The oxidation of azo dyes by peroxy acids and *tert*-butyl hydroperoxide in aqueous solution catalysed by iron(III) 5,10,15,20-tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin: product studies and mechanism

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Product studies on the oxidation of two 1-arylazo-2-hydroxynaphthalene-6-sulfonate dyes by peroxy acids and by *tert*-butyl hydroperoxide catalysed by iron(III) 5,10,15,20-tetra(2,6-dichloro-2-sulfonatophenyl)porphyrin in solution have been carried out. In single turnover experiments at pH 11.88, 9.30 and 6.93, dye bleaching by peroxy acids is a two-step process; an initial fast reaction, during which the oxoiron(IV) porphyrin is also formed, is followed by a slow phase involving the regeneration of the iron(III) porphyrin from the oxoiron(IV) porphyrin. The peroxy acid : dye stoichiometry is 1 : 1 for the initial fast dye bleaching and 2 : 1 for the slow phase; the latter is equivalent to a 4 : 1 stoichiometry of oxoiron(IV) porphyrin to dye. In multiple turnover reactions the dye bleaching occurs in two sequential oxidations by oxoiron(IV) porphyrin π-cation radical, each with a peroxy acid : substrate stoichiometry of 1 : 1.

Evidence is presented to show that, in multi-turnover reactions at pH 11.88 where the substrate is the dye anion, the initial product arises from the hydroxylation of the 1-position of the naphthol ring which in the second step is oxidised further to give an azoxy compound. At pH 9.30, where the dyes exist predominantly as the hydrazone tautomers, the initial oxidation generates an azoxy compound which following a Wallach rearrangement is further oxidised on the naphthol ring. More extensive oxidation results in the cleavage of the N–N bond.

The iron(III) porphyrin-catalysed dye oxidation with excess of *tert*-butyl hydroperoxide at pH 6.93, which occurs by hydrogen atom-abstraction, has a hydroperoxide : dye stoichiometry approaching 2 : 1 and gives the same azoxy product as obtained at pH 11.88 with the peroxyacids.

Mechanisms to account for the observed products and stoichiometries are discussed.

Introduction

The stability of azo dyes, with respect to oxidation, is of crucial importance in washing processes. Thus a dye on a fabric must be stable if fading of dyed materials is to be avoided; in contrast, however, in the same situation it is important to be able to oxidise the dye molecules in solution to prevent unwanted dye-transfer between fabrics. For these reasons there is much interest in the mechanisms and products of the oxidative bleaching of azo dyes and the factors that control their stability towards oxidation with a view to designing dye molecules or bleaching systems to optimise the desired properties.[1] The recent papers by Oakes and co-workers[2] have provided much insight into the mechanisms of uncatalysed oxidations of azo dyes by peroxy acids, hypochlorite, chlorine and hydrogen peroxide.

Biodegradation of azo dyes is of particular importance since this may provide new environmentally friendly methods for treating dye effluent in waste water. Both horseradish peroxidase[3] and lignin peroxidases[4] have been shown to be effective in catalysing the oxidation of a range of azo dyes by hydrogen peroxide, the latter bringing about the complete degradation of a number of azo dyes.[4c,5] Cytochrome P450 monooxygenases can also oxidise 1-phenylazo-2-naphthol dyes.[6]

The work of Spadaro and Renganathan[3b] and Crawford and co-workers[4d] shows that the peroxidase-catalysed oxidation of azo dyes by H_2O_2 can give dye-dimers and a range of products from the oxidative cleavage of the azo link; the relative proportions depending on the structure of the dye molecule. Based on these studies both groups propose that the initial steps involve two one-electron oxidations of the dye by the active oxidants (compounds I and II) to give the dye radical followed by the dye cation. In subsequent steps the cation is trapped by water and the resulting hydroxylated intermediates break down to give either the aryldiazene (Scheme 1, route a) or the nitrosoarene (Scheme 1, route b) which then react further to the observed products. Although there is broad agreement about the one-electron oxidation mechanism there is a difference of opinion about the relative importance of the alternative subsequent cleavage pathways.

At York, we have instigated a study of azo dye oxidation in aqueous solution using iron porphyrin-based models for peroxidases and cytochrome P450 monooxygenases. This research programme is designed, through kinetic and product studies, to determine the mechanisms of these reactions and, in particular, the role of the oxoiron(IV) porphyrin π-cation radical and the oxoiron(IV) porphyrin active oxidants (analogues of compounds I and II, respectively). In our previous paper we described the pH dependence of the mechanism of azo dye oxidation with oxoiron(IV) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin.[7] Here we report the products from azo dye oxidation with peroxy acids catalysed by the iron(III) analogue of the oxoiron porphyrin above (Fe^{III}TDCSPP) † and propose likely mechanisms for the reactions.

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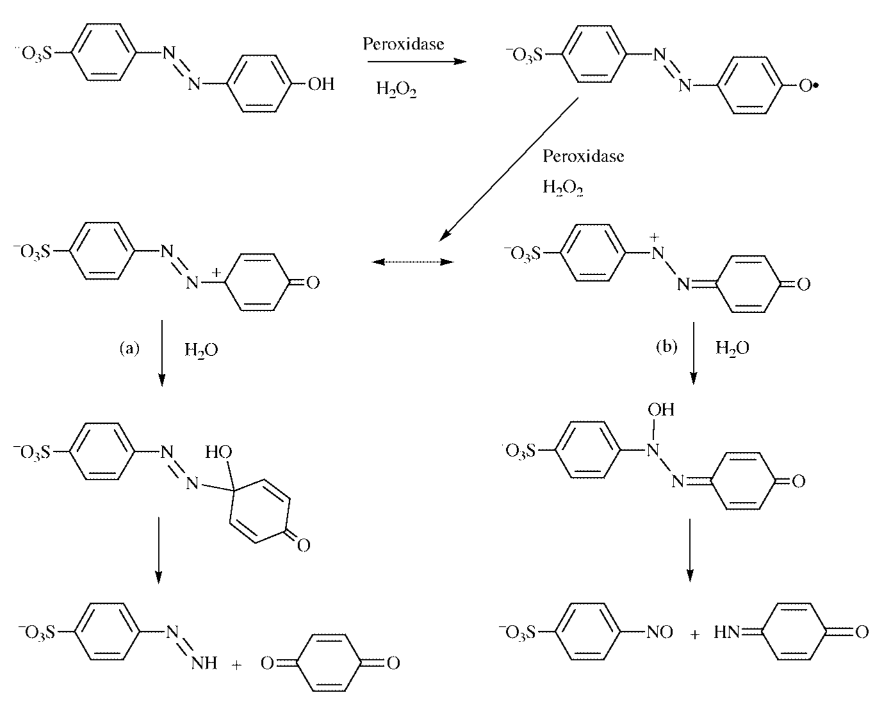
† The following abbreviations are used, TDCSPP = tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin ligand; P (as in Fe^{III}P) = porphyrin ligand in general; MCPBA = 3-chloroperoxybenzoic acid; MMPP = magnesium monoperoxyphthalate.

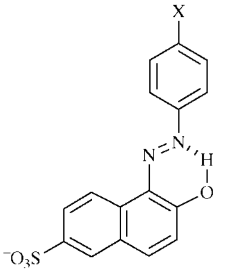


Scheme 1

Results and discussion

Oxidation system and procedure

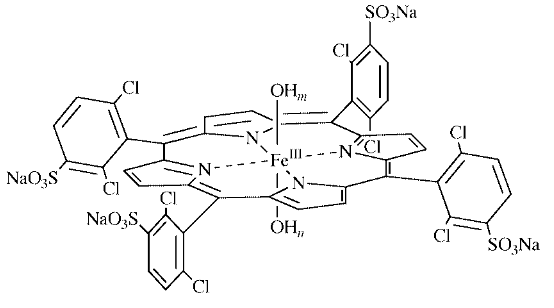
Two water soluble monosulfonated 1-(4-substituted-phenyl)-azo-2-naphthols (**1** and **2**) were used in this study. These were selected to investigate the influence of the substituents on the mechanisms of oxidation and also to help in the identification of the products. The analyses were mainly by UV-VIS spectroscopy and by solvent extraction followed by GC and GC-MS; the latter method allowed the simple separation, identification and estimation of the yields of the organic soluble oxidation products. This procedure also avoids the potential problem of the thermal decomposition of the unreacted dyes during GC analysis,[4e] since the azo dyes are all water soluble and as such were not injected into the gas chromatograph.



