydrogen [b]
2-Naphthol dyes		
2 (4-NO_2)	10.62	15.70
3 (4-COMe)	10.81	15.91
4 (3-CF_3)	10.31	15.56
5 (4-Cl)	10.36	15.53
6 (H)	10.66	15.79
7 (4-$CHMe_2$)	10.81	15.65
8 (4-Me)	10.71	15.64
9 (4-OMe)	10.69	15.05
4-Naphthol dyes		
10	8.11	
11	7.68	12.10

[a] Measured in deionised water (40 °C) and corrected for $\mu = 0.05$ mol dm^{-3}.[17] [b] ^{1}H NMR spectra recorded in $(CD_3)_2SO$.

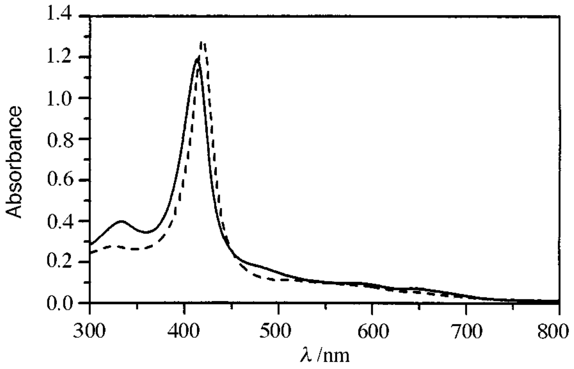
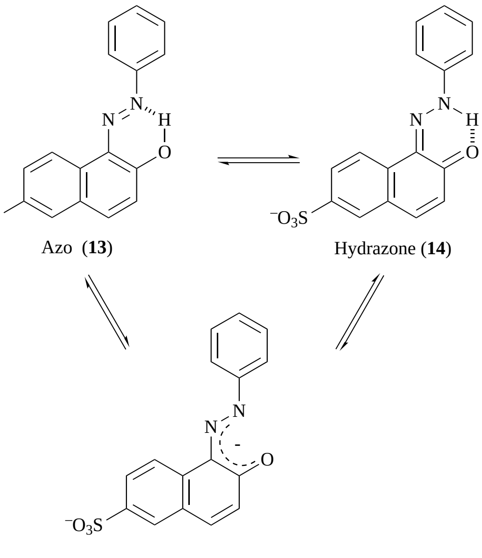


Fig. 1 UV–VIS spectrum of Fe^{III}TDCSPP (1×10^{-5} mol dm^{-3}) in aqueous buffer (pH 9.3) (——) before and (– – –) after the addition of one equivalent of 3-CPBA



Scheme 1

The required oxoiron(IV) porphyrin was prepared in a fast oxidation (<1 s) of Fe^{III}TDCSPP with 3-chloroperoxybenzoic acid (3-CPBA). The formation of the ferryl porphyrin can be readily monitored by UV–VIS spectroscopy by the bathochromic shift of the Soret band from 414 to 420 nm (Fig. 1). The reaction initially generates the oxoiron(IV) porphyrin radical-cation which is extremely rapidly reduced by comproportionation with iron(III) porphyrin to give the desired ferryl species (Scheme 2). The overall stoichiometry of the process predicts that a half-molar equivalent of peroxyacid should generate one

Table 2 Effect of the initial concentration of $Fe^{III}TDCSPP$ on the yield of $OFe^{IV}TDCSPP$ from the reaction of $Fe^{III}TDCSPP$ with 3-CPBA[a]

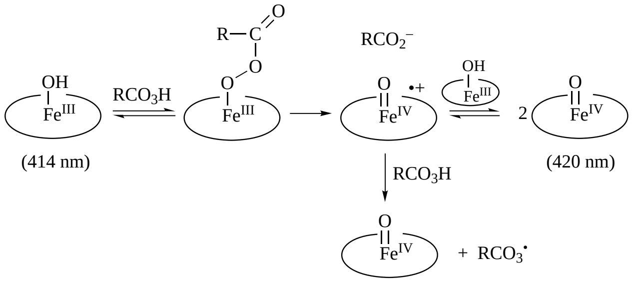
$[Fe^{III}TDCSPP]/10^{-6}\ mol\ dm^{-3}$	Yield (%)[a]
1	70
2	75
4	88
10	93

[a] 3-CPBA, 5×10^{-7} mol dm^{-3}; pH 9.3; ionic strength, 0.05 mol dm^{-3}; 30 °C. [b] % yields based on 3-CPBA.

Table 3 pH Dependence of $OFe^{IV}TDCSPP$ half-life[a]

pH	$t_{\frac{1}{2}}$/min
11.91	23.5
11.51	14.75
10.15	12.25
9.3	11.5
7.8	4.7

[a] $Fe^{III}TDCSPP$, 10^{-6} mol dm^{-3}; 3-CPBA, 5×10^{-7} mol dm^{-3}; ionic strength, 0.05 mol dm^{-3}; 30 °C.



Scheme 2

molar equivalent of $OFe^{IV}TDCSPP$. In the event, mixing equal volumes of 5×10^{-7} mol dm^{-3} 3-CPBA and 1×10^{-6} mol dm^{-3} $Fe^{III}TDCSPP$ results in a 70% conversion to the oxoiron(IV) porphyrin; the 30% unaccounted for oxidant being consumed in side-reactions of the initially formed oxoiron(IV) porphyrin radical-cation. We suspect that the major side-reaction involves oxidation of the peroxyacid which competes with the $OFe^{IV}P^{\bullet +}/Fe^{III}P$ comproportionation (Scheme 2). In agreement with this conclusion increasing the concentration of $Fe^{III}TDCSPP$ in the reaction increases the efficiency of the oxidation to give $OFe^{IV}TDCSPP$ (Table 2).

Stability of oxoiron(IV) tetra(2,6-dichloro-3-sulfonatophenyl)-porphyrin in the absence of azo dyes

The oxoiron(IV) porphyrin, generated from $Fe^{III}TDCSPP$ with a half-molar equivalent of 3-CPBA in the absence of substrate, slowly decays back to $Fe^{III}TDCSPP$. The rate of disappearance of the $OFe^{IV}P$ species, which follows first-order kinetics for over three half-lives, increases with decreasing pH (Table 3). The complete, rapid oxidation and slow decay, cycle above is unaffected by the addition of 3-chlorobenzoic acid and results in a 10–12% bleaching of $Fe^{III}TDCSPP$. In contrast, addition of a 100-fold excess of 4-methoxyphenol (a known reactive substrate for $OFe^{IV}P$)[12a] immediately after formation of the ferryl porphyrin regenerates the $Fe^{III}TDCSPP$ with *ca.* 1% bleaching. We conclude that the porphyrin bleaching, in the absence of added substrate, does not occur during the formation of $OFe^{IV}P$ but rather arises from a self-oxidation during the slow decay back to $Fe^{III}TDCSPP$. All the oxidising equivalents of the $OFe^{IV}P$ species can be accounted for in a multistep oxidation of the porphyrin ring[16] leading to the 10–12% bleaching. Thus, an initial oxidation of the porphyrin ring leads to relatively easy further oxidations of the partially oxidised ligand.

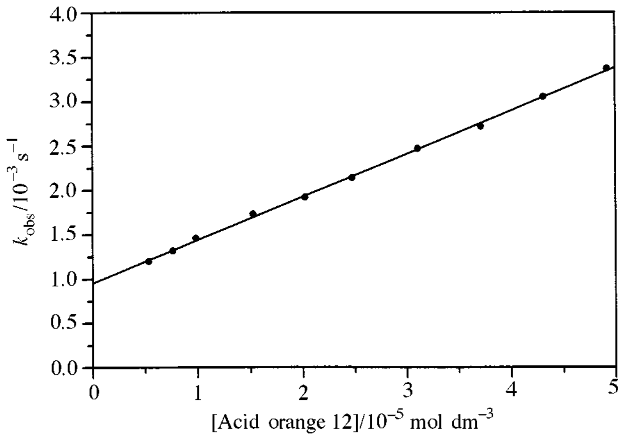


Fig. 2 Dependence of the pseudo first-order rate constant for reduction of $OFe^{IV}TDCSPP$ by acid orange 12 (**6**) on [Dye], pH 9.3; $\mu = 0.05$ mol dm^{-3}; 30 °C

Characterisation of the kinetic equation for the reduction of oxoiron(IV) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin by acid orange 12 (6)

The reactions were carried out in a thermostatted cuvette (30 °C) and followed by monitoring the disappearance of the Soret band of $OFe^{IV}TDCSPP$ (400–500 nm using a spectrum simulation programme to fit the data). In the standard procedure, the ferryl porphyrin was prepared by adding a half-molar equivalent of 3-CPBA to $Fe^{III}TDCSPP$ (1×10^{-6} mol dm^{-3}) in aqueous borate buffer (pH 9.3, 0.025 mol dm^{-3}) with an ionic strength of 0.05 mol dm^{-3} (maintained with $NaNO_3$). The reaction was initiated by mixing with a solution of acid orange 12 (**6**) (final concentration 5–50 × 10^{-6} mol dm^{-3}) in the same buffer. For the faster reactions a stopped-flow apparatus was employed.

