Kinetic investigation of the oxidation of substituted arylazonaphthol dyes by hydrogen peroxide in alkaline solution

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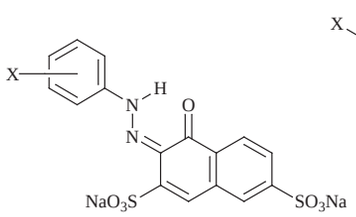
A number of arylazonaphthol dyes, namely substituted 2-arylazo-1-hydroxynaphthalene-3,6-disulfonates (**1**) and 1-arylazo-2-hydroxynaphthalene-6-sulfonates (**2**), have been synthesised and characterised by a range of techniques. All the dyes were found to exist predominantly in the hydrazone tautomeric form in aqueous media. *Ortho*-substituents on the aryl ring were found to increase dye pK_A values—irrespective of whether they are electron-withdrawing or -releasing—and the factors influencing pK_A values are discussed. Kinetic investigations have been made of the two dye series to pinpoint the active dye site and to identify the reactive species. In contrast to oxidation by HOCl and peracids, *ortho* substituents in the aryl ring of the 1-arylazo-2-naphthol dyes gave higher observed second-order rate constants, k_{2obs}, than corresponding *para* substituents; furthermore, k_{2obs} is not suppressed as the substituent increases in size or becomes charged. *Ortho*- and *para*-substituents gave similar rate constants, k_2^N, for nucleophilic reaction between the perhydroxy anion and the hydrazone tautomer and both gave good Hammett plots with slope ~1. Values of k_2^N for the 2-arylazo-1-naphthol dyes (10^{-3}–10^{-4} M^{-1} s^{-1}) were over an order of magnitude less than the corresponding values for substituted 1-arylazo-2-naphthol dyes (10^{-2} M^{-1} s^{-1}). Product analysis was carried out for dye **2** (X = H), and a reaction mechanism has been proposed which involves reaction of the perhydroxy anion at the imine carbon of the hydrazone tautomer, producing an unstable diazene intermediate which decomposes liberating nitrogen to form benzene.

Introduction

Although the oxidation of arylazonaphthol dyes by hydrogen peroxide in aqueous media has attracted much interest recently,[1–4] key mechanistic aspects of the reaction have not been elucidated. It is generally agreed[1–3] that observed rate constants exhibit a maximum in alkaline media and that the reaction involves nucleophilic reaction of the perhydroxy anion with the hydrazone tautomer.[1,2] One group of workers[2] investigated the influence of dye structure and reported that dye substituents do not influence reactivity towards peroxide, unlike oxidation by hypochlorite.[5] Others[4] have concluded that the presence of substituents in the aryl ring suppresses rates. Neither group reports having taken specific action to eliminate the influence of trace metal impurities, which can play a key role[6] in the oxidation of dyes, especially at high temperatures. Trace metals can catalyse the oxidation of dye, or they can exclusively catalyse oxidant decomposition, reducing oxidant concentration.

Earlier,[1,7] it was shown that a characteristic feature of dye oxidation is that the reactive bleach or catalyst species[8,9] are present in exceedingly low concentrations. Furthermore, it was found that oxidation by hydrogen peroxide proceeds *via* a different mechanism than with HOCl or Cl_2. In this investigation, a number of substituted arylazonaphthols have been examined to elucidate the mechanism of reaction. In particular, two series of dyes based on 2-arylazo-1-hydroxynaphthalene-3,6-disulfonic acid, sodium salts (**1**) and 1-arylazo-2-hydroxynaphthalene-6-sulfonic acid, sodium salt (**2**) were synthesised and characterised by UV–VIS spectroscopy and ^1H and ^{13}C NMR spectroscopy. Dye pK_A values were also determined, primarily to facilitate kinetic analyses. Systematic investigations have been carried out into a) the influence of *ortho* and *para* substituents upon the oxidation of substituted 1-arylazo-2-naphthol dyes **2** by hydrogen peroxide; and b) the effect of changing the dye structural motif from substituted 1-arylazo-2-naphthol (**2**) to 2-arylazo-1-naphthol (**1**); primarily to identify the active species and pinpoint the active site of the dye.