1 X = NO_2

2 X = OMe

The reactions were carried out at room temperature in buffered solution (ionic strength 0.05 mol dm^{-3}) using the sterically hindered anionic iron(III) tetra(2,6-dichloro-3-sulfonatophenyl)porphyrin (**3**) as the catalyst, at pH 11.88 and 9.3 with a peroxy acid and at pH 6.93 with $^tBuO_2H$ as the oxidant. The peroxy acid oxidants used in this study were magnesium monoperoxyphthalate (MMPP) and 3-chloroperoxybenzoic acid (MCPBA). To overcome problems from catalyst degradation, the iron porphyrin was added to the reaction mixture in two (pH 9.3) or three (pH 11.88) equal aliquots.



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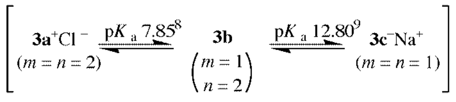


$$\left[\underset{(m=n=2)}{\mathrm{3a^+Cl^-}} \xrightleftharpoons{\mathrm{p}K_\mathrm{a}\,7.85^8} \underset{\binom{m=1}{n=2}}{\mathrm{3b}} \xrightleftharpoons{\mathrm{p}K_\mathrm{a}\,12.80^9} \underset{(m=n=1)}{\mathrm{3c^-Na^+}}\right]$$

Oxidation stoichiometry

Stoichiometry of dye oxidations involving a single turnover of catalyst. UV-VIS spectroscopy reveals that the addition of less than one equivalent peroxy acid to a solution of Fe^{III}TDCSPP in the presence of a dye at pH 11.88 leads to a two-step process (Fig. 1): initial fast competitive oxidations involving $OFe^{IV}P^{+\bullet}$ lead to dye bleaching and reaction with $Fe^{III}P$ to give the oxoiron(IV) porphyrin (λ_{max} 420 nm), followed by a slow regeneration of the iron(III) porphyrin (λ_{max} 414 nm) from $OFe^{IV}P$ accompanied by a further bleaching of the dye. To optimise the initial fast process and to ensure that the change in dye concentration was not too small for accurate measurement, the more reactive dye, **2**, was used at a concentration not greater than 10-fold that of the oxidant. A further complication arising from the background reduction of $OFe^{IV}P$ to $Fe^{III}P$ without concomitant dye bleaching was allowed for by using rate constants measured previously.[7] Two methods were used to quantify the dye bleaching; the first used spectral simulation effectively to subtract iron(III) and oxoiron(IV) absorptions at the λ_{max} of the dye, while in the second the dye loss at 458 nm (an isosbestic point for the $Fe^{III}P/OFe^{IV}P$ system) was monitored. Both methods consistently gave the same results.

Table 1 shows that, at the lowest concentration of MCPBA, assuming that in the fast reaction there is a 1 : 1 dye : peroxy acid stoichiometry for dye bleaching (reaction 1) and a 2 : 1

Table 1 Fast and slow bleaching of **2** and formation of $OFe^{IV}P$ in the reaction of dye **2** with MCPBA catalysed by $Fe^{III}TDCSPP$[a]

MCPBA/10^{-6} mol dm^{-3}	Bleached dye/ 10^{-6} mol dm^{-3} in initial FAST reaction	$OFe^{IV}P$[b] formed/10^{-6} mol dm^{-3} in initial FAST reaction	MCPBA[c] accounted for (%)	Stoichiometry[d] of $OFe^{IV}P$ consumed to dye bleached in SLOW reaction
0.35	0.20	0.30	99	4.2
0.71	0.41	0.51	94	4.0
1.06	0.62	0.72	93	4.2
1.42	0.86	0.84	90	3.8
2.82	1.73	1 (100% of FeP)	(79)[e]	—

[a] Iron porphyrin (10^{-6} mol dm^{-3}) and dye **2** (10^{-5} mol dm^{-3}) at pH 9.3, ionic strength 0.05 mol dm^{-3} and 30 °C. [b] Measured by UV-VIS spectroscopy by monitoring absorbance at 420 nm. [c] Assuming the dye oxidant stoichiometry is 1 : 1 and one peroxy acid oxidises two $Fe^{III}P$ to two $OFe^{IV}P$. [d] Calculated from the second slow bleaching of dye by $OFe^{IV}P$, allowing for a background loss of $OFe^{IV}P$. [e] This value cannot be compared with the others because there is an excess of oxidant.

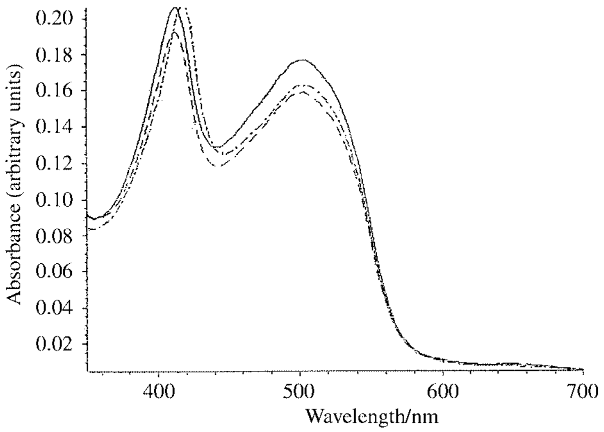


Fig. 1 The UV-VIS spectrum of $Fe^{III}TDCSPP$ (10^{-6} mol dm^{-3}) and dye **2** (10^{-5} mol dm^{-3}); (——) before, (-•-) 5 s after and (- - -) 30 min after the addition of MCPBA (10^{-6} mol dm^{-3}); pH 9.3, 30 °C and ionic strength 0.05 mol dm^{-3}.

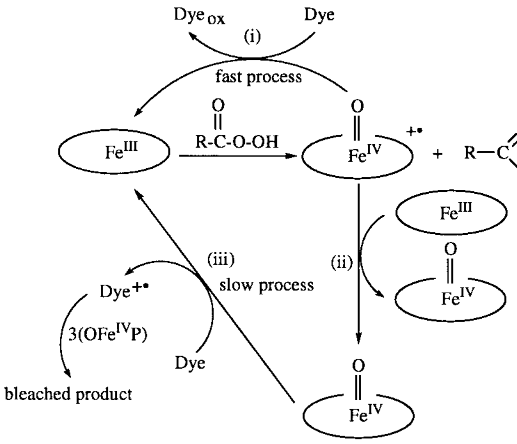
$$\text{Dye} + ArCO_3H \xrightarrow{Fe^{III}P} \begin{matrix}\text{Bleached}\\ \text{Dye}\end{matrix} + ArCO_2H \quad (1)$$

$$Fe^{III}P + ArCO_3H \longrightarrow OFe^{IV}P^{+\bullet} + ArCO_2H \quad (2)$$

$$Fe^{III}P + OFe^{IV}P^{+\bullet} \longrightarrow 2\,OFe^{IV}P \quad (3)$$

$Fe^{III}P$: peroxy acid stoichiometry for $OFe^{IV}P$ formation (reactions 2 and 3), the oxidant accountability is excellent. Interestingly, however, the slow second phase bleaching of the dye by the oxoiron(IV) porphyrin has a 4 : 1 $OFe^{IV}P$: dye stoichiometry; this is equivalent to a 2 : 1 stoichiometry of peroxy acid : dye. When the reactions were repeated at pH 6.93 and 9.30, the same 1 : 1 and 4 : 1 stoichiometries were observed for the fast and slow reactions, respectively. A mechanism to account for the biphasic oxidations is illustrated in Scheme 2 with dye and $Fe^{III}P$ competing for the initially formed $OFe^{IV}P^{+\bullet}$ in the fast phase of the oxidation [steps (i) and (ii)] and $OFe^{IV}P$ oxidising the dye [step (iii)] in the slow phase.