The loss of $OFe^{IV}TDCSPP$ in the presence of excess of the azo dye follows pseudo first-order kinetics (for more than three half-lives) and the pseudo first-order rate constants (k_{obs}) are proportional to the dye concentration (Fig. 2). The gradient (48 ± 3 dm^3 mol^{-1} s^{-1}) corresponds to the second-order rate constant (k_2) for acid orange 12 oxidation by $OFe^{IV}TDCSPP$ and the intercept (1×10^{-3} s^{-1}) to the first-order rate constant (k_{bg}) for the dye-independent background decay of $OFe^{IV}TDCSPP$. The overall rate law is described by eqn. (1) which with excess of the dye simplifies to eqn. (2).

$$-d[OFe^{IV}P]/dt = k_{bg}[OFe^{IV}P] + k_2[OFe^{IV}P][Dye] \qquad (1)$$

$$-d[OFe^{IV}P]/dt = k_{obs}[OFe^{IV}P] \qquad (2)$$

$$\text{where } k_{obs} = k_{bg} + k_2[Dye]$$

The expected non-dependence of the reaction on the peroxyacid was confirmed by using two other peroxybenzoic acids, magnesium monoperphthalate and 4-sulfonatoperoxybenzoic acid, to prepare the oxoiron(IV) porphyrin. The second-order rate constants, k_{obs}, obtained for $OFe^{IV}TDCSPP$ generated with these peroxyacids are identical to that obtained using 3-CPBA.

Stoichiometry of 1-arylazo-2-hydroxynaphthalene-6-sulfonate dye oxidation by $OFe^{IV}TDCSPP$

The stoichiometry of the oxidations was investigated at pH 6.93, 9.30 and 11.93 using 1-(4-methoxyphenylazo)-2-hydroxynaphthalene-6-sulfonate (**9**). This substrate, the most reactive of those studied, was selected to minimise any problems from the background self-reaction of the oxoiron(IV) porphyrin. These studies show that at each pH one dye molecule reduces four equivalents of the ferryl porphyrin. Thus the initial rate determining step is followed by three fast further oxidations and the true second-order rate constants for the

Table 4 pH Dependence of the second-order rate constant (k_2) for oxidation of 1-phenylazo-2-hydroxynaphthalene-6-sulfonate by $OFe^{IV}TDCSPP$ prepared from $Fe^{III}TDCSPP$[a]

pH	k_2/dm^3 mol^{-1} s^{-1}[b]	pH	k_2/dm^3 mol^{-1} s^{-1}[b]
6.93	131 ± 3.8	10.65	45 ± 0.8
7.40	67 ± 2.3	11.00	66 ± 1.0
7.95	23 ± 1.0	11.41	75 ± 0.8
8.65	12 ± 0.8	11.53	79 ± 0.5
9.30	12 ± 0.8	11.88	82 ± 2.0
9.87	22 ± 0.5	11.93	85 ± 1.3
10.40	38 ± 0.5	12.68	93 ± 2.0

[a] $Fe^{III}TDCSPP$, 10^{-6} mol dm^{-3}; 3-CPBA, 5×10^{-7} mol dm^{-3}; ionic strength, 0.05 mol dm^{-3}; 30 °C. [b] Average of at least two measurements. In regions of buffer overlap one measurement was carried out in each buffer.

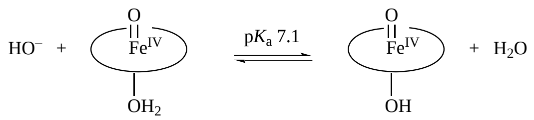
reactions are a quarter of the measured values. The values reported in this paper have all been corrected to allow for this factor of four.

pH dependence of the reaction of acid orange 12 (6) with oxoiron(IV) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin

Using the method described above, the oxidation of acid orange 12 (**6**) by $OFe^{IV}TDCSPP$ was examined at 14 pH values between 6.93 and 12.68. For each of these reactions the rate was found to be first-order in [Dye] and [$OFe^{IV}P$]. On increasing the pH of the reaction from 6.93 to 12.68 the measured k_2 values pass through a minimum between pH 8.65 and 9.30 (Table 4).

The pK_a of acid orange 12 (**6**) is 10.75 at an ionic strength of *ca.* 0 and is calculated to be 10.66 at ionic strength 0.05 mol dm^{-3},[17] consequently changing the pH will change the ratio of the concentrations of the dye and its anion present in the reaction mixtures. Monitoring the UV–VIS spectrum of **6** over the pH range 9.30–12.68 shows a clean equilibrium (sharp isosbestic points) between the dye and its anion (the same is true of all its substituted derivatives). No evidence for a pH dependent azo–hydrazone tautomeric equilibrium was detected.

Changing the pH of the reaction medium also affects the axial ligand on the ferryl porphyrin oxidant. Under the reaction conditions this will either be a water molecule or hydroxide ion (Scheme 3). Jeon and Bruice,[18] using pH dependent redox potential measurements on $Fe^{III}TDCSPP$, measured the pK_a value for this ionisation in Scheme 3 to be 7.1.



Scheme 3

Based on the dye and oxoiron(IV) porphyrin pH dependent equilibria, described above, four separate oxidations are possible and the overall rate of reaction is the sum of the rates of the separate reactions [eqn. (3)]. However, calculation of the

$$-d[OFe^{IV}P]/dt = k_a[OFe^{IV}P(OH_2)][Dye] + k_b[OFe^{IV}P(OH_2)][Dye^-] + k_c[OFe^{IV}P(OH)][Dye] + k_d[OFe^{IV}P(OH)][Dye^-] \quad (3)$$

pH-dependent mole fractions of the species in the reaction mixtures shows that at no pH are significant concentrations of both $OFe^{IV}P(OH_2)$ and dye anion present in the solutions (Fig. 3). Assuming the term in k_b is therefore unimportant, the rate equation reduces to the three terms given in eqn. (4).

$$-d[OFe^{IV}P]/dt = k_a[OFe^{IV}P(OH_2)][Dye] + k_c[OFe^{IV}P(OH)][Dye] + k_d[OFe^{IV}P(OH)][Dye^-] \quad (4)$$

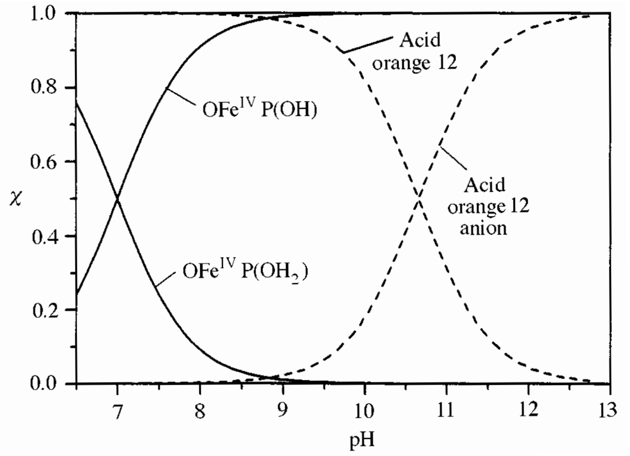


Fig. 3 Calculated dependence of the mole fractions of $OFe^{IV}TDCSPP(OH_2)$ and $OFe^{IV}TDCSPP(OH)$ and of acid orange 12 (**6**) and its anion on pH; μ = 0.05 mol dm^{-3}; 30 °C

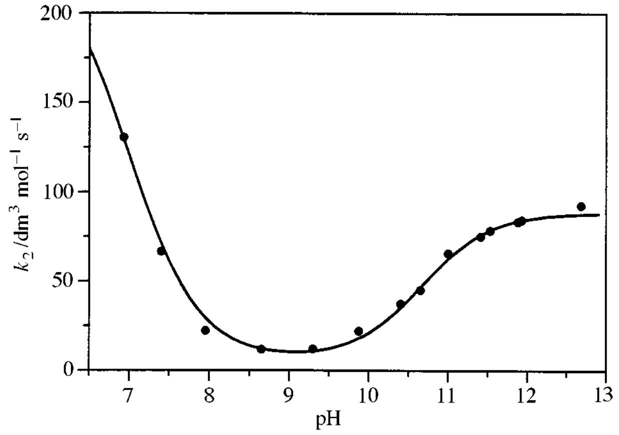


Fig. 4 pH dependence of the second-order rate constant for the reaction between $OFe^{IV}TDCSPP$ and acid orange 12 (**6**). The points are experimental and the line is generated using eqn. (5).

