PERKIN 2

Kinetic investigations of azo dye oxidation in aqueous media

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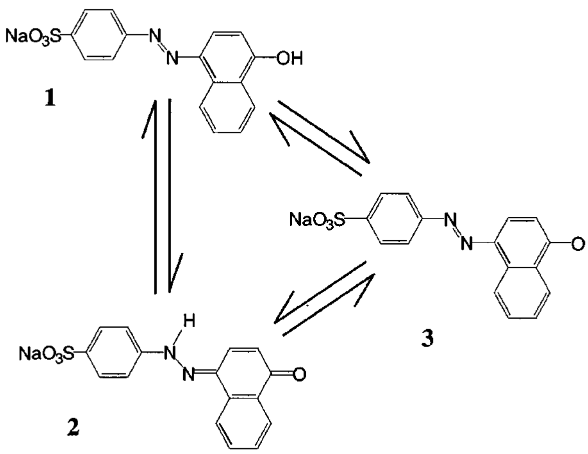
A detailed kinetic and spectroscopic investigation has been made of the oxidation of 4-(4-sulfophenylazo)-1-naphthol (Orange I, 4) and 1-(4-sulfophenylazo)-2-naphthol (Orange II, 5) and a series of specially synthesised, substituted 1-arylazo-2-naphthol dyes (6a, 6b) by hypochlorite, peracids and hydrogen peroxide in aqueous media. In all cases, observed second-order rate constants exhibit maxima in alkaline media at a pH equal to the midpoint of the pK_A values of dye and oxidant. It is found that substituents upon the aryl ring *ortho* to the azo group suppress dye reactivity towards hypochlorite and, in addition, it is shown that peracids exhibit similar trends. In contrast, oxidation by hydrogen peroxide is enhanced by *ortho* substituents, suggesting that it functions *via* a different mechanism. Surprisingly, the dye common anion has been identified as the form of the dye most susceptible to oxidation by peracids and hypochlorite, with the *undissociated* oxidant molecules acting as electrophiles. In contrast, dye oxidation by hydrogen peroxide proceeds *via* the perhydroxyl anion and the hydrazone tautomeric form of the dye. The main function of *ortho* substituents is to increase the dye pK_A, thereby influencing observed rates (k_{2obs}) by changing the equilibrium concentration of reactive species. Substituents also exert an electronic effect on absolute rate constants, k_2, giving good Hammett plots for both *ortho* and *para* substituents. Reactive oxygen species, *e.g.* singlet oxygen, superoxide or hydroxyl radicals, are not implicated in the rate-controlling step of the reaction.

Introduction

The oxidation of azo dyes has attracted much attention in recent years.[1–11] This has been stimulated by environmental, commercial and social pressures, particularly environmental concerns over residual dyes present in waste water streams,[9–11] dye fading due to hypochlorite[2–4] used as a disinfectant in water supplies or the presence of low temperature bleaches in detergents.[8] Although previous studies represent significant steps forward in generating empirical rules governing oxidation, further progress is required in developing the underlying science base. There are many misconceptions, particularly regarding the nature of the active species and the factors that control oxidation. Indeed, the role of hydroxyl groups in promoting oxidation of dyes has not been explicitly recognised, nor has the importance of the dye pK_A or the role of substituents thereupon.

Azo dyes that contain a hydroxyl group conjugated with the azo-linkage exist as an equilibrium mixture of two tautomeric forms in aqueous solution, azo or hydrazone[12,13] (Scheme 1). These are chemically distinct forms which have characteristically different visible spectra, the azo form **1** absorbing typically at 400–440 nm and the hydrazone **2** at 475–510 nm. When the hydroxyl group is positioned in a naphthol *ortho* to the azo group, the equilibrium favours the hydrazone form, particularly in aqueous media. Furthermore, another equilibrium has to be considered since the hydroxyl groups in azo dyes have pK_A values in the region 8–12. Thus, dissociation occurs in alkaline media to form a common anion **3**, in which the negative charge is delocalised throughout the molecule. The ion **3** is regarded to be predominantly azo in character.[14,15]

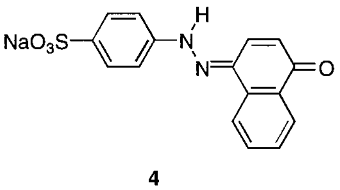
Such equilibria are important as one dye species tends to be a great deal more reactive than the others. A common misconception is that the hydrazone form is most easily oxidised. In fact, it will be shown that the common anion is 10^5 times more reactive than the hydrazone form towards hypochlorite. Hydroxyl groups play a key role in dye oxidation by promoting azo–hydrazone equilibria and formation of the common anion. Another important property is the pK_A of the hydroxyl group, as this controls the concentration of reactive species. In particular, when the hydroxyl group is located in the naphthol ring in a position *ortho* to the azo group, the pK_A tends to be over two units higher than in naphthols or when it occupies other positions in the naphthol ring, due to intramolecular hydrogen bonding.[12,13] Furthermore, *ortho* substituents in the aryl ring can further increase the pK_A.