When the concentration of the peroxy acid is increased, the overall oxidant accountability falls slightly. We attribute this to non-productive consumption of peroxy acid in reactions with the active oxidant that competes with the dye and $Fe^{III}P$ in the fast phase of the reaction.[10] These reactions involve one-electron redox cycling of the catalyst [reactions (4)–(6)] and/or the two-electron reaction of $OFe^{IV}P^{+\bullet}$ with the peroxy acid [reaction (7)]. (These will be discussed in more detail in a future paper describing the kinetics of these dye bleaching systems.) There is also a shift in favour of dye bleaching over $OFe^{IV}P$ formation since increasing the concentration of peroxy acid effectively reduces the concentration of $Fe^{III}P$ which favours step (i) over step (ii) (Scheme 2).



Scheme 2

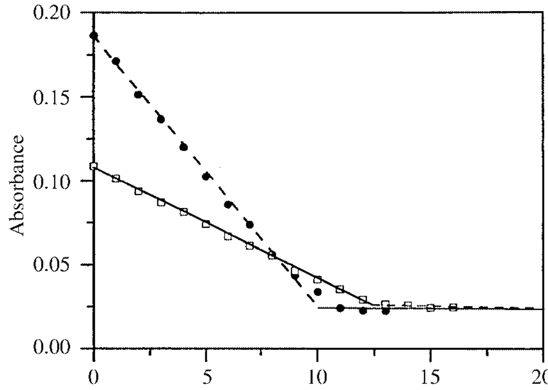


Fig. 2 The loss of dye **2** (10^{-5} mol dm^{-3}) absorbance on repeated addition of MCPBA (10^{-6} mol dm^{-3}) in the presence of $Fe^{III}TDCSPP$ (10^{-6} mol dm^{-3}) at pH 9.3 (●) (absorbance measured at 502 nm) and 11.88 (□) (absorbance measured at 498 nm), ionic strength 0.05 mol dm^{-3} and 30 °C.

$$OFe^{IV}P^{+\bullet} + ArCO_3H \longrightarrow OFe^{IV}P + ArCO_3^{\bullet} + H^+ \quad (4)$$

$$OFe^{IV}P + ArCO_3H \longrightarrow OFe^{IV}P^{+\bullet} + ArCO_2^{\bullet} + OH^- \quad (5)$$

$$OFe^{IV}P + ArCO_3H \longrightarrow OFe^{IV}P^{+\bullet} + ArCO_2^- + OH^{\bullet} \quad (6)$$

$$OFe^{IV}P^{+\bullet} + ArCO_3H \longrightarrow Fe^{III}P + ArCO_2H + O_2 \quad (7)$$

The single turnover experiments were repeated using a series of sequential additions of MCPBA to the same dye/$Fe^{III}P$ solution. The results (Fig. 2) show that there is essentially the same overall dye bleaching (from $OFe^{IV}P^{+\bullet}$ and $OFe^{IV}P$) for each aliquot of peroxy acid until dye oxidation is almost complete. This suggests that the products from dye oxidation with

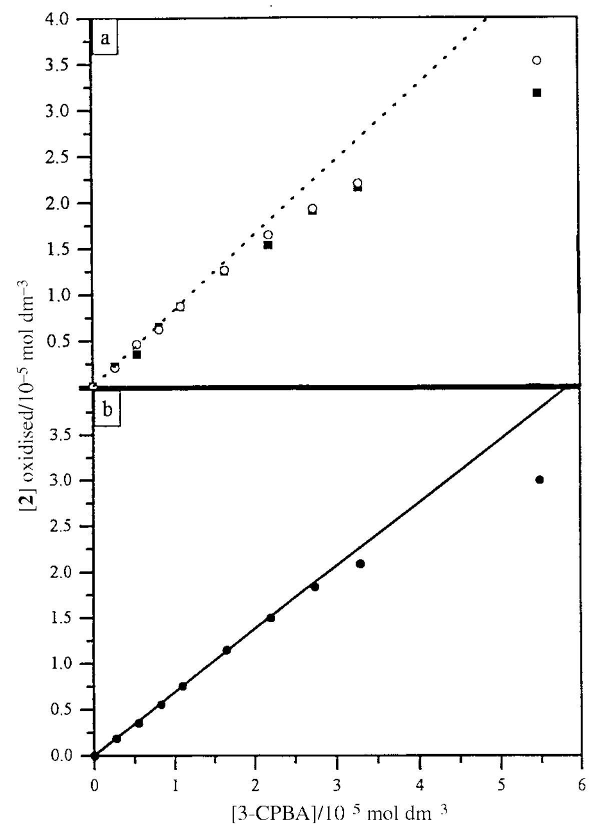


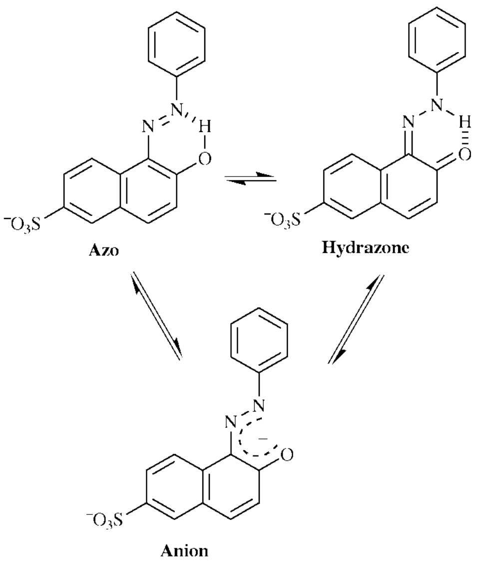
Fig. 3 The change in dye concentration on addition of MCPBA to fresh solutions of Fe^{III}TDCSPP (10^{-6} mol dm^{-3}) and **2** (5×10^{-5} mol dm^{-3}) at (a) pH 6.93 (○) and pH 9.3 (■) and (b) pH 11.88; 30 °C and ionic strength 0.05 mol dm^{-3}.

OFe^{IV}P$^{+\bullet}$ (1 : 1 stoichiometry) and with OFe^{IV}P (4 : 1 stoichiometry) have greater stability towards oxidation than the dyes themselves and are only oxidised further after the majority of the dye has been bleached.

Stoichiometry of dye oxidations involving multiple catalyst turnovers. To be able to generate sufficient products from the dye oxidations for their quantification and identification, a large excess of the peroxy acid was required to recycle the iron porphyrin catalyst. Under these conditions the major oxidant is OFe^{IV}P$^{+\bullet}$ and this brings about the bulk of the dye oxidation,[10] however, stoichiometric studies under these conditions are potentially complicated by competitive oxidations of the dye oxidation products and by side-reactions of the peroxy acid with the active oxidant that do not involve dye bleaching [reactions (4)–(7)].[10] These were investigated by oxidising a 50-fold excess of dye **2** over catalyst with progressively higher concentrations of MCPBA. The results (Fig. 3) show that there is a non-linear relationship between dye bleaching and oxidant concentration. The cause of the deviation from linearity in Fig. 3 was examined further by adding the oxidant to the reaction in several rather than in one aliquot. It was argued that if the non-linearity arises from competitive side-reactions of the peroxy acid, due to its initial high concentration in the solution, then the linearity should be improved by adding it over a period of time in several smaller aliquots. However, if it arises from the initial oxidation products competing with the dye for the active oxidant, the non-linearity should persist. For the oxidations at pH 6.93 and 9.3, the linearity was significantly improved giving the stoichiometries 1.83 and 1.73, respectively, suggesting that the non-linearity for these oxidations arises from peroxy acid side-reactions. Under these conditions the initial product from the first equivalent of active oxidant is further oxidised and the stoichiometry approaches 2. In contrast, the oxidations at pH 11.88 showed no improvement in linearity with the stoichiometry being dependent on the extent of reaction; rising for dye **2** from 1.78 to 1.94 as the extent of dye bleaching increased from 68 to 92%. We conclude that at all the pHs studied the dye oxidation occurs in two sequential steps, each of which has a peroxy acid : substrate stoichiometry of 1 : 1, giving an overall stoichiometry for both steps of 2 : 1. Under strongly basic conditions (pH 11.88) the initial product builds up in the early stages of the reaction and only substrate oxidation is important. At pH 11.88 the dyes will be predominantly present as anions and it is likely that the build-up of the initial oxidation product arises from the enhanced reactivity of the anion compared with unionised dye. As the reaction proceeds, however, the concentration of the first product increases at the expense of the substrate and it begins to compete for the active oxidant and the stoichiometry increases to give a final value of ~2.0 when dye bleaching is complete.