Since the concentrations of the active species are pH dependent so too are the measured rates and k_2 values. The concentrations of dye and iron porphyrin species can be calculated as a function of proton concentration from their k_a values [eqn. (5)].

$$k_2 = \{k_a/(1 + K_P/[H^+])(1 + K_D[H^+])\} + \{k_c/(1 + [H^+]/K_D)(1 + K_D/[H^+])\} + \{k_d/(1 + [H^+]/K_P)(1 + [H^+]/K_D)\} \quad (5)$$

This allows a partition of the measured overall rate constant, k_2, into those of the individual reactions, k_a, k_c and k_d, where K_P and K_D are the dissociation constants of the oxoiron(IV) porphyrin and dye respectively.

Assuming only the pK_a of acid orange 12 (**6**), eqn. (5) was used to obtain values for k_a, k_c, k_d and K_P from the pH dependence of the measured k_2 values. The best fit to the data (Fig. 4) gives k_a 235 ± 7, k_c 6.3 ± 1.9 and k_d 88.5 ± 2.3 dm^3 mol^{-1} s^{-1} and a pK_a for the oxoiron(IV) porphyrin ionisation of 7.0 ± 0.2. The last value is in excellent agreement with the pK_a of $OFe^{IV}TDCSPP$ (7.1 ± 0.2) measured by Jeon and Bruice.[18] Using these data, it is possible to calculate the rates of the three individual oxidations over the pH range studied (Fig. 5). This shows, as expected, that at pH $\leqslant$ 7.0 essentially all the reaction occurs between $OFe^{IV}P(OH_2)$ and dye whereas at pH $\geqslant$ 11.0 only the reaction of $OFe^{IV}P(OH)$ and dye anion is important. In the intermediate pH region all three reactions contribute with dye oxidation by $OFe^{IV}P(OH)$ dominating at pH *ca.* 9.0.

Table 5 Measured second-order rate constants for the oxidation of substituted 1-phenylazo-2-hydroxynaphthalene-6-sulfonates **2**–**9** by OFe^{IV}-TDCSPP at pH 6.93, 9.30 and 11.93 and calculated second-order rate constants k_a, k_c and k_d[a]

	k_2[b]/dm^3 mol^{-1} s^{-1}					
Dye **2**–**9** (Subst.)	pH = 6.93	9.30	11.93	k_a[c]/dm^3 mol^{-1} s^{-1}	k_c[c]/dm^3 mol^{-1} s^{-1}	k_d[c]/dm^3 mol^{-1} s^{-1}
2 (4-NO$_2$)	17	16	38	19 ± 1.5	15 ± 0.8	39 ± 1.5
3 (4-COMe)	26	10	73	41 ± 2.8	8 ± 0.8	78 ± 1.0
4 (3-CF$_3$)	29	18	42	40 ± 1.3	16 ± 0.8	43 ± 0.5
5 (4-Cl)	123	26	100	212 ± 9.0	18 ± 1.3	102 ± 6.8
6 (H)	131	12	85	235 ± 7.2	8 ± 2.0	89 ± 1.3
7 (4-CHMe$_2$)	693	26	141	1269 ± 14	16 ± 3.5	151 ± 4.5
8 (4-Me)	721	29	149	1320 ± 19	18 ± 1.0	157 ± 2.8
9 (4-OMe)	4735	99	280	8725 ± 139	48 ± 4.5	293 ± 4.0

[a] OFe^{IV}TDCSPP prepared from Fe^{III}TDCSPP, 10^{-6} mol dm^{-3}; 3-CPBA, 5×10^{-7} mol dm^{-3}; ionic strength, 0.05 mol dm^{-3}; 30 °C. [b] Average of at least two measurements. [c] Calculated from eqn. (5) using pK_a = 7.0 for OFe^{IV}TDCSPP and pK_a of dye in Table 1.

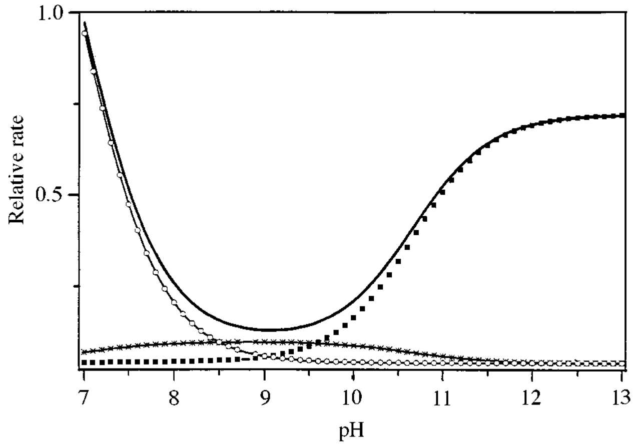


Fig. 5 pH dependence of the contributions of the rate of reaction of (—○—) OFe^{IV}TDCSPP(OH$_2$) with **6**; (—×—) OFe^{IV}TDCSPP(OH) with **6** and (--■--) OFe^{IV}TDCSPP(OH) with the anion of **6** to (——) the overall rate of oxidation; μ = 0.05 mol dm^{-3}; 30 °C

Determination of k_a, k_c and k_d values for the oxidation of a series of 1-(substituted phenylazo)-2-hydroxynaphthalene-6-sulfonate dyes by OFe^{IV}TDCSPP

The method described above can be simplified and applied to the oxidation of other dyes related to acid orange 12 (**6**). Thus knowing the pK_a values of the dye and of the oxoiron(IV) porphyrin and the second-order rate constant, k_2, at a minimum of three pH values, k_a, k_c and k_d can be calculated. To minimise the errors, the three pH values should be selected so that a different one of the three reactions dominates under each condition. This approach was tested with acid orange 12 (**6**), using pH 6.93, 9.30 and 11.93, and it gave k_a, 235 ± 9.8; k_c, 6.3 ± 2.0 and k_d, 88.5 ± 2.3 dm^3 mol^{-1} s^{-1}. These values are in excellent agreement with those obtained by fitting the pH-dependence of all the measured second-order rate constants, k_2.

It is important to note that at pH 9.0, the low concentrations of dye anion and of OFe^{IV}P(OH$_2$) (Fig. 5) means that even a small increase in the contribution of the terms k_a[OFe^{IV}P(OH$_2$)][Dye] and k_d[OFe^{IV}P(OH)][Dye$^-$] to the overall rate at this pH would require a large increase in their rate constants, k_a and k_d. This in turn would lead to a large effect at pH 6.93 or 11.93. Thus despite k_c being small, it is not possible to fit the measured k_2 values using k_a and k_d alone. This method provides a self-consistent check and means that the three rate constants can be calculated with a high degree of accuracy.

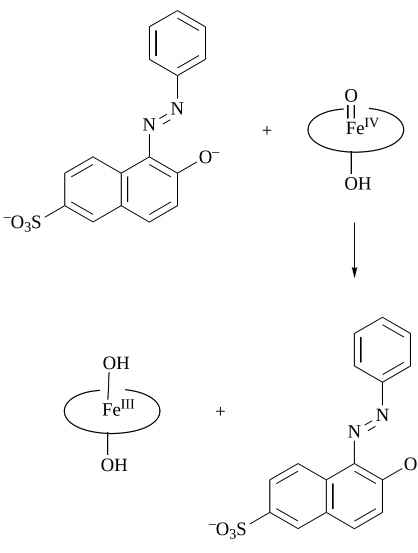
To help elucidate the mechanisms of the three oxoiron(IV) porphyrin oxidations of acid orange 12 (**6**) the reactions of a series of analogues, with substituents on the phenyl ring, have been investigated at pH 6.93, 9.30 and 11.93. The measured k_2 values and the calculated rate constants, k_a, k_c and k_d are shown in Table 5.