(Orange I : λ_{max} values: *azo* = 403 nm, *hydrazone* = 477 nm, common ion = 513 nm)

Scheme 1

One of the most significant early papers on dye oxidation appeared some twenty years ago, with hypochlorite[1] as oxidant. A systematic investigation of the influence of dye subsituents showed that *ortho* substituents in the aryl ring of 2-arylazo-1-naphthol dyes suppressed dye oxidation, with *para* substituents having little effect. These trends were subsequently confirmed for a related set of dyes,[2] although the authors took issue with the mechanistic analysis; indeed, it was assumed that hypochlorous acid was the active oxidant, although no comment was made about it having insignificant concentrations at the rate maximum. More recently, a series of papers have appeared[2–4] which have generated a number of empirical rules governing



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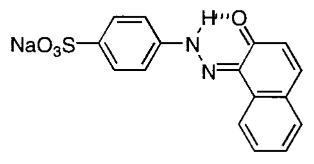
Orange I

pK_A = 8.2, λ_{max} = 477 nm



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Orange II

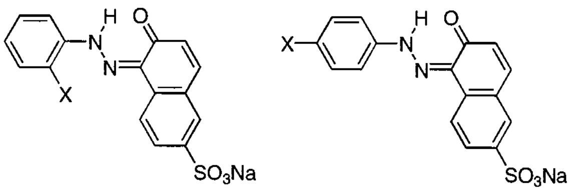
pK_A = 11.4, λ_{max} = 484 nm

oxidation, particularly regarding the influence of dye substituents for a variety of dye structures. There have been three previous publications on hydrogen peroxide oxidation of dyes.[5,6] It was found that dye oxidation may[6] or may not[5] depend upon the presence of *ortho* substituents but, in our opinion, this may critically rest upon the dye examined, *i.e.* whether 2-arylazo-1-naphthol or 1-arylazo-2-naphthol. It was concluded that the hydrazone form of the dye was more susceptible to oxidation than the azo form[5] or that superoxide radicals were the active oxidant species.[6] Only one paper has appeared upon the interaction of peracids with dyes,[7] which reinforced earlier findings that indigenous trace metals are a major source of experimental irreproducibility. However, the scientific approach was let down by the high ionic strength, coupled with the unfortunate selection of the azo dye, Acid Red 27 (Amaranth). Dyes having such structural motifs tend[16] to aggregate readily at low concentrations and ionic strengths to produce unusually complicated kinetic data. Thus, conclusions drawn about the nature of the active oxidant (*i.e.* the peracid anion) or effects of substituent thereupon and implications for stain oxidation in detergency are not generally true and must be treated with caution for dye oxidation. In our case we avoided such problems by eliminating buffers and trace metals from our system and by careful dye selection.

The main focus of this investigation is two-fold: (a) to identify the reactive species responsible for oxidation of dyes, and (b) to elucidate the factors controlling dye oxidation, particularly the role of dye substituents.

It is imperative that well-characterised dyes are investigated. In general, we have tended to avoid commercial dyes as they are often impure, complicated molecules that aggregate in aqueous solution. Even some of the simpler dyes, *e.g.* Acid Red 88 or Amaranth (naphthylazonaphthol dyes) tend to aggregate readily at low ionic strength[16] or be inextricably associated with indigenous trace metals. Consequently, our approach has been to select even smaller, much more soluble, well-characterised dyes, *i.e.* with well-defined solution physical chemistry, and we have found simple arylazonaphthol dyes to be most appropriate. Initially, we investigated two available dyes, 4-(4-sulfophenylazo)-1-naphthol (Orange I, **4**) and 1-(4-sulfophenylazo)-2-naphthol (Orange II, **5**), which exist predominantly in the hydrazone form in aqueous media. We have also endeavoured[17] to synthesise, purify and characterise a series of substituted 1-arylazo-2-naphthol dyes (**6a**,**6b**)—all of which exist predominantly in the hydrazone tautomeric form—specifically for the purpose of examining the role of dye substituents.

Dye oxidation has been evaluated on these common dye sets by hypochlorite, hydrogen peroxide and a range of peracids. No previous study has been made of the influence of hypochlorite on 1-arylazo-2-naphthol dyes. A range of peracids have been examined, but particular emphasis has been given to *p*-sulfonated perbenzoic acid (PSPBA) and potassium peroxosulfate, $KHSO_5$. In later experiments, *m*-chloroperbenzoic acid (MCPBA) was selected as an example of an uncharged peracid. Experiments were conducted in the presence of sequestrant (edta) to deactivate trace metals. Additionally, the use of buffers/high ionic strength was avoided to preclude dye aggregation.



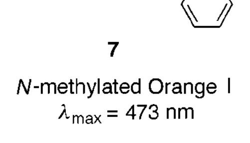
6a **6b**

o- and *p*-substituted 1-arylazo-2-naphthol dyes

Experimental

Sodium hypochlorite was obtained from BDH in the form of a 12% active chlorine solution. Peracids were used as received from manufacturers: *p*-nitroperbenzoic acid (PNPBA) from Lancaster Synthesis, *m*-chloroperbenzoic acid (MCPBA) from Aldrich and *p*-sulfonated perbenzoic acid (PSPBA), potassium peroxosulfate ($KHSO_5$) and *sec*-butylimidoperoxy trimetallic acid (BIPTA) and *N*,*N*-phthaloylaminoperoxycaproic acid (PAP) were all from Interox. Two further peracids: bicyclo-[2,2,2]heptane-3-methyl-2-peroxycarboxylic acid (PN) and tricyclo[3,3,1,1]decane-1-peroxycarboxylic acid (PAD), based on the cyclic alkanes norbornane and adamantane, respectively, were prepared in-house using standard preparative procedures.[18] Hydrogen peroxide (8.08 M) was obtained from Aldrich. Other chemicals used were potassium hydroxide (Fluka Puriss), nitric acid (BDH Analar) and edta (BDH analytical concentrate). The pK_A values of some oxidants are known from the literature,[19,20] and are indicated below,† others were calculated using Hammett–Taft relationships for the acid and normalised to the peracid.[21]

Strenuous efforts were made to ensure all the dyes used were of the highest purity obtainable and the resulting solutions were characterised[17] using a number of physical techniques (^1H and ^{13}C NMR, HPLC, and UV-Visible Spectroscopy). Solutions were prepared using water that was double-distilled from demineralised water using a Fisons ‘Fi-Streem’ 4BD Still. A series of *ortho* and *para* substituted dyes based upon 1-arylazo-2-naphthol-6-sulfonic acid (sodium salt) were synthesised using standard diazotisation and coupling procedures.[12] These dyes were purified by recrystallisation from water–ethanol mixtures.[17] Orange I (λ_{max} = 477 nm, $\varepsilon = 2.7 \times 10^4$) was obtained from Fluka and Orange II (λ_{max} = 484 nm, $\varepsilon = 1.6 \times 10^4$) was obtained from Sigma; both dyes were purified by recrystallisation. The *N*-Me and *O*-Me derivatives of Orange I (**7**,**8**) were used as supplied by Peter Gregory (Zeneca) and Richard Clark of this Laboratory.