Products from the catalysed oxidation of 1-arylazo-2-naphthol dyes by peroxy acids at pH 11.88

The initial product studies were carried out with dye solutions at pH 11.88. Under these conditions the dyes employed are ~90% ionised[2a] and, from our previous studies on azo dye oxidation with OFe^{IV}TDCSPP,[7] we expect the dye anion rather than the dye itself to be the substrate. This eliminates potential problems arising from the dye being a mixture of azo and hydrazone tautomers since the isomers ionise to a common anion (Scheme 3).



Scheme 3

The peroxy acid was added to a solution of the dye (**1** or **2**) and Fe^{III}TDCSPP to give molar ratios of oxidant : dye : catalyst of 1600 : 800 : 1. Two further batches of the catalyst were added subsequently to ensure that all the peroxy acid had been consumed. UV-VIS spectroscopy indicated that each dye's visible absorbance was extensively bleached and that two new shorter wavelength absorption bands (λ_{max} ~330 and ~390 nm) were formed (Fig. 4). Control reactions showed that, in the absence of the iron porphyrin catalyst, < 10% of dyes **1** and **2** was oxidised by either MMPP or MCPBA in 48 h so that by comparison with the catalysed oxidation, effectively 100% complete in 2 h, the background reaction can be neglected.

Assuming that the oxidation products do not absorb in the region of the main visible absorbance of the dyes, the extent of dye bleaching was 68 and 73% for **1** and **2**, respectively. Exhaustive extraction of these reaction mixtures with diethyl ether followed by GC analysis, however, only detected one product in very low yield from each reaction, nitrobenzene (1.5%) and anisole (0.8%) based on bleached **1** and **2**, respect-

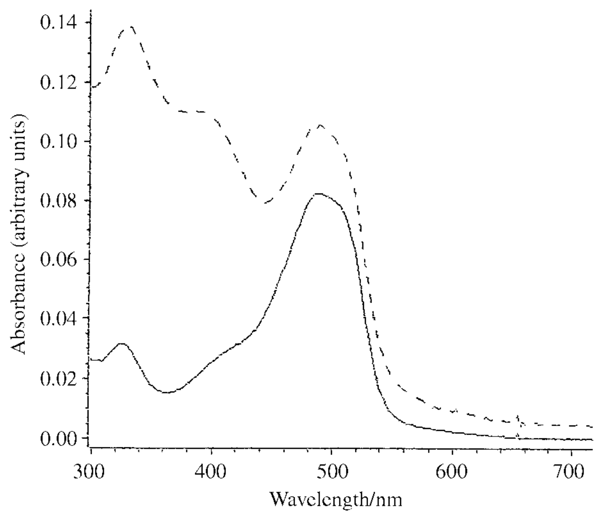
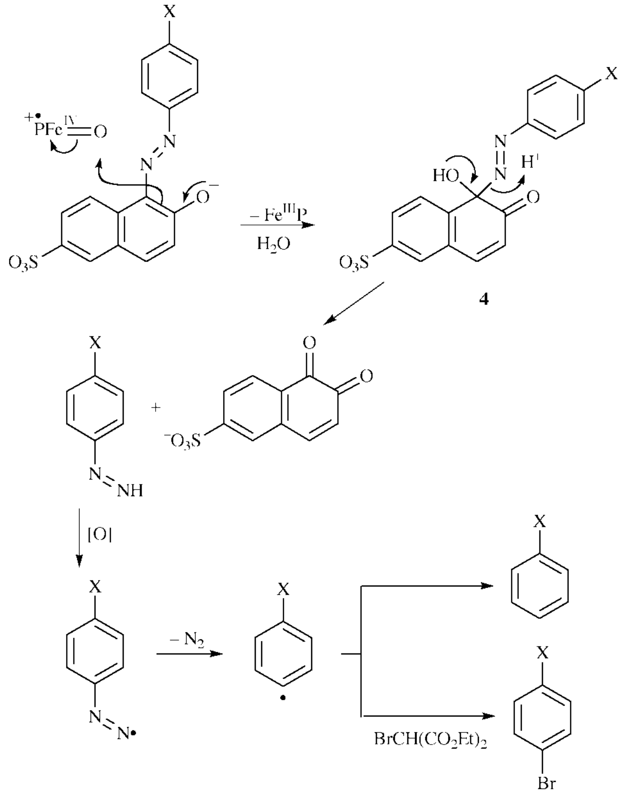


Fig. 4 The UV-VIS spectrum of dye **1** (5×10^{-4} mol dm^{-3}) before (——, spectrum 1/5 scale) and after (– – –) extensive oxidation with MMPP (1×10^{-3} mol dm^{-3}) catalysed by Fe^{III}TDCSPP [$3 \times (6.25 \times 10^{-7}$ mol dm^{-3})] in aqueous buffer, pH 11.88 at 30 °C; spectra recorded at pH 9.3.

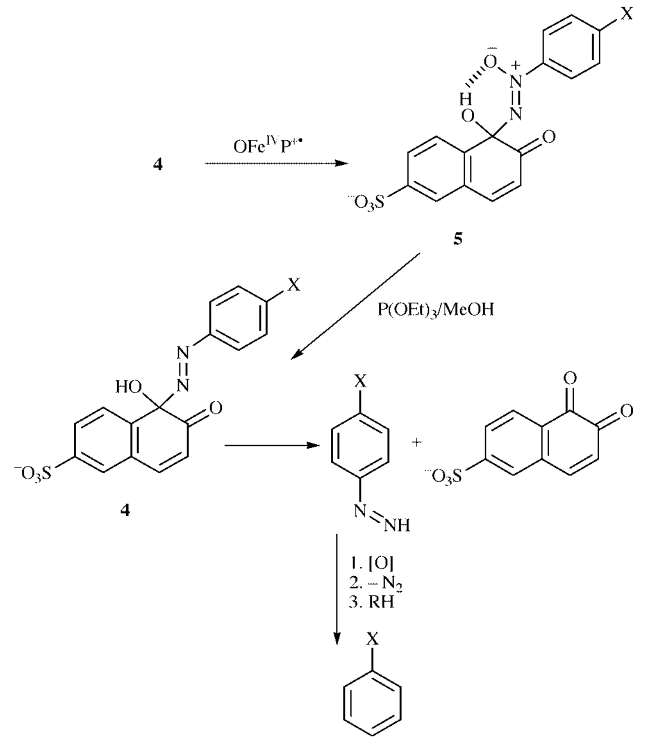
ively. (A control experiment showed that the total self-bleaching of the catalyst using a large excess of MMPP or MCPBA in the absence of dye did not lead to any GC detectable products following extraction of the aqueous solution with diethyl ether.) These results suggest that the oxidation products are water-soluble and consequently that the azo link of the dyes had not been cleaved.

Information about the identity of the water-soluble products (**4** and **5**, Schemes 4 and 5), assigned to the new absorbances in product mixture UV-VIS spectrum, was obtained from the experiments below.



Scheme 4

(i) Changing the solvent from aqueous buffer to methanol effects the azo/hydrazone equilibrium of dye **2** used in this study and leads to a significant shift in its UV-VIS spectrum.[11] Indeed, dilution of an aliquot of the reaction mixture for **2** with methanol (30- to 100-fold) before the addition of peroxy acid showed the expected change in the absorbance of the azo dye; however, the analogous experiment with the products did not result in a shift in the absorbance of either product **4** or **5** (although it did lead to the spontaneous decay of the peak from **4**), suggesting that neither product is an equilibrium mixture of azo and hydrazone tautomers.



Scheme 5

(ii) Addition of MMPP to a reaction mixture containing dye, products **4**, **5** and Fe^{III}TDCSPP resulted in the decay of the UV-VIS bands of the dye and **4** with an increase in that of **5**. Further oxidation led to the bleaching of the iron porphyrin but not of the product **5**. We conclude that the dye oxidation leads initially to **4** which, in agreement with the stoichiometric studies, is oxidised further in competition with the dye to give the relatively stable product **5**.