Oxidation of the *O*-methylated derivative of acid orange 12 (6) by OFe^{IV}TDCSPP

The *O*-methylation of **6** to give **12** locks the dye in the azo tautomer and also eliminates the dye–anion equilibrium in basic solution. As a result only two oxidation processes need to be considered, those between the dye and the two oxoiron(IV) porphyrin species. The rate of oxidation of **12** at two pH values (7.07 and 9.30) was measured and the second-order rate constants were found to be low and independent of pH (4.8 ± 1.3 and 4.3 ± 0.5 dm^3 mol^{-1} s^{-1}, respectively).

Mechanism of the reaction between OFe^{IV}TDCSPP(OH) and anions of 1-arylazo-2-hydroxynaphthalene-6-sulfonate dyes with second-order rate constant k_d

Oxoiron(IV) porphyrins can in principle oxidise substrates by oxygen-transfer, hydrogen atom-abstraction and electron-transfer. The first reaction has been reported for alkenes,[19] however, it has not been observed with oxoiron(IV) tetra(*N*-methyl-2-pyridyl)porphyrin in aqueous solution; instead the latter species readily oxidises substrates susceptible to single electron-transfer or hydrogen atom-abstraction.[20] For the dye anion, in the absence of an easily abstracted hydrogen atom, only electron-transfer is likely (Scheme 4). In agreement with this conclusion the redox potentials of the species involved [acid orange 12 (**6**) anion, $E_{\frac{1}{2}}$ = 0.46 V[21] and OFe^{IV}TDCSPP, $E_{\frac{1}{2}}$ = 1.06 V *vs.* SCE[18]] show that this is a thermodynamically favoured process.



Scheme 4

Plots of the log k_d values against the substituent constants σ and σ^+ show that each gives a linear correlation although the correlation coefficient of the latter is significantly better

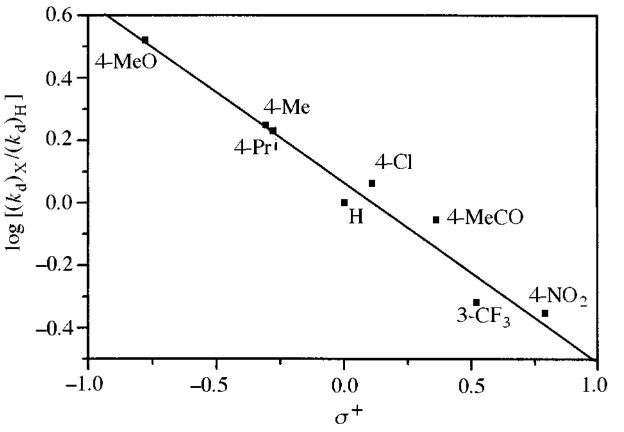


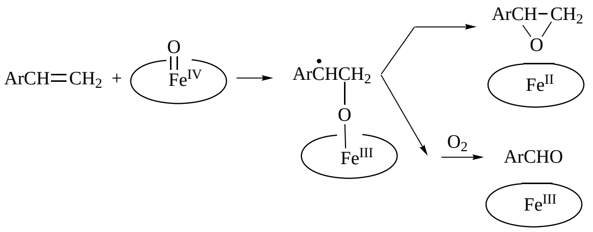
Fig. 6 Hammett plot of log[k_dX/k_dH] *vs.* σ^+ for the oxidation of dyes **2**–**9** by $OFe^{IV}TDCSPP(OH)$

($\rho = -0.73$, $r = 0.907$ and $\rho^+ = -0.568$, $r = 0.980$) (Fig. 6). The reaction constant is negative, as expected for an electron-transfer process, however, it is smaller than typical values for electron-transfer from simple benzenoid systems. We attribute this to the extensive delocalisation in the dye anion and the radical oxidation product, as a consequence, the substituent effect on the electron-transfer will be relatively small and significantly less than in simple benzenoid systems.

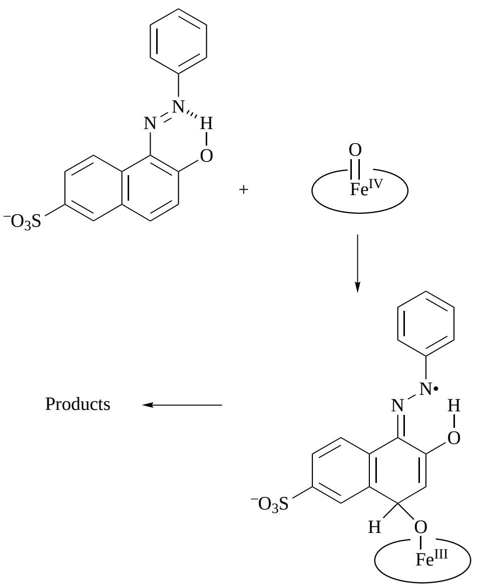
Mechanism of the reaction between 1-arylazo-2-hydroxynaphthalene-6-sulfonate dyes and $OFe^{IV}TDCSPP(OH)$ with second-order rate constant k_c

The rate of this reaction is almost independent of the substituent on the dye (Table 5). This might arise, as has been noted before,[22] from the substituent having two counteracting effects on the rate of reaction. Thus, in the present study, these could involve the known shift of the substrate equilibrium in favour of the hydrazone tautomer by electron-withdrawing substituents[23] and the oxidation of this tautomer by the $OFe^{IV}P$ species which would be enhanced by electron-donation. However, this cannot be the cause of the small substituent effect since for all the dyes the hydrazone is the major tautomer and consequently the substituent effect on the rate, arising from changes in the hydrazone concentration, will be small. For the substituent to have a marked effect on the rate the azo tautomer would have to be the substrate. However, electron-donation favours the azo tautomer so that this would not produce the required substituent effect to counteract that of the oxidation step.

Alternative mechanisms include hydrogen atom-abstraction and radical addition of $OFe^{IV}TDCSPP(OH)$ to the dye. We do not believe the former to be correct since *O*-methylated acid orange 12 (**12**) at pH 9.30 reacts at a similar rate to acid orange 12 (**6**) itself ($k_c = 4.3 \pm 0.5$ and 8.0 ± 2.0 dm^3 mol^{-1} s^{-1}, respectively), furthermore the substituent effects are quite different to those from oxidations with $OFe^{IV}TDCSPP(OH_2)$ which are considered to occur by hydrogen-abstraction (see below). Support for the radical addition mechanism comes from a recent study on the oxidation of styrene by $OFe^{IV}TMP$ in benzene for which Groves *et al.*[24] proposed a mechanism involving a radical attack by the oxoiron(IV) porphyrin on the alkene; similar mechanisms have been proposed before for other group VII oxidants derived from ruthenium porphyrins[25] and ruthenium complexes.[26] The small substituent effects in the styrene oxidation were attributed to the influence of the substituents on the stability of the benzylic radical intermediates that would be formed by addition of $OFe^{IV}TMP$ to styrenes (Scheme 5). In the azo dye oxidation an equivalent neutral nitrogen radical could be formed by addition of $OFe^{IV}P$ to either the azo group or to the 4-position of the 2-naphthol group of the azo tautomer (the latter is illustrated in Scheme 6). However, this cannot be occurring in the present study since the substituent effect on the proportion of azo dye in the tautomeric equilibrium would result in a significant negative ρ value (see below). Addition instead to the naphthalene ring of the hydrazone tautomer would, however, not be expected to show a significant ρ value. Work is currently in hand to identify the mechanism of this oxidation. Note that the contribution of this reaction to the overall oxidation is small compared with those of $OFe^{IV}TDCSPP(OH_2)$ with dye (low pH) and $OFe^{IV}TDCSPP(OH)$ with dye anion (high pH).