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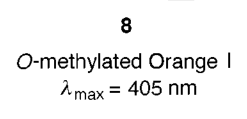
N-methylated Orange I

λ_{max} = 473 nm



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O-methylated Orange I

λ_{max} = 405 nm

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† pK_A values are: PNPBA = 7.1,[19,20] MCPBA = 7.6,[19,20] PSPBA = 7.7, $KHSO_5$ = 9.5,[19,20] BIPTA = 7.3, PAP = 8.2, PAD = 7.8 and PN = 7.8.

The reactions were carried out in a double-walled glass water jacket, thermostatted with a digital reading circulator. A small overhead stirrer was used to achieve homogeneity. The pH was controlled by a VIT90 titration system in conjunction with an ABU93 autoburette and pH electrodes PHG 201 and REF 401, all by Radiometer. The reaction liquor was circulated with a peristaltic pump *via* silicone rubber tubing through a quartz flow cell (path length 10 mm) mounted in a double-beam Perkin-Elmer Lambda 14 spectrophotometer. The flow was maintained at such a rate that no significant temperature losses occurred between the reaction vessel and the flow cell. In a typical reaction sequence, 200 ml of dye solution was brought to the set temperature (±1 °C) and pH (±0.05) in the reaction vessel. The spectrometer was set to record absorbance at the required wavelength with a 2 s sampling interval. With the reaction liquor circulating, the oxidant was added—dispersing almost instantaneously—and measurement was initiated. Any gross changes in pH at this point were corrected by immediate manual addition of small volumes of KOH(aq) or NHO_3(aq). In between reactions the reaction circuit was flushed with edta(aq) to remove any trace metals and at least three more times with distilled water. All parts (except electrodes) were soaked in alkaline detergent solution containing excess edta when not in use.

Kinetic measurements were made using absorbance values at the dye isosbestic points. The absorbances of undissociated and dissociated forms of the dye were found to obey the Beer–Lambert law over the experimental range of interest (up to 1×10^{-4} M dye). There was no interference from product absorbances. Measurements of decolorisation of dye were conducted under pseudo first-order conditions, *i.e.* $[\text{Oxidant}]_T \gg [D]_T$. Although there were a few exceptions—particularly with peroxide at high pH or hypochlorite at high concentrations[17]—absorbance *vs.* time traces were generally found to exhibit simple kinetic behaviour; logarithmic plots of absorbance *vs.* time were linear over a substantial fraction of the reaction and plots of k_{obs} (obtained from the gradient) varied linearly with initial $[\text{Oxidant}]_T$. The rate law for well-characterised dye solutions is described by eqn. (1):

$$-d[D]/dt = k_{obs}[D]_T = k_{2obs}[D]_T[\text{Oxidant}]_T \qquad (1)$$

Observed rate constants, k_{2obs}, invariably exhibited maxima with change in solution pH. All experiments were conducted at 40 °C, unless otherwise stated and in the presence of 20 μM edta to remove effects due to trace metal impurities. Values of k_{obs} quoted in the tables represent maximum values recorded at pH 10, 10.5 and 11, for hypochlorite, peroxosulfate and hydrogen peroxide, respectively. From a knowledge of the pK_A values of the dye and that of oxidants pH-independent rate constants (k_2) were calculated from observed rates.

Results and discussion

Kinetic analysis

Initial investigations were carried out using *p*-sulfonated perbenzoic acid (PSPBA) as oxidant ($pK_A = 7.7$) since a systematic study of interactions between dyes (D) and peracids (PA) has not previously been reported, and since only two solution species need be considered over a wide pH range compared to three for hypochlorite. Similarly, the experiments were carried out at 25 °C to minimise potential complications arising from peracid self-decomposition.[20]

The rate law is described by eqn. (2), where $[D]_T$ and $[PA]_T$

$$-d[D]/dt = k_{obs}[D]_T = k_{2obs}[D]_T[PA]_T \qquad (2)$$

denote total concentrations of dye and peracid, respectively. Experimentally determined second-order rate constants, k_{2obs}, for Orange I were found to pass through a maximum with change in solution pH (Fig. 1) and the maximum rate was found to occur at a pH midway between the pK_A of the dye and that of the peracid.

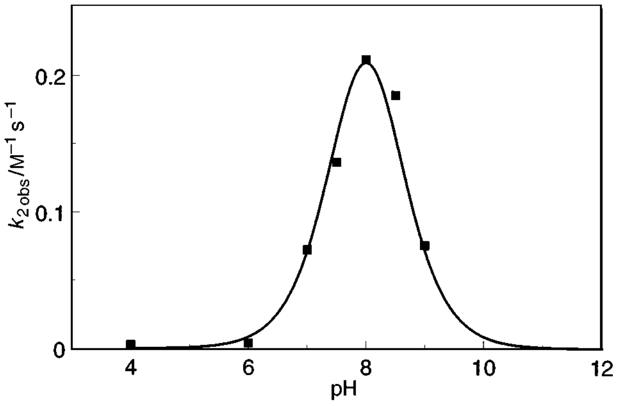

Fig. 1 Observed second-order rate constants for oxidation of Orange I with 5 mM PSPBA as a function of pH at 25 °C. The solid line is the theoretical fit to the experimental data (■).