(iii) In support of the conclusions in (ii) above, heating a reaction mixture, containing MMPP, in which all the catalyst had been degraded led to the conversion of **4** to **5** with little change in the absorption of the unreacted dye.

(iv) On lowering the pH of the product mixture to 7.0, product **4** decomposes rapidly leading to the formation of nitrobenzene (21%) and anisole (26%) from the reactions of **1** and **2**, respectively. ES-MS analysis of the aqueous reaction mixture from **1** showed the presence of an anion with *m*/*z* 237 which is consistent with the formation of 1,2-naphthoquinone-6-sulfonate.

(v) Repeating the oxidation of **1** in the presence of diethyl 2-bromomalonate, a radical trap that is more water-soluble than the commonly used bromotrichloromethane,[12] gave the expected products **4** and **5**. However, after neutralisation and work-up nitrobenzene (1.6%) and 4-bromonitrobenzene (20.8%) were formed. Effectively the same product yields were also obtained when the radical trap was added after the oxidation but prior to the neutralisation. These results show conclusively that product **4** decomposes *via* a 4-substituted phenyl radical (Scheme 4).

The single turnover stoichiometry studies show that dyes **1** and **2** each consume one equivalent of peroxy acid in the fast reaction involving OFe^{IV}TDCSPP$^{+\bullet}$ to give product **4**. This initial oxidation does not involve hydroxylation of the aryl ring or of positions 3 to 8 on the naphthol group since these would not cleave to give nitrobenzene or anisole in water at pH 7. Nor can product **4** be a β-azoxy compound, a known oxidation product of azo compounds by peroxy acids,[13] since the N–N bond of 1-aryl-β-azoxy-2-naphthols is known to cleave spontaneously to give arylnitroso products which would be readily further oxidised, so that **1** and **2** would form 1,4-dinitrobenzene and 4-nitroanisole, respectively (Scheme 1) and would not form aryl radicals. The isomeric α-azoxy compound is an unlikely oxidation product since resonance in the dye anion makes the β-nitrogen more electron-rich and more reactive towards the electrophilic active oxidant. Instead we assign a C-1 hydroxylated naphthol structure to **4**, the initial oxidation product from **1** and **2** (Scheme 4), formed either by direct oxygen-transfer or *via* an electron-transfer process. Products analogous to **4** have been proposed as intermediates in the oxidation of 1-arylazo-2-naphthol dyes by peroxidases,[3b,4d] hypochlorite[2b] and peroxy acids[2c] and at pH 7 they would be expected to cleave to an aryldiazene[3b,4d–f] which in turn would readily undergo radical oxidation to an aryl radical (Scheme 4).[14] The aryl radical either abstracts a hydrogen atom from one of the organic species in the mixture or, in the presence of the radical trap diethyl 2-bromomalonate, it preferentially picks up a bromine atom (Scheme 4). The cleavage of **4** would also account for the formation of the 1,2-naphthoquinone detected by ES-MS.

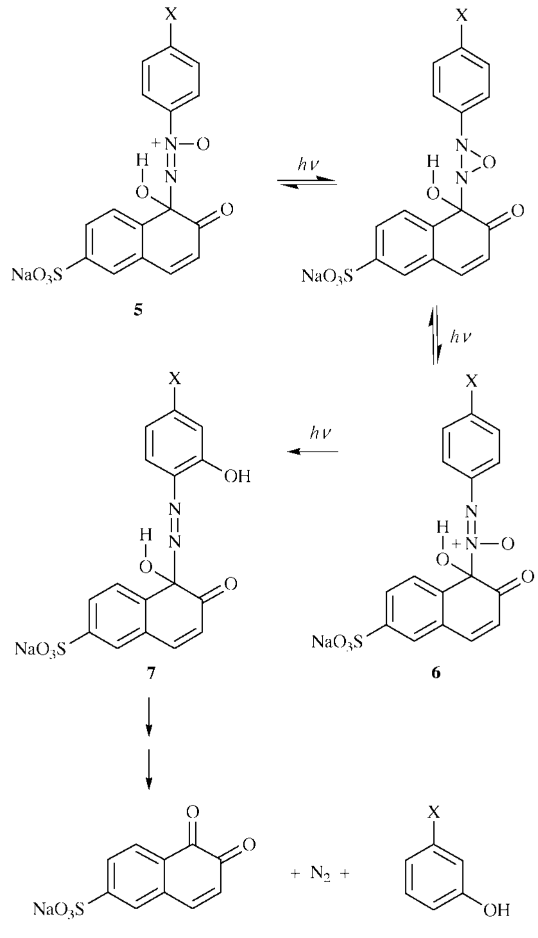
Product **5** is formed by the further oxidation of **4** and, from the stoichiometry studies, this oxidation involves a further one equivalent of peroxy acid. Species **5** is stable to hydrolysis even at pH 2 at 60 °C and is not readily oxidised further by the peroxy acid/Fe^{III}TDCSPP system. The simplest oxidation that fulfils these requirements is to form an azoxy compound. Based on the peroxybenzoic acid oxidation of phenylazomethane (this is analogous to **4** since it is a mixed arylalkylazo compound) which oxygenates the nitrogen next to the phenyl ring,[15] steric arguments and on intramolecular H-bonding, we assign structure **5** to the β-azoxy derivative of **4** (Scheme 5).

That **5** is an azoxy compound was confirmed by reducing it with a large excess of triethyl phosphite[16] in methanol. This resulted in the disappearance of the UV-VIS absorption associated with **5** without the appearance of any new bands. Deoxygenation of **5** would give **4**, however, under the experimental conditions used this would be cleaved further as described above (Scheme 5). In agreement with the reactions outlined in Scheme 5, removal of the methanol from a product mixture from an extensive oxidation of **1**, after triethyl phosphite reduction followed by diethyl ether extraction, gave 88.2% nitrobenzene with no other GC-detectable products.

An estimate of the extinction coefficient of the azoxy compound was made by carrying out an oxidation of **1** aimed at converting all the dye and product **4** into product **5**. The value obtained (1.1×10^3 m^2 mol^{-1} at λ_{max} 402 nm) is very comparable with those of other azoxy compounds.[17]

Further confirmation that product **5** is an azoxy compound was obtained by examining its photochemistry. Illumination of aromatic azoxy compounds leads to intramolecular 1,2- and 1,4-photorearrangements of the oxygen, the former to give the isomeric azoxy compounds, *via* an oxadiaziridine intermediate, and the latter an *ortho*-hydroxyazo compound.[18] In the case of **5**, since a direct 1,4-shift is not possible, irradiation was expected to give the isomeric azoxy compound **6** *via* a 1,2-shift, which would then photoisomerise further to give the hydroxyazo compound **7** and cleave (*cf.* the cleavage of compound **4**) to give a 3-substituted phenol (Scheme 6). In agreement with these predictions, a reaction mixture from **1**, which had been carried out to give effectively a complete conversion to **5**, was irradiated (pH 4.0) until the absorption band of **5** was bleached, extracted with diethyl ether (pH 9.3) and analysed by GC to give a 79.0% yield of 3-nitrophenol together with 5.1% of nitrobenzene.

The evidence presented above suggests that the azo dye anions at pH 11.88 are oxidised by two sequential oxygen-transfers from $OFe^{IV}TDCSPP^{+\bullet}$; thus one equivalent of peroxy acid gives product **4** and a second equivalent is required to convert **4** to **5**. From this it follows that bleached dye not detected as **4** can be accounted for as **5** and the product distribution for dye **1** is 21% of **4** (detected as nitrobenzene when the product mixture was adjusted to pH 7) and 79% of **5**; for dye **2** the corresponding values are 26 and 74%, respectively. Using these data, it is possible to calculate the predicted oxidant to dye stoichiometry of the reactions as being 1.79 for **1** [21 + (2 × 79)] and 1.74 **2** [26 + (2 × 74)]. These values compare well with the measured stoichiometry for the oxidation of **2** (*vide supra*) where at 68% dye bleaching the value was 1.78.