Scheme 5



Scheme 6

Mechanism of the reaction between 1-arylazo-2-hydroxynaphthalene-6-sulfonate dyes and $OFe^{IV}TDCSPP(OH_2)$ with second-order rate constant k_a

Changing the axial ligand from OH^- to H_2O is reported to have only a minor effect on the iron porphyrin's redox potential, increasing it from 1.06 to 1.10 V *vs.* SCE.[18] Consequently, it is surprising that this change has such a large effect on the rate of dye oxidation, for example the second-order rate constant for acid orange 12 (**6**) oxidation increases 31-fold whilst for its 4-methoxyphenyl analogue (**9**) the increase is 184-fold. A further distinction between the two oxidants is the marked substituent effect on the k_a values compared with the very small effect on k_c. The former is apparent in the good linear correlation ($r = 0.988$) of log k_a *vs.* σ^+ with $\rho = -1.79$ (Fig. 7).

The difference between $OFe^{IV}TDCSPP(OH)$ and $OFe^{IV}TDCSPP(OH_2)$ is also revealed by comparing their second-order rate constants for the oxidation of acid orange 12 (**6**) (Table 5) and its *O*-methyl derivative **12** at pH 7.07 and 9.30. For the former oxidant, the rate constants are very comparable whilst for the latter the *O*-methylated dye reacts almost 50 times slower. The above evidence suggests that the two oxidants react with azo dyes by different mechanisms.

There are two plausible mechanisms for the oxidation, electron-transfer and hydrogen atom-abstraction. The ρ value for the log k_a/σ^+ correlation is consistent with the former which would generate a dye radical cation (Scheme 7); presumably of

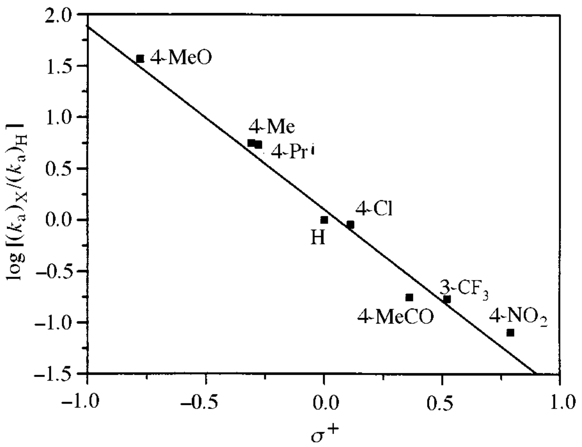
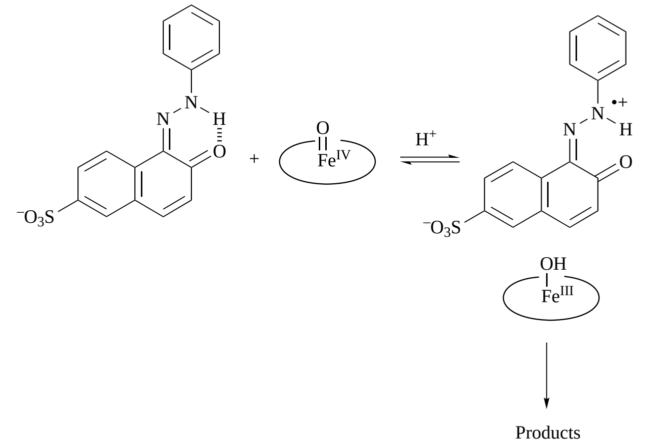


Fig. 7 Hammett plot of log[k_aX/k_aH] *vs.* σ^+ for the oxidation of dyes **2**–**9** by $OFe^{IV}TDCSPP(OH_2)$

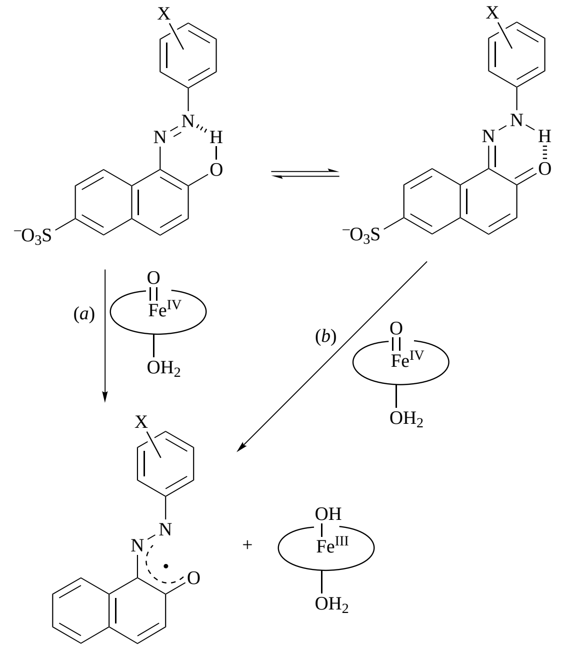


Scheme 7

the hydrazone tautomer since this has the lower oxidation potential. The latter mechanism, however, would be in agreement with our previous studies on the oxidation of phenols at pH 7.6 by the cationic oxoiron(IV) tetra(*N*-methyl-2-pyridyl)porphyrin which we showed occurred by abstraction of the phenolic hydrogen to give a phenoxyl radical.[12a] This mechanism would also account for the dramatic difference in reactivity between **6** and **12** since the latter has no readily abstractable hydrogen atoms.

To test whether or not the reactions of $OFe^{IV}TDCSPP(OH_2)$ and the azo dyes involve hydrogen atom-abstraction, we have measured the kinetic isotope effect for the reaction using the monodeuterated derivative of 1-(4-methylphenylazo)-2-hydroxynaphthalene-6-sulfonate (**8**). The reaction was carried out in phosphate buffer in D_2O (99.9% deuterated), prepared as for pH 6.93 in H_2O, at ionic strength 0.05 mol dm^{-3}. Under these conditions, allowing for exchangeable protons in the dye and H_2O in the buffer salts and porphyrin, the acidic hydrogen of **8** will be >99% deuterated. The pH meter gave a value of 7.12 for the reaction solution which after correction (addition of 0.38) for using a glass pH electrode in D_2O,[27] equates to a pD value of 7.50. This change on going from H_2O to D_2O arises from an increase in the buffer pK_a and is expected. The pK_a of the dye (10.66 in H_2O at ionic strength 0.05 mol dm^{-3}) will also increase with the result that at pD 7.50, as at pH 6.93, dye ionisation will be negligible. The pK_a for $Fe^{IV}TDCSPP(OD_2)$ has not been reported, however, those of the iron(III) analogues $Fe^{III}TDCSPP(OH_2)$ and $Fe^{III}TDCSPP(OD_2)$ are 7.85 and 8.68, respectively.[14] This gives $K_{aH}/K_{aD} = 6.76$, a value that is close to K_{wH}/K_{wD} of water.[28] Assuming that K_{aH}/K_{aD} is the same for both the iron(III) and oxoiron(IV) species, the pK_a for $OFe^{IV}TDCSPP(OD_2)$ is calculated to be 7.8. Bruice and co-workers[29] have shown that changing the solvent from H_2O to D_2O has no effect on the Fe^{III}/Fe^{IV} redox potential for $Fe^{III}TDMSPP$ and we assume that the same is true for the octachloro analogue, $Fe^{III}TDCSPP$, used in this study. UV–VIS spectra of the dye in the protic and deuterated buffers show no difference indicating that deuteration has no detectable isotope effect on the position of the azo–hydrazone tautomeric equilibrium.

The reaction of the oxoiron(IV) porphyrin and dye at pD 7.50 is first-order in each reactant with a second-order rate constant of 455 ± 12 $dm^3\ mol^{-1}\ s^{-1}$. The contribution to this value from k_c, the reaction between $OFe^{IV}TDCSPP(OD)$ and dye, will be very small and can effectively be neglected (assuming no isotope effect for k_c, the value is 24 $dm^3\ mol^{-1}\ s^{-1}$). The second-order rate constant k_a, corrected for the proportion of oxidant present as $OFe^{IV}TDCSPP(OD_2)$, becomes 675 ± 23 $dm^3\ mol^{-1}\ s^{-1}$. This gives a kinetic isotope effect (k_{aH}/k_{aD}) of 1.96 for the oxidation of **8** by aqueous $OFe^{IV}TDCSPP$ and clearly indicates that the rate determining step in the reaction involves hydrogen atom-abstraction from either the N–H (hydrazone) or O–H (azo) bond, depending on which tautomer is the substrate (Scheme 8).