Generally speaking, all oxidants and dyes examined exhibit such maxima. However, the maximum with Orange I is much sharper than with other dyes, as the pK_A values for oxidant and dye are similar.

The overall rate can be expressed as follows:

$$-d[D]/dt = k_1[PA][HD] + k_2[PA][D^-] + k_3[PA^-][HD] + k_3[PA^-][D^-] \qquad (3)$$

As all rate profiles exhibit maxima at $pH = [pK_A^{(PA)} + pK_A^{(HD)}]/2$ and are generally symmetrical, the 1st and 4th terms of eqn. (3) can be ignored (Appendix). Thus the rate profiles can be explained in terms of i, reaction of undissociated peracid moiety (PA) with ionised dye (D^-), and/or ii, reaction of ionised peracid moiety (PA^-) with undissociated dye (HD). Assuming one reaction predominates, then:

$$-d[D]/dt = k_2^E[PA][D^-] = k_2^N[PA^-][HD] \qquad (4)$$

where superscripts refer to electrophilic (E) and nucleophilic (N) reaction by peracid. In the appendix, it is shown that by combining this rate equation with equilibria and mass balance between species, the observed second-rate constant, k_{2obs} can be expressed in terms of measurable quantities as follows:

$$k_{2obs} = k_2^E\{1/(1 + K_A/[H^+])\}\{1/(1 + [H^+]/K_D)\} = k_2^N\{1/(1 + [H^+]/K_A)\}\{1/(1 + K_D/[H^+])\} \qquad (5)$$

where K_A and K_D are the acid dissociation constants for the peracid and dye, respectively. Differentiation of both these expressions with respect to $[H^+]$ leads to a maximum value for k_{2obs} at a pH given by:

$$\text{pH at } k_{2obs}(\text{max}) = (pK_A + pK_D)/2 \qquad (6)$$

This analysis is important as it shows that the reaction proceeds *via* one reactant that is dissociated and another that is undissociated, *i.e.* both are involved in the rate-determining step. Although there are two possible ionic reactions that could contribute to the overall rates, later on we will see that only one reaction is significant in all cases. Furthermore, it will be seen that rates strongly depend upon the leaving group character of the parent acids, implicating heterolytic peroxide bond scission in the transition state as the kinetically significant step. This suggests that oxygen radicals are not involved in the initial stage of dye oxidation, at least when trace metals are deactivated. This is an important conclusion derived from an elegantly simple, non-invasive route that may not necessarily be derived

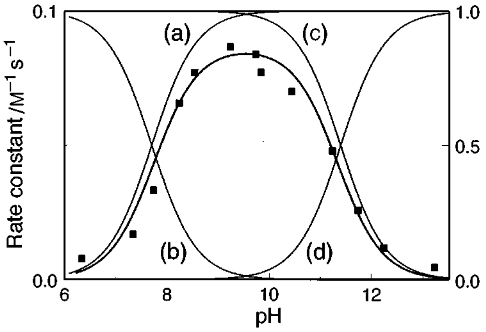

Fig. 2 Observed second-order rate constants for oxidation of Orange II with 5 mM PSPBA as a function of pH at 25 °C together with corresponding speciation profiles. The heavy line is the theoretical fit to the experimental data (■) and lines (a) to (d) are the mole fractions of PA^-, PA, HD and D^-, respectively.

from radical trap studies; for example, radicals may be involved in subsequent reaction steps or radical traps may react with oxidant. Overall, kinetic studies can provide valuable information about the reactants involved in the rate-determining step and subsequent breakdown of the activated complex.

Although the analysis indicates that one reactive species is dissociated and the other undissociated, it does not tell us which they are. Furthermore, the maximum occurs at pH 8 (Fig. 1) where the concentrations of ionised and unionised forms of both reactants are similar. In order to facilitate identification of reactants, it is necessary to select reactants with well-separated pK_A values so that one species of either reactant predominates, *i.e.* product of concentrations of one pair of potential reactants increase relative to the other. Consequently, we have examined the oxidation of Orange II ($pK_A = 11.4$) with PSPBA (pK_A 7.7). Their rate and speciation profiles with pH are depicted in Fig. 2.

As anticipated from the widely separated pK_A values, the speciation profiles for the ionised peracid and neutral dye closely match the rate profile, with the concentrations of the undissociated peracid and ionised dye being minimal at the pH where the rate is at a maximum. If it is assumed that the peracid anion is the reactive species, the experimental data can be fitted with rate constant, $k_2^N = 0.08$ M^{-1} s^{-1} at 25 °C; however, the corresponding rate constant for reaction of undissociated peracid with dissociated dye can be fitted equally well with a rate constant $k_2^E = 350$ M^{-1} s^{-1} at 25 °C. Although this rate constant is orders of magnitude higher, it is not unrealistically high for reactions involving undissociated peracid[20] so that the analysis does not permit unambiguous identification of reactive species, even when reactants have widely separated pK_A values.

In order to distinguish between the two possibilities, the main approach was switched to an examination of the specially synthesised series of *para*- and *ortho*-substituted 1-arylazo-2-naphthol dyes (**6a**,**6b**). In particular, the influence of dye substituents was investigated in three main areas:

(a) Effect of dye substituents on pK_A values.
(b) Influence on dye oxidation with three oxidant types: hypochlorite, hydrogen peroxide and peracid (peroxosulfate or MCPBA).
(c) The effect of 'fixing' dye (Orange I) in the azo and hydrazone forms.