Scheme 6

Products from the catalysed oxidation of 1-arylazo-2-naphthol dyes for peroxy acids at pH 9.30

The product studies were extended to dye solutions at pH 9.30 where the dyes are >95% unionised. Under these conditions the dye exists as an azo/hydrazone equilibrium with the latter tautomer predominating (Scheme 3).[19]

The oxidations at pH 9.30 were carried out as described above for pH 11.88 with an initial molar ratio of oxidant : dye : catalyst of 1600 : 800 : 1. A further batch of the catalyst was added subsequently to ensure that all the peroxy acid had been consumed. UV-VIS spectroscopy showed that each dye's visible absorbance was extensively bleached, typically 55 and 60% of **1** and **2**, respectively and that a new shorter wavelength absorption band ($\lambda_{max} \sim 315$ nm) (assigned to product **8**) was formed. The formation of **8** was most apparent with dye **2** and at higher concentrations of the catalyst.

Subjecting **1** and **2** to more extensive oxidation (repeated additions of peroxy acid and Fe^{III}TDCSPP) led to the formation of 1,4-dinitrobenzene and 4-nitroanisole, respectively, in increasing yields (Table 2). These results suggest that the initial

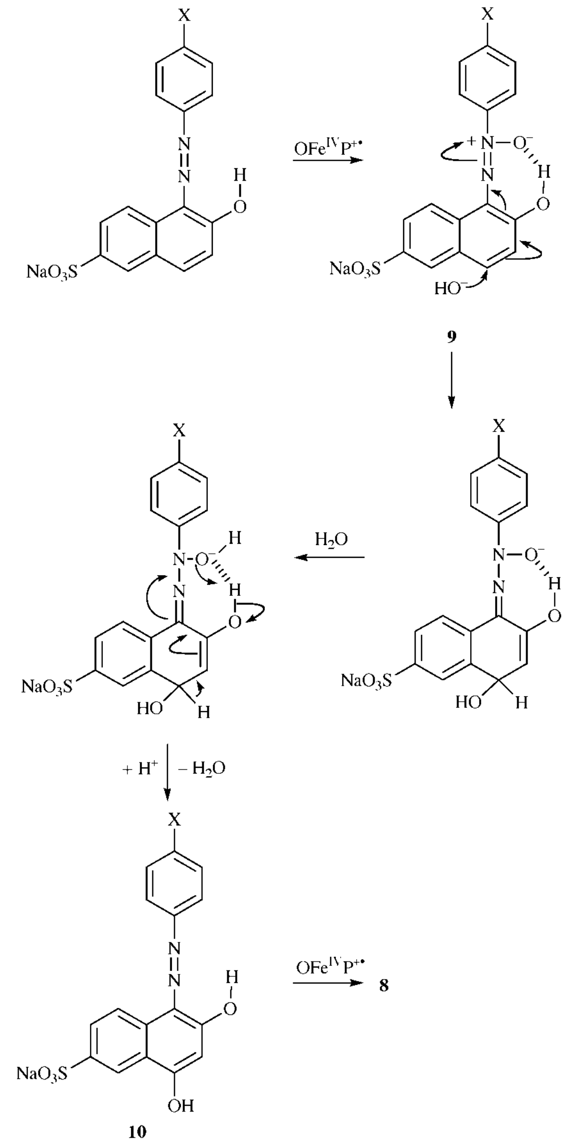
Table 2 Yields of organic products detected by GC analysis after oxidation of dyes **1** and **2** by MMPP catalysed by $\mathrm{Fe^{III}TDCSPP}$ at pH 9.30

Dye[a]	No. of oxidations[b]	Yield[c] of nitrobenzene or anisole (%)	Yield[c] of 1,4-dinitrobenzene or 4-nitroanisole
1	1	2.1	None
1	4	2.1	4.6
1	10	2.3	27.8
1	16	2.3	55.2
2	1	1.7	None
2	16	1.9	73.4

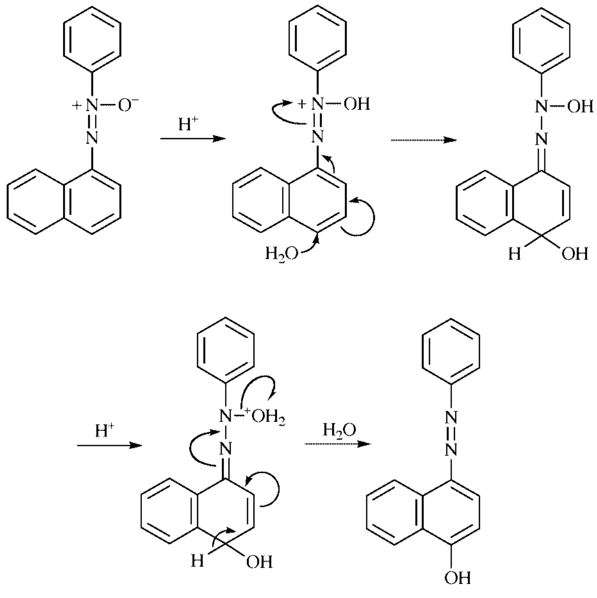
[a] 2.5×10^{-5} mol. [b] Each oxidation was performed after the previous one was complete (as identified by the reformation of $\mathrm{Fe^{III}P}$) and involved addition of 5×10^{-5} mol MMPP and 6.25×10^{-8} (for the first oxidation) and 2.5×10^{-7} mol (for subsequent oxidations) iron porphyrin. [c] Only one major organic product was detected from each substrate.

oxidation of the dyes by the electrophilic active oxidant $\mathrm{OFe^{IV}TDCSPP^{+\bullet}}$ gives water-soluble products with an intact azolink. Further oxidation is required to cleave the N–N bond to give the organic soluble 4-substituted nitrobenzenes. The initial dye oxidation does not occur on the phenyl ring or at positions 5–8 on the naphthol group since these would give coloured products. Furthermore, oxidation of the phenyl ring would not lead, on extensive oxidation, to the observed 4-substituted nitrobenzenes, consequently this oxidation pathway can be eliminated. Initial oxidation of C-1 of the naphthol can also be rejected since this would give compounds **4** which at pH 9.30 spontaneously cleave to give nitrobenzene and anisole from **1** and **2** respectively (Scheme 4). However, GC analysis of the reaction mixtures showed only 2.1% nitrobenzene and 1.7% anisole were formed. The 3,4-bond of the naphthol group is a potential site of attack and forming the 3,4-epoxide would, by loss of conjugation, lead to the bleaching of the dye. In support of this explanation $\mathrm{OFe^{IV}P^{+\bullet}}$ species are active epoxidising agents that are capable of epoxidising polycyclic aromatic rings.[20] However, the azo-substituted naphthol group in the dye is relatively unreactive and electrophiles prefer to attack the azo link (*e.g.* peroxy acids give azoxy compounds[13,21]). Consequently we propose that the initial site of attack is the azo linkage to give azoxy compound **9**, possibly *via* an unstable oxadiaziridine intermediate,[18c] and the azoxy compound, which would absorb between 350 and 415 nm in the UV-VIS spectrum, reacts further by a Wallach type rearrangement (Scheme 7).[22] That the bleached product was not an azoxy compound was confirmed by treating it with triethyl phosphite: this did not regenerate a coloured azo compound.

The Wallach rearrangement of arylazoxy compounds to 4-hydroxyarylazo compounds normally requires strongly acidic conditions to protonate the oxygen and bring about the elimination of water (Scheme 8).[22] However, for compound **9** the naphthol OH–azoxy hydrogen bond might be expected to circumvent the need for an external acid and allow rearrangement to occur at pH 9.30 with hydroxide as the attacking nucleophile. The resulting product, **10**, would be coloured. However, since no build-up of a coloured intermediate was detected it must be rapidly further oxidised in preference to the dye substrate. This is not surprising since **10** is a 2,4-dihydroxynaphthalene azo dye and, as noted previously,[7,10] such compounds and 4-naphthol azo dyes are much more readily oxidised than their 2-naphthol analogues. The overall oxidant : azo dye stoichiometry for the oxidation in Scheme 7 would be 2.0 : 1, which is in fair agreement with the measured value of 1.73 (*vide supra*). The precise identity of the colourless product is unclear and further research is needed to isolate and obtain its structure.