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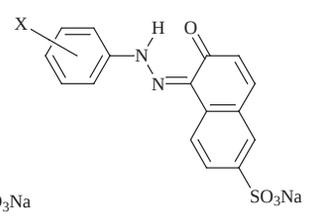

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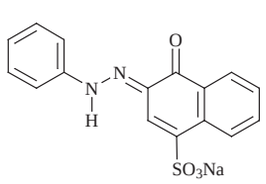

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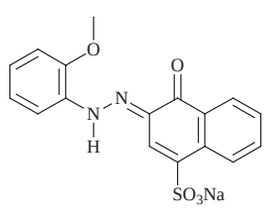
pK_A = 8.5, λ_{max} = 493 nm



4

pK_A = 9.5, λ_{max} = 509 nm

Kinetic investigations were complemented by product analysis of dye **2** (X = H) to deduce the reaction mechanism. Special care was taken to eliminate the influence of trace metals by carrying out experiments in the presence of the sequestrant EDTA.

Experimental

Hydrogen peroxide (8.08 M) was sourced from Aldrich. Potassium hydroxide was *ex*. Fluka (puriss), nitric acid was *ex*. BDH (Analar) and ethylenediaminetetraacetic acid disodium salt, EDTA, was diluted from a BDH analytical concentrate. All solutions were made up using water doubly distilled from a Fisons "Fi-Streem" still.

Two series of *ortho*- and *para*-substituted dyes based upon 2-arylazo-1-hydroxynaphthalene-3,6-disulfonic acid sodium

Table 1 Characteristics of substituted arylazonaphthol dyes

Substituent	pK_A	^{1}H–N shift δ (ppm)	^{13}C=O shift δ (ppm)	λ_{max}/nm	ε_{max} [a] ($\times 10^4$)/l mol^{-1} cm^{-1}	Yield (%) [a]	Purity (NMR) (%)	Purity (HPLC) (%)
1-Arylazo-2-naphthol dyes								
o-H	10.8	15.86	177.7	483	1.90	67	98.0	99.6
o-CH_3	11.4	16.78	174.0	488	2.02	93	99.6	90.5
o-$CH(CH_3)_2$	11.4	16.45	171.2	490	1.53	56	91.2	78.4
o-Cl	11.3	16.23	176.6	481	1.70	76	99.0	80.7
o-OCH_3	11.7	16.56	182.0	498	2.14	60	98.5	93.5
o-OCH_3, *m*-CH_3	12.0	16.58	177.9	500	1.90	70	93.9	97.5
o-CO_2H	12.2	17.34	173.7	486	—	37	89.8	73.3
o-SO_3Na	12.1	15.84	170.9	479	1.52	41	83.7	98.8
o-NO_2	11.6	16.62	184.1	487	1.70	92	99.2	95.1
o-OH, *m*-CH_3 (i)	8.5	—	—	501	1.16	—	—	—
(ii)	12.6	—	—	586	—	—	—	—
p-CH_3	10.9	15.73	168.7	490	1.77	88	97.2	97.5
p-$CH(CH_3)_2$	10.9	15.73	168.3	488	1.62	91	95.4	73.7
p-Cl	10.5	15.66	172.0	483	1.76	90	98.4	97.7
p-OCH_3 [b]	10.8	15.16	165.1	498	1.39	77	95.5	96.1
p-CO_2H [c]	11.2	—	180.3	487	—	86	96.3	96.2
p-SO_3Na	10.8	15.95	173.5	482	1.47	99	78.8	96.0
p-NO_2 [d]	10.7	15.72	—	492	—	—	—	—
p-$COCH_3$ [d]	10.9	15.91	—	490	—	—	—	—
2-Arylazo-1-naphthol dyes								
o-H	11.5	16.27	178.2	491	1.60	17	71.2	75.6
o-CH_3 [b]	12.0	16.41	178.5	500	2.19	45	90.5	91.3
o-$CH(CH_3)_2$	12.0	16.99	177.4	502	1.29	21	67.5	88.9
o-Cl	11.7	16.34	164.4	494	1.84	66	91.3	79.0
o-OCH_3	12.5	16.49	156.0	512	1.73	—	79.5	98.0
o-CO_2H	13.2	—	175.1	492	1.64	44	78.4	93.8
o-SO_3Na [b]	13.2	16.09	181.1	488	1.82	32	87.4	98.8
p-SO_3Na	11.3	16.27	180.7	490	1.56	19	73.1	68.7