These studies were complemented by an investigation of the oxidation of a selected dye, Orange II, with a range of peracids of differing pK_A values. As oxidation of some of these dyes was slow, subsequent experiments were conducted at 40 °C. Oxidant loss due to self decomposition[20] at 40 °C remained insignificant on the timescale for dye oxidation.

Dye pK_A values

The UV-VIS spectra of all the dyes exhibited isosbestic points as solution pH was modulated in the alkaline pH region, due to formation of the common anion. A typical example is given in Fig. 3 for Orange II.

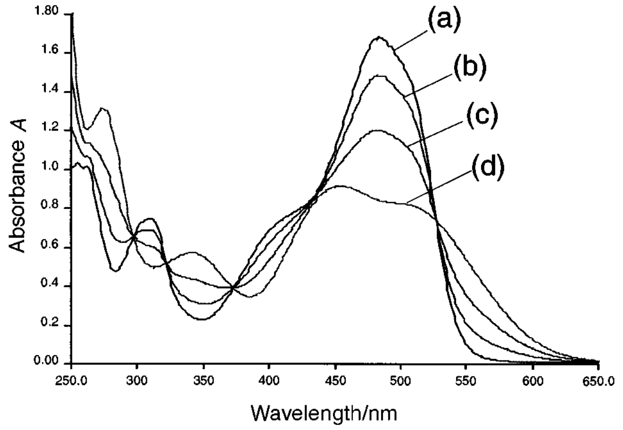

Fig. 3 Influence of pH on the UV-VIS spectrum of Orange II at 40 °C. Spectra (a) to (d) are at pH 7.2, 11.0, 11.6 and 13.4, respectively.

Table 1 Influence of aryl substituent upon dye pK_A and upon k_{2obs} (M^{-1} s^{-1}) for reaction of 1-arylazo-2-naphthol dyes with peroxosulfate at 40 °C

	para-		*ortho-*	
Dye substituent	pK_A	k_{2obs} (pH 10.5)	pK_A	k_{2obs} (pH 10.5)
-H	10.8	7.2	10.8	7.2
$-CH_3$	10.9	10.8	11.4	1.6
$-CH(CH_3)_2$	10.9	11.2	11.4	1.4
-Cl	10.5	9.6	11.3	0.42
$-OCH_3$	10.8	16.5	11.7	0.29
$-COCH_3$	10.9	6.5	—	—
$-NO_2$	10.7	8.9	11.6	0.28
$-CO_2^-$	11.2	3.2	12.2	0.20
$-SO_3^-$	10.8	4.9	12.1	0.053

Dye pK_A values were determined from the solution spectra[15] at 40 °C using dilute solutions of dye (~50 μM) at natural ionic strength to discourage aggregation. Dye pK_A values are given in Table 1. The pK_A values for these dyes are higher than those for corresponding naphthols (9.3 and 9.5 for 1- and 2-naphthols) due to intramolecular hydrogen bonding between the naphthol oxygen atom and the N–H proton of the hydrazone group.[12,13]

Inspection of Table 1 shows that *para* substituents have little influence upon dye pK_A values, indicating that intramolecular hydrogen bonding plays a dominant role. On the other hand, *ortho* substituents increase pK_A values, partly by reinforcing hydrogen bonding,[17] and it appears that charged substituents are most influential. The influence of *ortho* substituents in increasing dye pK_A values has been noted previously[15] for a related set of dyes.

Oxidation of 1-arylazo-2-napthol dyes by various oxidants

Initially restricting attention to observed second-order rates with the negatively charged peroxosulfate anion, it is clear that the influence of the *para* substituent is small (Table 1). In contrast, *ortho* substituents have a marked effect—suppressing observed rated by 50–100 fold—paralleling the increase in dye pK_A. The effect of *ortho* substituents upon observed rates with various other oxidants is given in Table 2.

To provide a comparison with organic peracids, MCPBA was selected in preference to PSPBA as it is uncharged and gives more convenient rates. Inspection of Table 2 shows that MCPBA and HOCl show the same trends: *ortho* substituents suppress rates by 50-fold in both cases. Clearly, HOCl behaves similarly to peracids and the results are consistent with literature results for a different dye series.[1,2] If the results for hydrogen peroxide are examined, it is clear that the observed rates

Table 2 Influence of *ortho* substitution upon $k_{2\text{obs}}$ (M^{-1} s^{-1}) for reaction of 1-arylazo-2-naphthol dyes with various oxidants at 40 °C

ortho substituent	pK_A	MCPBA $k_{2\text{obs}}$ (pH 10)	HOCl $k_{2\text{obs}}$ (pH 10)	H_2O_2 $k_{2\text{obs}}$ (pH 11)
-H	10.8	0.50	147	0.0020
-CH_3	11.4	—	52	0.0077
-$CH(CH_3)_2$	11.4	0.087	68	0.0079
-Cl	11.3	0.044	35	0.026
-OCH_3	11.7	—	16	0.0061
-NO_2	11.6	—	8.5	0.042
-CO_2^-	12.2	—	2.9	0.0074
-SO_3^-	12.1	0.011	3.8	0.030

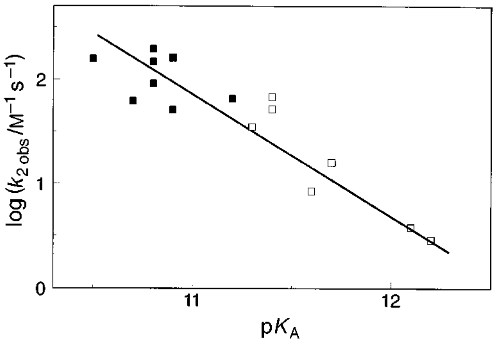

Fig. 4 Plot of observed second-order rate constant ($k_{2\text{obs}}$) *vs.* pK_A for reaction of 2×10^{-4} M NaOCl with 50 μM arylazonaphthol dye in the presence of 20 μM edta at pH 10 and 40 °C. (■ = *para*-substituted 1-arylazo-2-naphthol dye, □ = *ortho*-substituted 1-arylazo-2-naphthol dye).

actually increase with substituent, *i.e.* show opposing trends (Table 2). Evidently, the influence of substituent can either increase or decrease the rate depending upon the oxidant. This provides the first indication that peroxide may function by a different mechanism from hypochlorite. Close examination indicates that a good correlation exists between observed rate constant for peracids or hypochlorite and dye pK_A over several orders of magnitude. The results for hypochlorite oxidation are given in Fig. 4.