Scheme 7



Scheme 8

The more extensive oxidation of dyes **1** and **2** must result in further oxidation of the product **8** to an azoxy compound followed by the heterolytic cleavage of the N–N bond to give a 4-substituted nitrosobenzene (Scheme 1, route b), which in turn is oxidised to the corresponding nitro compound detected by GC.

The oxidation of 1-arylazo-2-naphthol dyes with *tert*-butyl hydroperoxide catalysed by $\mathrm{Fe^{III}TDCSPP}$ at pH 6.93

In our previous paper, we reported our extensive kinetic and mechanistic studies on azo dye bleaching by the oxoiron(IV) porphyrin $\mathrm{OFe^{IV}TDCSPP}$.[7] In the light of this we thought it would be of interest to compare the products from the reactions of this species with those of the corresponding π-cation radical (*vide supra*); however, to obtain sufficient materials for the product studies it was necessary to use a catalytic cycle free from the more potent oxidant $\mathrm{OFe^{IV}TDCSPP^{+\bullet}}$. For this purpose we chose the reaction of *tert*-butyl hydroperoxide with the iron(III) porphyrin which involves homolysis of the O–O bond [reaction (8)],[23] although it is complicated by the concomitant generation of $^t\mathrm{BuO}^\bullet$ and also, by further reaction, by $^t\mathrm{BuOO}^\bullet$, $\mathrm{Me}^\bullet$ and $\mathrm{MeOO}^\bullet$ [reactions (8)–(11)]. We selected pH 6.93 for this study since we have shown that at this pH $\mathrm{OFe^{IV}TDCSPP}$ oxidises azonaphthol dyes by hydrogen atom abstraction,[7] and we argued that this would minimise problems that might arise from $^t\mathrm{BuO}^\bullet$ which is also a potent H-atom abstractor.

$$\mathrm{Fe^{III}P} + {}^t\mathrm{BuO_2H} \longrightarrow \mathrm{OFe^{IV}P} + {}^t\mathrm{BuO}^\bullet \qquad (8)$$

$$^t\mathrm{BuO}^\bullet + {}^t\mathrm{BuO_2H} \longrightarrow {}^t\mathrm{BuOH} + {}^t\mathrm{BuO_2}^\bullet \qquad (9)$$

$$^t\mathrm{BuO}^\bullet \longrightarrow \mathrm{Me}^\bullet + \mathrm{Me_2CO} \qquad (10)$$

$$\mathrm{Me}^\bullet + \mathrm{O_2} \longrightarrow \mathrm{MeO_2}^\bullet \qquad (11)$$

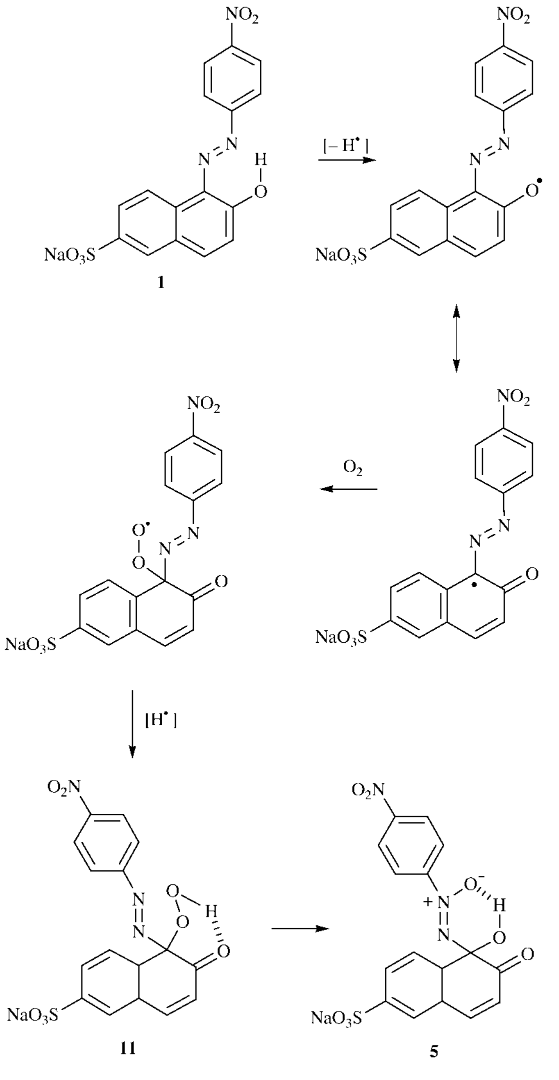
Control reactions showed that in the absence of the iron(III) porphyrin negligible bleaching of dye **1** occurs and that the yield of $^t\mathrm{BuOH}$, from the $^t\mathrm{BuOOH/Fe^{III}TDCSPP}$ system, is significantly higher in the presence of the dye than in its absence. The latter observation is consistent with some of the *tert*-butoxyl radicals abstracting hydrogen atoms from the dye.

In a typical oxidation, **1**, oxidant and catalyst (in the molar ratios 1600 : 2200 : 1) were reacted together for 2 h, and a further batch of catalyst was then added to ensure the complete consumption of the oxidant. Under these conditions UV-VIS spectroscopy showed that 82% of the dye's visible absorption ($\lambda_{\max}$ 486 nm) was bleached, with the appearance of a new absorption at $\lambda_{\max}$ 398 nm. This gives a reaction stoichiometry of $^t\mathrm{BuOOH}$: dye of 1.73 : 1. Extraction of the organic soluble products into diethyl ether, as described above, gave 0.92% nitrobenzene and 7.25% 1,4-dinitrobenzene (based on dye bleached).

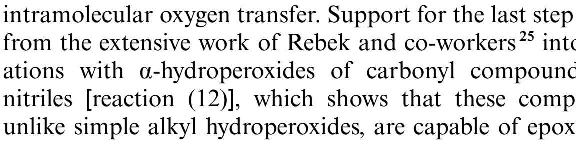
We attribute the product spectrum to **5**, the same water-soluble azoxy compound formed by the oxidation of the dye anion by $\mathrm{OFe^{IV}TDCSPP^{+\bullet}}$ at pH 11.88, and as expected treatment of the product mixture with triethyl phosphite led to the decay of the 398 nm band without the appearance of a new visible absorbance. Diethyl ether extraction of the $\mathrm{(EtO)_3P}$-treated reaction gave nitrobenzene in 82.4% yield (Scheme 5) which with the 7.25% yield of 1,4-dinitrobenzene gives an overall product accountability of ~90%, based on dye bleached. Confirmation for the product being **5** came from its photolysis, which gave 3-nitrophenol (Scheme 6).

The conversion of **1** to **5** requires oxidation to occur at both the 1-position of the naphthol ring and the β-nitrogen of the azo link, although it is unlikely that these arise from direct oxygen transfer from $\mathrm{OFe^{IV}TDCSPP}$ to the dye since oxoiron(IV) porphyrins are poor oxygen-transfer reagents (unlike their $\mathrm{OFe^{IV}P^{+\bullet}}$ analogues).[7,24] Furthermore it is unlikely that either **4** or **9** is an intermediate in the process since neither is stable under the reaction conditions: **4** would be cleaved to give nitrobenzene (Scheme 4) and **9** would rearrange to **10** (Scheme 7).

Based on our kinetic studies, the initial step in the oxidation is hydrogen abstraction to give the resonance stabilised dye radical.[7] This we propose is too hindered to couple and is not converted to the dye cation by oxidation or disproportionation, since the latter would react with water to give either **4** (attack on 1-position of the naphthol ring) or **9** (attack on β-nitrogen of the azo link).[3b,4d] Instead it is trapped by dioxygen to give a peroxyl radical (Scheme 9). This reacts further to give the hydroperoxide **11** which, unlike **4**, would not lead to the cleavage of the azo link. We believe that **11** rearranges to **5** by an intramolecular oxygen transfer. Support for the last step comes from the extensive work of Rebek and co-workers[25] into oxidations with α-hydroperoxides of carbonyl compounds and nitriles [reaction (12)], which shows that these compounds, unlike simple alkyl hydroperoxides, are capable of epoxidising alkenes. This increased activity is attributed to internal hydrogen bonding which increases the electrophilicity of the terminal oxygen, making it behave more like a peroxy acid. Compound **11** is an α-hydroperoxy ketone whose structure would allow it to bring about an intramolecular oxidation of the β-nitrogen of the azo link to give the azoxy compound **5**; the intermolecular equivalent is a typical reaction of peroxy acids.[13,21]



Scheme 9



(12)

R = Me or Ph ; X = $\mathrm{CHMe_2}$; $\mathrm{NMe_2}$ or OMe

The possibility that the conversion of **11** into **5** involves the participation of the iron(III) porphyrin was also investigated by carrying out the Fe^{III}TDCSPP-catalysed oxidation of **1** by adding the oxidant in seven aliquots. It was argued that this should alter the relative concentration of **11** and Fe^{III}TDCSPP and might therefore affect the yield of **5**. However, the UV-VIS spectral changes observed at the end of the reaction were very similar to those from the standard experiment, as were the yields of the two products (nitrobenzene and 1,4-dinitrobenzene) extracted into diethyl ether, suggesting that the conversion of **11** into **5** is not catalysed by the iron(III) porphyrin.