Scheme 8

The moderate sized ρ value (-1.79 *versus* σ^+), however, is larger than would be expected for hydrogen atom-abstraction and is significantly greater than that obtained from the single electron transfer from the dye anion to $OFe^{IV}TDCSPP(OH)$ ($\rho = -0.568$ *versus* σ^+) and that from our previous studies on phenol oxidations ($\rho = -1.10$ *versus* σ^+ [12a]). A possible explanation is that the substituents have two effects on the rate of reaction that reinforce each other. Thus the substituents will influence the rate of hydrogen atom-abstraction by the ferryl porphyrin, as noted previously,[12a] and they will also affect the position of the azo–hydrazone tautomeric equilibrium.

Berrie *et al.*,[23] used ^1H NMR spectroscopy to examine the azo–hydrazone equilibrium in chloroform for a series of non-sulfonated 1-(substituted phenylazo)-2-naphthol dyes, analogous to those in the present study. Their data show the azo tautomer is favoured by electron-donating substituents and *vice versa*. We have used their tautomer distributions, from eight dyes, to calculate equilibrium constants (K_{taut}) for a Hammett analysis of the equilibria and have obtained a linear correlation ($r = 0.930$) of log K_{taut} *versus* σ^+ with $\rho = 0.46$ (the calculated K_{taut} for the 4-cyano-substituted dye was not used since it

Table 6 Second-order rate constants, k_a, k_b, k_c and k_d (dm^3 mol^{-1} s^{-1}), calculated from the measured, pH-dependent rate constants, for the oxidation of dyes **10** and **11** by OFe^{IV}TDCSPP using eqn. (3)[a]

Dye	k_a	k_b	k_c	k_d
10	17 165 ± 1154	2 177 ± 344	2 277 ± 270	2 242 ± 192
11	3 624 ± 218	921 ± 108	2 418 ± 241	593 ± 49

[a] OFe^{IV}TDCSPP prepared from Fe^{III}TDCSPP, 10^{-6} mol dm^{-3}; 3-CPBA, 5×10^{-7} mol dm^{-3}; ionic strength, 0.05 mol dm^{-3}; 30 °C.

showed a large deviation from the line). Although we have been unable to obtain quantitative data for the equilibria in water, it is clear from UV–VIS spectra that, in agreement with the study in chloroform, the electron-withdrawing 4-nitro group shifts the equilibrium almost completely to the hydrazone tautomer (λ_{max} 486 nm), whereas with the electron-donating 4-methoxy group there is a significant amount of the minor azo tautomer (λ_{max} 410 and 502 nm). Another difference between the organic and aqueous solutions is that the azo content of the dyes in water is lower than that in chloroform.[30]

From the above it follows that the oxidation must occur *via* the azo tautomer [Scheme 8, path (*a*)], electron-donating substituents will then favour the reaction by increasing the concentration of this tautomer in the reaction mixture. Consequently the measured ρ value will be the sum of the ρ values for the azo–hydrazone tautomerisation and for the hydrogen atom-abstraction [eqn. (6)]. This gives an estimated $\rho_{H.abs}$ value of

$$\rho_{obs} = \rho_{taut} + \rho_{H.abs} \qquad (6)$$

−1.33. We believe this is a maximum value and the true $\rho_{H.abs}$ is of a smaller magnitude than this since our qualitative studies on the azo–hydrazone equilibrium in water suggest the azo concentration is smaller and the substituent effects are bigger than those in chloroform (larger ρ_{taut}).

Oxidation of sulfonated 1-arylazo-4-naphthol dyes with OFe^{IV}TDCSPP

The very strong intramolecular H-bonding in the 1-arylazo-2-naphthol dyes is not present in the corresponding 4-naphthol compounds and pK_a values of the latter are dramatically lower. Thus in the pH range 7–8, in contrast to the 1-arylazo-2-naphthols, the 1-arylazo-4-naphthols are extensively ionised, so that in the presence of OFe^{IV}TDCSPP substantial concentrations of both OFe^{IV}TDCSPP(OH$_2$) and dye anion will be present. As a consequence all four possible reactions between the two oxoiron(IV) species and the dye and its anion should be kinetically important and the rate law for loss of oxoiron(IV) porphyrin is that given in eqn. (3). This was tested with two dyes, 1-(4-sulfonatophenylazo)-4-naphthol (**10**) (pK_a 8.11) and 1-(4-nitrophenylazo)-4-hydroxynaphthalene-6-sulfonate (**11**) (pK_a 7.68) by measuring k_2 at 6 and 5 pH values, respectively. Computer fitting of the data to eqn. (3) gave the second-order rate constants of the four reactions (Table 6). These rate constants allow the contribution of each of the individual reactions to the overall reaction over the complete pH range to be calculated (see, for example, Fig. 8 for the oxidation of **11**). This shows that, although the rate constant for the oxidation of the dye anion by OFe^{IV}TDCSPP(OH$_2$) (k_b) is comparable with those for oxidation of the dye and dye anion by OFe^{IV}TDCSPP(OH) (k_c and k_d, respectively), the contribution from the first reaction to the overall rate is small because the concentrations of the two reacting species are small.

Interestingly for each of the 1-arylazo-4-naphthol dyes, the rate constants k_b and k_d for oxidation are very similar in size, indicating that the rate of electron-transfer from the dye anion to each oxoiron(IV) species is independent of the axial ligand [NB this might be expected for an outer sphere electron-transfer since the redox potentials of OFe^{IV}TDCSPP(OH$_2$) and OFe^{IV}TDCSPP(OH) are very similar].[18] Furthermore, assuming the same would be true for the 2-naphthol dyes, this provides a further justification for ignoring the reaction of the dye anion with OFe^{IV}TDCSPP(OH$_2$) in the oxidation of the 1-arylazo-2-naphthol dyes, since a combination of a k_b of comparable magnitude to k_d and very low concentrations of dye anion and OFe^{IV}TDCSPP(OH$_2$) make the term k_b[OFe^{IV}P-(OH$_2$)][Dye$^-$] in eqn. (3) insignificant.

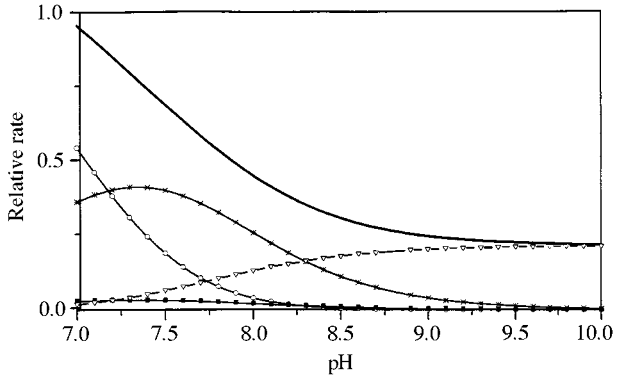


Fig. 8 pH dependence of the contributions of the rate of reaction of (—○—) OFe^{IV}TDCSPP(OH$_2$) with **11**; (—■—) OFe^{IV}TDCSPP(OH$_2$) with the anion of **11**; (—×—) OFe^{IV}TDCSPP(OH) with **11**; (—▽—) OFe^{IV}TDCSPP(OH) with the anion of **11** to (——) the overall rate of oxidation; μ = 0.05 mol dm^{-3}; 30 °C

Comparison of the rate constants, k_a, k_c and k_d, for the two 1-(4-nitrophenylazo)hydroxynaphthalene-6-sulfonate dyes (**2** and **11**) reveals that particularly dye **2** but also its anion are significantly less reactive than their 4-naphthol isomers. This can be attributed to the strong internal H-bonding in the 2-naphthol dye which makes hydrogen atom-abstraction harder and also to the higher oxidation potential of the 2-naphthol dye relative to its 4-naphthol isomer.[31] It is interesting to note that a similar trend has been reported for the horseradish peroxidase (HRP) and liginase-catalysed oxidations of azo dyes by hydrogen peroxide.[9a] Thus HRP bleaches 1-(4-sulfonatophenylazo)-4-naphthol (**10**) 7.5 times faster than the 2-naphthol isomer and for the 1-phenylazohydroxynaphthalene-6-sulfonate dyes the difference is nearly 50-fold.[9a]

Comparison of the oxidation of azo dyes by OFe^{IV}TDCSPP(OH$_2$) and OFe^{IV}TDCSPP(OH)

It is interesting to consider why the oxidations of the naphthol dyes by OFe^{IV}TDCSPP(OH$_2$) and OFe^{IV}TDCSPP(OH) differ so significantly, since changing the axial ligand has only a small effect on the reduction potentials of the two oxoiron(IV) species.[18] Thus, with an axial water the oxidation proceeds by hydrogen atom-abstraction whereas with an axial hydroxide it does not.