In order to analyse the dependence upon dye pK_A, the first step in kinetic analysis is to examine the influence upon the concentration of potential reactants. Accordingly, pH-independent rate constants were calculated (Table 3) from eqn. (4).

Calculated nucleophile second-order rate constants, k_2^N, are similar to observed rate constants, since the peracid anion and undissociated dye are the predominant species.

On the other hand, consideration of the second-order electrophilic rate constants, k_2^E, shows that those for the *ortho*-substituted dyes are remarkably similar to those for the corresponding *para*-substituted dyes (Table 3), *i.e. ortho* substituent does not affect absolute rate more than the corresponding *para* substituent. This is compelling evidence that HOCl functions as an electrophile. Contrary to literature reports, there is no evidence that the reactivity of arylazonaphthol dyes towards HOCl (a small, non-charged but effective oxidant) is influenced at all by steric or charge effects due to *ortho* substituents. The results suggest that the primary role of *ortho* substituents is to increase the pK_A of the dye, thereby lowering the equilibrium concentration of the reactive common anion species.

Although k_2^E for *ortho*-substituted dyes are identical to corresponding *para*-substituted dyes within experimental error, nevertheless, there is still a small affect of substituent (Table 3). Indeed, a correlation with Hammett σ constant[22] is anticipated for reaction with an azo dye and such a plot is shown in Fig. 5.

The plot of k_2^E *vs.* Hammett σ constant gives the anticipated

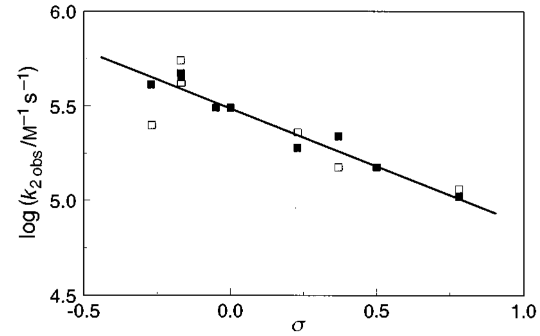

Fig. 5 Variation of k_2^E for reaction of NaOCl with 1-arylazo-2-naphthol dyes at 40 °C as a function of Hammett σ constant in the presence of 20 μM edta. (■ = *para*-substituted 1-arylazo-2-naphthol dye, □ = *ortho*-substituted 1-arylazo-2-naphthol dye).

negative slope for HOCl acting as an electrophile, *i.e.* electron-donating substituents give enhanced rates *via* an increase in negative charge density upon the anion. The magnitude of the slope is −0.5 and this will be discussed elsewhere.[17] Although a repeat of this analysis presents a similar picture with peracids,[17] it emerges that oxidation with hydrogen peroxide proceeds by an entirely different mechanism. In this case, calculated rate constants for *para*- and *ortho*-substituted dyes are similar[17] only when k_2^N is considered, suggesting that nucleophilic reaction occurs between the perhydroxyl anion and the neutral form of the dye. Accordingly, plots of k_2^N *vs.* Hammett σ constants (Fig. 6) for aryl substituents produce a strong positive correlation with slope +1, *i.e.* electron-withdrawing groups increase the electropositive character of the dye.

To provide reinforcement of these views, the next section will examine the influence of substituents upon the peracid molecule. As only a limited range of perbenzoic acids were available, a selection of other peracids having a wide pK_A range was additionally examined.

Oxidation of Orange II with a range of peracids

It has been suggested[23] that reactions of peroxygen compounds with substrates can be considered to occur by a two-step model, which initially involves complexation between the two reactants, followed by reaction between them:

$$\text{Peracid} + \text{Dye} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{Complex I}}{[\text{Peracid/Dye}]} \overset{k_r}{\rightleftharpoons} \text{Dye Oxidation}$$

For a second-order reaction:

$$-\mathrm{d}[\text{Dye}]/\mathrm{d}t = k_2[\text{Peracid}][\text{Dye}] \qquad (7)$$

Assuming steady steady in complex I,

$$k_2 = k_f k_r/(k_b + k_r) \qquad (8)$$

In particular, peracid anions are known to react with unsaturated imines, carbon double bonds or carbonyl-containing compounds[19,24–26] and the scheme has been applied to nucleophilic attack on carbonyl compounds to form a tetrahedral intermediate, when the fate of the intermediate depends upon the relative pK_A values of the conjugate acids of the attacking nucleophile and the leaving group. When nucleophiles have conjugates with higher pK_A values than the leaving group, *e.g.* with HO_2^- as oxidant and phenols as leaving groups, the transition state mainly involves bond formation, since once formed the intermediate will tend to proceed more easily into products, *i.e.* condition $k_r > k_b$. In such a case, rates will increase with electron-donating substituents on the attacking

Table 3 Rate constants ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) for reaction of *ortho*-substituted 1-arylazo-2-naphthol dyes with hypochlorite at 40 °C