It is noteworthy that compounds analogous to **11** have been proposed as intermediates in the photo-oxidation of 1-phenylazo-4-naphthol dyes.[26] These, it is suggested, cleave to the 1,4-naphthaquinone and an aryldiazonium which couples with unreacted dye. This route was not observed in the present study on the water-soluble dyes, perhaps because the cleavage of the intermediate is a photo-oxidation rather than a thermal process.

Conclusions and general comments

(1) The initial steps in the iron(III) porphyrin-catalysed oxidation of 1-arylazo-2-hydroxynaphthalene-6-sulfonate dyes with peroxy acids (pH 11.88 and 9.30) or with *tert*-butyl peroxide (pH 6.93) involve oxidation of the naphthol ring and the azo group but not the cleavage of the N–N bond.

(2) The bleaching of arylazo 2-naphthol dyes in multiple turnover reactions by peroxy acids catalysed by iron(III) porphyrins involves oxygenation of the dye or its anion by $OFeP^{+\bullet}$. The oxidant to dye stoichiometry for dye bleaching is 2 : 1.

(3) At pH 11.88, with peroxy acids, the sequential oxidation of the dye anion involves hydroxylation of C-1 of the naphthol group followed by *N*-oxygenation of the azo link. In contrast at pH 9.3 oxidation involves *N*-oxygenation of the dye followed by a Wallach rearrangement and further oxidation of the naphthol ring.

(4) Extensive oxidation of the dyes with the peroxy acid is required to cleave the N–N bond. Under these circumstances 1,4-dinitrobenzene and 4-nitroanisole are major products from **1** and **2**, respectively.

(5) With $^tBuO_2H$ at pH 6.93, it is proposed that initial hydrogen atom-abstraction by $OFe^{IV}P$ or $^tBuO^\bullet$ is followed by reaction of the dye radical with dioxygen to give a peroxyl radical and subsequently the C-1 naphthol hydroperoxide. The latter undergoes a novel intramolecular oxidation to give the detected azoxy product.

Experimental

Instrumentation

UV-VIS spectra and kinetic data were recorded on Hewlett Packard HP8452 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. EI mass spectra were obtained with a VG Analytical Autospec instrument and for GC-MS the mixtures were separated by capillary GC using a Hewlett Packard 5896 series II gas chromatograph coupled to the mass spectrometer. Electrospray mass spectra of the degraded dye samples were recorded on an LCQ Finnigan MAT mass spectrometer. Gas chromatographic analysis of the reaction mixtures used a Pye Unicam PU 4500 chromatograph with a flame ionisation detector and an Alltech capillary column (Carbowax, length 30 m, id 0.25 mm and phase thickness 2.5 μ). The results were recorded and processed on a Viglen 486 PC running JCL 6000 software from Jones Chromatography Ltd. pH measurements were made with a Corning 200 pH meter equipped with a Reagecom combined pH/reference electrode. UV irradiation photolyses were carried out using a ILC302 UV Xenon high intensity light source (300 W) directed by a liquid light guide (Laser Lines Ltd.).

Materials

The syntheses and purification of the dyes and the iron(III) porphyrin used in this study were reported previously.[7] All the other materials were commercially available and used without purification. The buffer solutions (ionic strength 0.05 mol dm^{-3}) were prepared with deionised water following Bates[27] and Gomori.[28]

Spectral simulation to obtain the stoichiometry of dye bleaching by $OFe^{IV}P$

The MCPBA was added to the dye and Fe^{III}TDCSPP in buffered solution (3 cm^3 total volume) in a quartz cuvette to give final concentrations of 10^{-6}, 10^{-5} and 10^{-6} mol dm^{-3}, respectively. The changes in the UV-VIS spectrum were followed using the diode array spectrometer. The stoichiometry of the fast phase of the reaction was obtained by measuring the yield of $OFe^{IV}P$ (λ_{max} 420 nm) and the loss of dye after 5 s of reaction (the end of the fast phase of the reaction when essentially all the oxidant has been consumed). The stoichiometry for the slow dye oxidation by $OFe^{IV}P$ used spectral simulation and required the spectra of $Fe^{III}P$ and $OFe^{IV}P$, and rate constants for the reaction of $OFe^{IV}P$ with the dye[7] and the background spontaneous reduction of $OFe^{IV}P$,[7] to determine how much of the $OFe^{IV}P$ was consumed in the dye bleaching.

Product studies

Oxidation procedure. The general method involved adding an aliquot (125 μl) of a stock solution of Fe^{III}TDCSPP (1.25×10^{-4} mol dm^{-3}) to the azo dye (2.5×10^{-5} mol) in the aqueous buffer (50 cm^3). The reaction was initiated by the addition of magnesium monoperoxyphthalate (0.016 g, 5×10^{-5} mol) followed by a second aliquot of catalyst. The reaction was left at room temperature overnight before the GC internal standard (biphenyl) (100 μl of a 1.5×10^{-2} mol dm^{-3} solution in methanol) was added. The solution was then shaken with sufficient diethyl ether to give an organic layer of 1–2 cm^3. The organic layer was removed and the aqueous mixture was repeatedly extracted with diethyl ether (5 × 1 cm^3). The organic extracts were combined, reduced in volume to 2 cm^3 by evaporation in a stream of air and analysed by GC. The peaks were identified by both comparison of their retention times and GC-mass spectra with those of authentic samples.

The extent of dye bleaching was obtained by measuring the concentration of the dye by UV-VIS spectroscopy before and after the oxidation.

Electrospray analyses of the degraded dye were carried out on the aqueous solution of the reaction products after the diethyl ether extraction.

The reactions using $^tBuO_2H$ as the oxidant followed the procedure above except that the peroxy acid was replaced by $^tBuO_2H$ (65% w/v, in water).

Triethyl phosphite reduction of azoxy compound 5. Product **5** was obtained by adding magnesium monoperoxyphthalate (16 mg) to a solution of 1-(4-nitrophenylazo)-2-hydroxynaphthalene-6-sulfonate (5 mg) and Fe^{III}TDCSPP (1.6×10^{-8} mol in 125 μl water) in aqueous buffer (25 cm^3) at pH 11.88. Two further batches of Fe^{III}TDCSPP (1.6×10^{-8} mol in 125 μl water) were added after approximately 10 s and 1 h and the reaction was left to stand for 24 h. UV-VIS analysis confirmed that the substrate and product **4** had been oxidised to **5**, methanol (225 cm^3) and triethyl phosphite (0.4 cm^3) were added and the solution was heated to 50 °C. During the reaction gas (presumably N_2) was evolved. After 8 h the methanol was removed under vacuum, biphenyl (GC internal standard) was added and the organic products were extracted into diethyl ether and analysed by GC.

The oxidation of the azo dye was also carried out at pH 7.0 using the same procedure with ^{t}BuO$_2$H (3.6×10^{-5} mol) instead of the peroxy acid. The product was reduced and analysed as described above.

Photolysis of product 5. The oxidation of 1-(4-nitrophenylazo)-2-hydroxynaphthalene-6-sulfonate was carried out as described above to give product **5** using either magnesium monoperoxyphthalate or ^{t}BuO$_2$H. Dilute HCl was then added to lower the pH to 4.0 and the solution was irradiated in a quartz test tube with UV light. After 18 h the organic products were extracted and analysed by GC as described above.

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