Resonance Raman studies on both cationic and anionic iron(III) porphyrins in aqueous solution reveal the pH dependence of the species present.[32] These data show that, in strongly basic solution, cationic iron(III) porphyrins exist as dihydroxy complexes whilst the analogous species of anionic iron(III) porphyrins are not formed, instead a monohydroxy complex is obtained.[34] The reluctance of anionic iron(III) porphyrins to ligate two negatively charged species has also been noted previously by Bruice and co-workers.[14,33]

A possible explanation for the different oxidation behaviour of OFe^{IV}TDCSPP(OH$_2$) and OFe^{IV}TDCSPP(OH) is that hydrogen atom-abstraction by the former gives the relatively stable aqua hydroxy iron(III) porphyrin whereas with the latter the unfavourable dihydroxy complex is formed. This difference in stability is reflected in the transition states for two processes accounting for why OFe^{IV}TDCSPP(OH$_2$) abstracts a hydrogen atom but OFe^{IV}TDCSPP(OH) does not.

Conclusions

(1) $OFe^{IV}TDCSPP$ is an efficient oxidant for 1-arylazo-2-hydroxynaphthalene-6-sulfonate dyes in aqueous solution in the pH range 6.93–12.68. (2) Under all conditions studied, the rate of $OFe^{IV}TDCSPP$ reduction is first-order in both [Dye] and [$OFe^{IV}TDCSPP$], and has a 1:4 stoichiometry of dye:$OFe^{IV}TDCSPP$. (3) The variation of the second-order rate constant with pH can be accurately simulated with three reactions, namely $OFe^{IV}TDCSPP(OH_2)$ with dye and OFe^{IV}-TDCSPP(OH) with dye and with dye anion, whose contributions to the overall rate are pH-dependent. (4) At high pH (>11.0), the predominant reaction involves initial electron-transfer between the dye anion and the oxidant OFe^{IV}-TDCSPP(OH). (5) At neutral pH, hydrogen-abstraction by $OFe^{IV}TDCSPP(OH_2)$ from the azo tautomer of the unionised dye is the major reaction. (6) The mechanism of the reaction between the dye and $OFe^{IV}TDCSPP(OH)$, which is significant in the pH range 8–10, is less well defined but may involve a radical addition of the oxoiron(IV) species to the hydrazone tautomer.

Experimental

Instrumentation

UV–VIS spectra and kinetic data were recorded on Hewlett Packard HP4582 and HP8453 diode array spectrometers and analysed using a Hewlett Packard HP9500 UV–VIS Chemstation and kinetic software 89512A or a PC with software A.02.05. Spectral simulations were carried out by spectral fitting using the QUANT II software package. Kinetic data were fitted with a non-linear regression programme SPSS 6.1 (SPSS Inc.). For kinetic studies with the fastest reactions, an Applied Photophysics RX 1000 stopped-flow apparatus, equipped with 2.5 cm^3 drive syringes and a dual pathlength (10/2 mm) cuvette, was attached to the spectrometer. The syringes and the reaction chamber were thermostatted at 30 °C. EI, CI and FAB (+ and −) mass spectra were obtained with a VG Analytical Autospec instrument. ^1H and ^{13}C NMR spectra were recorded on either JEOL JNM-Ex270 (270 MHz), Bruker MSL300 (300 MHz) or AMX500 (500 MHz) spectrometers. *J* values are given in Hz. Atomic absorption spectra (for Na and Fe) were obtained using a Philips PU9200 spectrometer. pH measurements were made with a Corning 200 pH meter equipped with a Reagecon PCFC8 combined pH/reference electrode.

Materials

All materials were commercially available and used without purification unless otherwise stated. The azo dyes 1-(4-chlorophenylazo)-, 1-(4-isopropylphenylazo)- and 1-(4-methylphenylazo)-2-hydroxynaphthalene-6-sulfonates (**5**, **7** and **8**) were supplied by Unilever Research. These compounds were organically pure although they contained small quantities of NaCl from the purification procedure (**5**, 4.7; **7**, 4.6 and **8**, 2.8%).

1-Phenylazo-2-hydroxynaphthalene-6-sulfonate (**6**) (Aldrich) was purified by making a saturated solution of the dye in DMF (10 cm^3) at 50 °C to which, after filtration, acetone was added dropwise to give a precipitate. The solid was recovered by filtration, slurried with fresh acetone, refiltered and dried. This led to a sharp increase in the dye's UV–VIS absorbance. Repeating the procedure twice did not lead to a further increase in absorption. The dye was finally recrystallised three times from ethanol–water (50:50 v/v) and had λ_{max}(aqueous buffer, pH 9.3; μ 0.05 mol dm^{-3}; 30 °C)/nm 484 (1.88×10^3 m^2 mol^{-1}) (Found: C, 54.55; H, 3.28; N, 8.01. $C_{16}H_{11}N_2NaO_4S{\cdot}0.5H_2O$ requires C, 54.86; H, 3.16; N, 8.01%). No impurities were detectable by ^1H NMR spectroscopy; *m*/*z* (FAB^-) 327 (M^-).

1-(4-Nitrophenylazo)-, 1-(4-acetylphenylazo)-, 1-(3-trifluoromethylphenylazo)- and 1-(4-methoxyphenylazo)-2-hydroxynaphthalene-6-sulfonate (**2**, **3**, **4** and **9**) were all prepared by the same procedure, illustrated with the synthesis of **2**. Sodium nitrite (4.15 g in 15 cm^3 water) was added slowly to a solution of 4-nitroaniline (8.29 g) in 1 mol dm^{-3} sulfuric acid (100 cm^3), keeping the temperature <3 °C. This cold solution was slowly added to 6-hydroxy-2-naphthalene sulfonic acid (12.3 g) and sodium hydroxide (4.0 g) dissolved in water (100 cm^3). The mixture was then heated until the red solid product was dissolved and sodium chloride (20 g) was added. The solution was cooled to 5 °C and the product recovered by filtration, washed with saturated brine and purified as described above for dye **6**. **2**: λ_{max}-(aqueous buffer, pH 9.3; μ 0.05 mol dm^{-3}; 30 °C)/nm 486 (2.78×10^3 m^2 mol^{-1}); *m*/*z* (FAB^-) 372 (M^-) (Found: C, 47.20; H, 2.93; N, 10.12. $C_{16}H_{10}N_3NaO_6S{\cdot}0.5H_2O$ requires C, 47.53; H, 2.74; N, 10.39%). **3**: λ_{max}(aqueous buffer, pH 9.3; μ 0.05 mol dm^{-3}, 30 °C)/nm 482 (2.47×10^3 m^2 mol^{-1}); *m*/*z* (FAB^-) 369 (M^-) (Found: C, 53.75; H, 3.55; N, 6.80. $C_{18}H_{13}N_2NaO_5S$ requires C, 53.86; H, 3.52; N, 6.98%). **4**: λ_{max}(aqueous buffer, pH 9.3; μ 0.05 mol dm^{-3}, 30 °C)/nm 474 (1.73×10^3 m^2 mol^{-1}); *m*/*z* (FAB^-) 395 (M^-) (Found: C, 48.87; H, 2.45; N, 6.48. $C_{17}H_{10}F_3N_2NaO_4S$ requires C, 48.81; H, 2.41; N, 6.70%). **9**: λ_{max}-(aqueous buffer, pH 9.3; μ 0.05 mol dm^{-3}; 30 °C)/nm 502 (1.71×10^3 m^2 mol^{-1}); *m*/*z* (FAB^-) 357 (M^-) [Found: C, 52.76; H, 3.36; N, 7.07. $C_{17}H_{13}N_2NaO_5S$ (2% NaCl) requires C, 52.63; H, 3.38; N, 7.22%].