	$k_{2\mathrm{obs}}$		pK_A[a]		$10^3\,k_2^\mathrm{E}$		k_2^N	
Dye substituent	*para*	*ortho*	*para*	*ortho*	*para*	*ortho*	*para*	*ortho*
-H	147	147	10.8	10.8	310	310	171	171
-CH_3	158	52	10.9	11.4	450	420	178	54
-$CH(CH_3)_2$	161	68	10.9	11.4	470	550	181	68
-Cl	157	35	10.5	11.3	190	230	213	37
-OCH_3	196	16	10.8	11.7	410	250	231	16
-$COCH_3$	51	—	10.9	—	150	—	58	—
-NO_2	62	8.5	10.7	11.6	110	110	66	8.7
-CO_2^-	66	2.9	11.2	12.2	310	140	71	2.9
-SO_3^-	92	3.8	10.8	12.1	220	150	106	3.8

[a] Experimental error in pK_A is ±0.1, which in certain cases may translate to an uncertainty of ±50% in k_2 values.

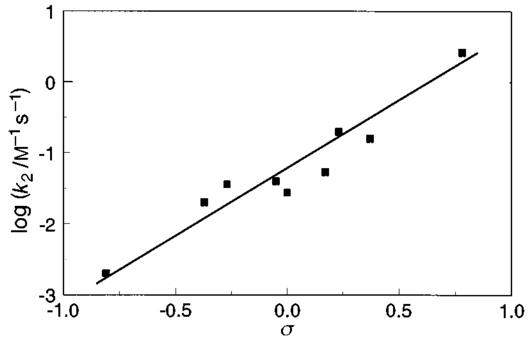

Fig. 6 Variation of k_2^N for reaction of hydrogen peroxide with *ortho*-substituted 1-arylazo-2-naphthol dyes at 40 °C as a function of Hammett σ constant in the presence of 20 μM edta.

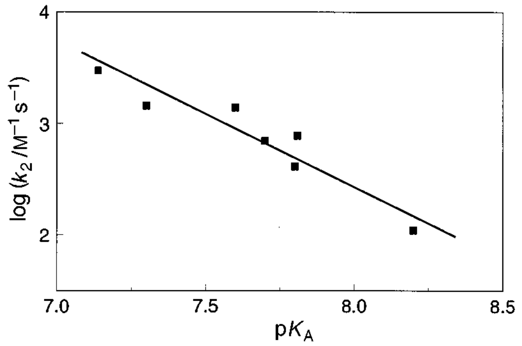

Fig. 7 Second-order rate constants, k_2^E, for oxidation of Orange II with 1 mM peracid in the presence of 20 μM edta as a function of peracid pK_A at 40 °C.

nucleophile. On the other hand, when the conjugate acid of the attacking nucleophile has a lower pK_A than that of the leaving group (*i.e.* $k_\mathrm{r} < k_\mathrm{b}$) peroxide bond scission in the transition state becomes the determining factor and the rate will decrease with electron-donating substituents due to the poorer leaving group character of the parent acids. Peracids tend to be intermediate cases, $k_\mathrm{r} \sim k_\mathrm{b}$; the anions are much less effective nucleophiles than HO_2^- due to the presence of the neighbouring electron-withdrawing acyl group, but the associated reduction in parent acid pK_A means that O–O bond rupture in the transition state will be facilitated. In this case, nucleophilic reaction tends to be less influenced by substituent since the rate decrease due to the poorer leaving-group character of parent acids upon introduction of electron-donating substituents is opposed by the tendency for the rate to increase by the enhanced nucleophilic character of the peracid anion.

Intermediate formation is less well-defined for electrophilic reactions with substrates, but similar concepts may be applied to the transition state. For example, electron-donating substituents will decrease both the electrophilic properties of the peracid and the leaving-group character of the parent acid. Thus a rate decrease occurs independent of whether bond formation or peroxide bond scission is characteristic of the transition state, resulting in a strong negative dependence upon the pK_A.

Using the above concepts, a number of peracids with different pK_A values were investigated, partly to confirm earlier mechanistic findings and partly to examine whether all peracids behave in the same manner towards oxidation of dyes. Observed rate constants for oxidation of Orange II were measured at pH 10 and converted into corresponding pH-independent electrophilic rate constants (k_2^E) utilising speciation profiles. The corresponding plot *vs.* peracid pK_A is illustrated in Fig. 7.

Clearly, a strong correlation with peracid pK_A is achieved, suggesting that all peracids behave similarly. There are two other interesting facets of this plot, firstly that the gradient is negative and secondly, that its value is ~1. This provides convincing support for the view that peracids act as electrophiles and, furthermore, the strong dependence upon peracid pK_A suggests that heterolytic peroxide bond scission in the activated complex is the kinetically significant step. It also provides good evidence that radicals are not implicated in the rate determining step, though they may be involved in subsequent steps.

Oxidation of Orange I 'fixed' in azo and hydrazone forms

In this approach, Orange I was 'fixed' in the hydrazone and azo tautomeric forms using its *N*- and *O*-methylated derivatives (**7**, **8**) and their reactivity towards hypochlorite, hydrogen peroxide and the inorganic peracid potassium peroxosulfate were compared to Orange I. The reactivity of both the *O*-Me and *N*-Me derivatives are much lower than the native dye and they respond differently towards the various oxidants with pH. In particular, the fixed azo dye exhibits a dependency on pH that is indicative of oxidation by electrophilic oxidants, consistent with literature studies on oxidation of azo compounds.[27] However, it is so unreactive that only the result for HOCl is given in Table 4. Evidently, the azo form is a relatively unreactive form of the dye towards oxidation. In contrast, the *N*-Me derivative generates a rate profile with pH which indicates that nucleophilic reaction is kinetically significant for all oxidants. All experimental results are quoted in Table 4 at 25 °C, with units of rate constant equal to $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Also included in the Table are rates calculated from the oxidation of Orange I by various oxidants at 25 °C, assuming first nucleophilic attack upon the neutral form (k_2^N) and, secondly, electrophilic attack on the dye anion (k_2^E).

The measured rate constant for the nucleophilic reaction of hydrogen peroxide with the *N*-Me hydrazone dye is similar to that calculated from results for Orange I. The close similarity in rates supports the view that the perhydroxyl anion, a powerful nucleophile,[19,23] is the active oxidant and that this initiates oxidation of the hydrazone tautomeric form of the dye. It also suggests that methylation of the dye does not hinder reaction with such nucleophiles. Peracids are much less effective[19,23]

Table 4 Influence of various oxidants upon oxidation of Orange I and its *N*-Me and *O*-Me derivatives at 25 °C

	HOCl		HSO_5^-		PSPBA		H_2O_2	
	k_2^N	k_2^E	k_2^N	k_2^E	k_2^N	k_2^E	k_2^N	k_2^E
Orange I	9500	1×10^5	2.3	1.5	0.56	1.4	0.30	2×10^{-4}
N-Me derivative	0.050	—	0.054	—	0.050	—	0.032	—
O-Me derivative	—	<6	—	—	—	—	—	—

nucleophiles and this may explain their lower reactivity. Indeed, calculated nucleophilic rate constants for Orange I with peracids and hypochlorite (Table 4) are much higher than those measured for the 'fixed' hydrazone dye, and even higher than that recorded for reaction with the powerful perhydroxyl anion. This study provides further supporting evidence that oxidation by peracids or hypochlorite occurs by electrophilic reaction between undissociated oxidant and the anionic dye.

The low reactivity of the hydrazone dye towards nucleophiles and its inertness towards electrophiles may reflect: i, the electron-donor properties of the nitrogen of the N–H fragment of the hydrazone unit,[28] particularly donation into the neighbouring imine group and ii, the low basicity of this nitrogen atom as it is difficult to protonate in acidic media, even when methylated.

Furthermore, a prevailing view that dyes capable of adopting the hydrazone tautomeric form are more reactive[2,12] towards specific oxidants than simple azo forms is not strictly true. Whilst oxidation by hydrogen peroxide does indeed proceed *via* attack of the perhydroxyl anion on the hydrazone form of dyes, the common anion is the reactive form towards peracids and hypochlorite. The common anion exhibits largely azo character[14,15] but is 10^6 fold more reactive towards HOCl than dyes that adopt the simple azo form; this arises from extensive delocalisation of the negative charge throughout the molecule. The switch in mechanism probably arises because peracids and HOCl are much less effective nucleophiles[19,23] than the perhydroxyl anion; on the other hand, the presence of neighbouring electron-withdrawing groups makes these oxidants not only more effective electrophiles but also promotes the leaving group properties of the parent acids.

Finally, it must be acknowledged that the conclusions specifically refer to oxidation of azonaphthol dyes and to non-metal catalysed reactions; they do not necessarily apply to other types or to metal catalysed reactions.[29,30]

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Appendix

Calculation of k_{2obs} (max)

Assuming rate law:

$$-d[D]/dt = k_{2obs}[PA]_T[D]_T \qquad (9)$$

$$= k_2^E[PA][D^-] \qquad (10)$$

Now:

$$[PA]_T = [PA] + [PA^-] \qquad (11)$$

$$[D]_T = [HD] + [D^-] \qquad (12)$$

and

$$K_A = [PA^-][H^+]/[PA] \qquad (13)$$

$$K_D = [D^-][H^+]/[HD] \qquad (14)$$

From eqns. (9) and (10)

$$k_{2obs} = k_2^E\{[PA]/[PA]_T\}\{[D^-]/[D]_T\} \qquad (15)$$

From eqns. (11) and (13)

$$K_A/[H^+] = \{[PA]_T - [PA]\}/[PA] \qquad (16)$$

Therefore:

$$[PA]_T/[PA] = 1 + K_A/[H^+] \qquad (17)$$

or

$$[PA]/[PA]_T = 1/(1 + K_A/[H^+]) \qquad (18)$$

Similarly, from eqns. (12) and (14):

$$[D^-]/[D]_T = 1/(1 + [H^+]/K_D) \qquad (19)$$

Substituting eqns. (18) and (19) into eqn. (15):

$$k_{2obs} = k_2^E\{1/(1 + K_A/[H^+])\}\{1/(1 + [H^+]/K_D)\} \qquad (20)$$

Let

$$f = (1 + K_A/[H^+])(1 + [H^+]/K_D) \qquad (21)$$

Then

$$f = 1 + K_A/[H^+] + [H^+]/K_D + K_A/K_D \qquad (22)$$

$$df/d[H^+] = -K_A/[H^+]^2 + 1/K_D;\ d_2f/d[H^+]^2 = 2K_A/[H^+]^3 \qquad (23)$$

Thus eqn. (20) has a maximum value at $df/d[H^+] = 0$, *i.e.*

$$-K_A/[H^+]^2 + 1/K_D = 0 \text{ or } [H^+]^2 = K_AK_D \qquad (24)$$

Thus

$$-2\log[H^+] = -(\log K_A + \log K_D) \qquad (25)$$

i.e.

$$\mathrm{pH}\ (k_{2obs}\ \mathrm{max}) = (pK_A + pK_D)/2 \qquad (26)$$

A similar conclusion is drawn where rate is expressed by eqn. (27),

$$-d[D]/dt = k_2^N[PA^-][HD] \qquad (27)$$

and eqn. (20) becomes:

$$k_{2obs} = k_2^N\ \{1/1 + [H^+]/K_A)\}\{1/(1 + K_D/[H^+])\} \qquad (28)$$

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