1-(4-Nitrophenylazo)-4-hydroxynaphthalene-6-sulfonate (**11**) was prepared by heating a solution of 4-(4-nitrophenylazo)-1-naphthol (1 g) in sulfuric acid (50 cm^3) at 50 °C for 3 h. The addition of sodium hydroxide (15 g) in water (50 cm^3) led to the precipitation of the product. The product was recovered by filtration, dissolved in aqueous buffer (pH 9.3, 10 cm^3) and washed three times with dichloromethane to remove unreacted substrate. The dye was then extracted into dichloromethane using the phase transfer reagent tetrabutylammonium chloride and washed five times with water. Ion-exchange chromatography with macroporous Dowex MSC-1 (H^+ form, 20–50 mesh) gave the dye **11**, 32 mg (3.2%). Although the yield is low, ^1H NMR spectroscopy shows the compound to be pure and to be the required 6-sulfonated compound. λ_{max}(aqueous buffer, pH 7.0; μ 0.05 mol dm^{-3}; 30 °C)/nm 560 (2.53×10^3 m^2 mol^{-1}); δ_H(DMSO) 12.10 (1H, s), 8.83 (1H, d), 8.42 (1H, s), 8.33 (1H, d), 8.32 (2H, d), 7.96 (2H, d), 7.64 (1H, m) and 7.51 (1H, m); *m*/*z* (FAB^-) 372 (M^-).

The synthesis of 2-methoxy-1-phenylazonaphthalene-6-sulfonate (**12**) was initially attempted by methylation of 1-phenylazo-2-hydroxynaphthalene-6-sulfonate, using several literature methods for methylating the non-sulfonated analogue,[34] however, these were unsuccessful. The method that succeeded involved first preparing 2-methoxy-1-phenylazonaphthalene followed by sulfonation. Potassium hydride (1.4 g in oil) was added slowly to 1-phenylazo-2-naphthol (3.2 g) in benzene (100 cm^3) followed by dry DMSO (5 cm^3), to ensure complete solution of the naphthol anion, and finally iodomethane (1.9 g). The mixture was heated to 70 °C for 3 h, cooled and washed three times with water and the organic solution was removed under vacuum. Column chromatography on silica gel, using cyclohexane–dichloromethane, gave the required product 2.1 g (62%), λ_{max}(MeOH)/nm 390; δ_H($CDCl_3$) 8.48 (1H, d), 8.12 (1H, d), 8.09 (2H, d), 7.81 (1H, d), 7.60–7.25 (5H, m), 7.29 (1H, d) and 3.9 (3H, s); *m*/*z* (EI) 262 (M^+). Sulfonation was achieved by adding, with stirring, concentrated sulfuric acid (25 cm^3) to 2-methoxy-1-phenylazonaphthalene (1.5 g) at room temperature. After 10 min, the reaction was cooled, ice (*ca.* 80 g) was slowly added and the mixture was poured into iced water (100 cm^3) containing sodium hydroxide (10 g). The resulting solid was collected by filtration, washed with brine prepared in buffer (pH 9.3) and shaken thoroughly with dichloromethane. The methylated dye is very readily demethylated in acidic solution, however, the two compounds can be separated by making a solution in dichloromethane, using the phase transfer agent tetrabutylammonium chloride, and extracting the naphthol into aqueous sodium hydroxide. The success of this separation can be checked by ^{1}H NMR spectroscopy by monitoring the downfield shifted peak of the strongly H-bonded proton of the naphthol dye (δ 15.5). The tetrabutylammonium salt of the methylated dye was converted to the sodium salt by ion-exchange chromatography using Duolite C225 SRC 9, sodium form (14–52 mesh). Removal of the solvent gave 2-methoxy-1-phenylazonaphthalene-6-sulfonate (**12**) 0.59 g (28%); λ_{max}(aqueous buffer, pH 9.3; μ 0.05 mol dm^{-3}; 30 °C)/nm 380 (7.5×10^2 m^2 mol^{-1}); δ_H(CDCl$_3$) 8.42 (1H, d), 8.11 (1H, d), 7.97 (2H, d), 7.85 (1H, dd), 7.79 (1H, d), 7.52 (2H, m), 7.38 (1H, d), 7.35 (1H, dd) and 3.9 (3H, s); *m*/*z* (FAB$^-$) 341 (M^-) (Found: C, 56.13; H, 3.47; N, 7.46. $C_{17}H_{13}N_2NaO_4S$ requires C, 56.04; H, 3.60; N, 7.69%).

5,10,15,20-Tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin was prepared from 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin[35] by the method of Gonsalves *et al.*[36] This involved making 5,10,15,20-tetra(2,6-dichloro-3-chlorosulfonatophenyl)porphyrin, followed by hydrolysis to the tetrasulfonato analogue (overall yield 75%), λ_{max}(water)/nm 414, 512 and 572; δ_H 9.04 (s, 8H, β-pyrrole), 8.51 (d, 4H, *J* 8.6, *p*-phenyl), 8.09 (d, 4H, *J* 8.6, *m*-phenyl); *m*/*z* (FAB$^+$, tetrabutylammonium salt) 2176 (M^+), 1935, 1693, 1452; *m*/*z* (ES) 301 (M^{4-}), 402 (M^{3-}), 604 (M^{2-}).

The sulfonatoporphyrin was metallated using iron powder by a modification of the method of Herrmann *et al.*[37] The porphyrin (0.107 g) was dissolved in water (100 cm^3) and passed through a short column of Amberlite CG-120, sodium form (5 g, 100–120 mesh). The eluent was refluxed with iron powder (2.5 g) until all the free base porphyrin had been consumed (monitored by UV–VIS spectroscopy) and the excess of iron was removed by filtration. The product was purified by adding dichloromethane and stirring with sufficient of the phase transfer agent, tetrabutylammonium chloride, to ensure all the metalloporphyrin was in the organic layer. This was then washed with water and the metalloporphyrin was converted to its sodium salt by adding the organic solution to a column of Amberlite CG-120, sodium form (20 g, 100–120 mesh) and eluting it with water. The recovered Fe^{III}TDCSPP was further purified by passing it through a second batch of the ion-exchange resin. Removal of the water gave the required metalloporphyrin (0.085 g, 79.7%). λ_{max}(water)/nm 398, 412 (1.2×10^3 m^2 mol^{-1}), 514, 584 and 650 *m*/*z* (FAB$^+$, tetrabutylammonium salt) 2230 [M^+ with 4(NBu$_4^+$)], 1989 [3(NBu$_4^+$) and H$^+$], 1747 [2(NBu$_4^+$) and 2H$^+$], 1505 (NBu$_4^+$ and 3H$^+$), 1263 (4H$^+$), 1037; *m*/*z* (ES) 315 (M^{4-}), 420 (M^{3-}) (Found: C, 30.00; H, 2.51; N, 2.98; Fe, 3.21; Na, 7.69. $C_{44}H_{17}Cl_8FeN_4Na_4O_{12}S_4 \cdot 16H_2O \cdot 1.85NaCl$ requires C, 30.20; H, 2.82; N, 3.20; Fe, 3.19; Na, 7.69%).

Kinetic procedure

Stock aqueous solutions of Fe^{III}TDCSPP and the dyes (typically 1.5×10^{-4} and 1.5×10^{-3} mol dm^{-3}, respectively) were prepared and kept for a maximum of two weeks. Fresh 3-CPBA solutions in methanol were made up at the beginning of each experiment (methanol rather than water was used as the solvent to prevent hydrolysis to hydrogen peroxide).

The standard procedure, for all but the fastest reactions, involved preparing OFe^{IV}TDCSPP by adding a half-molar equivalent of 3-CPBA (in 10 μl of methanol) to the iron(III) porphyrin in the required buffer solution in a quartz cuvette. The reaction was initiated by adding a solution of the dye in the same buffer to give a total volume of 3 cm^3.

For the fastest reactions a stopped-flow apparatus was used. One drive syringe was filled with freshly prepared OFe^{IV}TDCSPP, formed by the addition of a half-molar equivalent of 3-CPBA to Fe^{III}TDCSPP in aqueous buffer to give a final ionic strength (NaNO$_3$) of 0.05 mol dm^{-3}, the other was filled with a buffered solution of the azo dye. Following rapid mixing of equal volumes of the two solutions, the reactions were monitored by recording spectra 400–500 nm at fixed time intervals.

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