[a] Yields and ε_{max} values calculated from NMR purities. [b] NMR samples run in D_2O–DMSO. [c] NMR samples run in D_2O. [d] Samples prepared by G. Hodges,[20] University of York.

salts (**1**) and 1-arylazo-2-hydroxynaphthalene-6-sulfonic acid sodium salt (**2**) were synthesised using standard diazotisation and coupling procedures.[10] Isolation of dye was done by salting out. The crude paste was heated with NaCl to aggregate the dye so that it would filter easily. After isolation, the crude dye was recrystallised from ethanol–water. The recrystallised dye was boiled in excess acetone to remove most of the water and leave a product that was quickly vacuum dried to produce a free flowing powder.

The dyes were characterised by ^{1}H and ^{13}C NMR, HPLC, and UV–VIS spectroscopy. The purities according to NMR and HPLC are given in Table 1, together with yield. Residual salt levels were found to be < 100 ppm. NMR spectra were obtained in dimethyl sulfoxide (DMSO) as spectra in water were poorly resolved due to aggregation. All dyes were assayed against trioxan, and ^{13}C, APT and COSY spectra were recorded. The tautomeric (*N*–H) proton shifts and carbonyl ^{13}C shifts are given in Table 1. It must be emphasised that NMR spectra were obtained in DMSO and not water, and so may reflect different azo–hydrazone tautomeric equilibrium positions, as UV–VIS spectra tended to depend upon solvent. This is particularly true of dyes containing electron-releasing substituents,† *e.g.* *p*-methoxy substituted 1-arylazo-2-naphthol dyes, which exhibit‡ much more of the azo form in non-aqueous solvents (Fig. 1). Strictly speaking, the tautomeric proton shift quoted is actually a weighted average for the *N*–H of the hydrazone tautomer and the hydroxy proton of the azo tautomeric form. Also, NMR spectra were recorded at high dye concentrations and may be influenced by water of hydration associated with the dye. Indeed, in some cases, no *N*–H proton could be detected and this was because the spectrum was either run in D_2O or because some water was present.

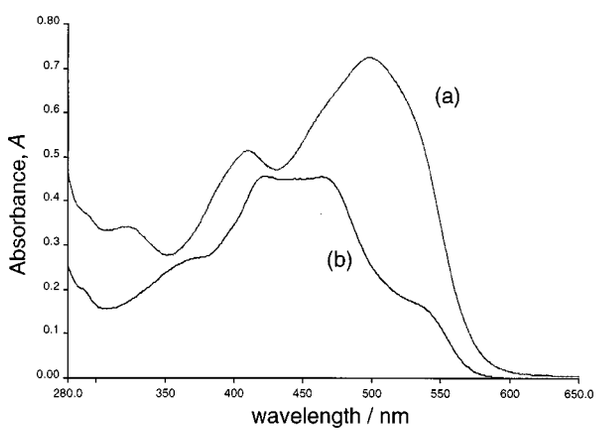


Fig. 1 UV–VIS spectra of *p*-methoxy substituted 1-arylazo-2-naphthol dye in (a) H_2O and (b) DMSO solutions at 25 °C.

Dyes were analysed using reversed phase HPLC with UV detection at 254 nm on a Hewlett Packard HP1090M Liquid Chromatograph. A 250 × 4.6 mm 5 μm Hypersil MOS column was used and the eluent was 40:60 acetonitrile–40 mM tetrabutylammonium hydrogen sulfate (TBAHS) in 0.05 M phosphoric acid adjusted to pH 3. The flow rate was 1.5 ml min^{-1} and the injection volume 10 μl. Extinction coefficients at the dye λ_{max} in aqueous solution were measured from UV–VIS spectra obtained using a Perkin-Elmer Lambda 14

† The azo form is stabilised by electron-releasing substituents since the azo group is an electron acceptor.

‡ Although spectra for the *p*-methoxy derivatives may additionally reflect other solvatochromic effects, firm evidence is provided by comparison of spectra of a range of *para*- and *ortho*-substituted arylazonaphthol dyes in acetonitrile. As anticipated, the *para*-isomer invariably exhibited more of the azo form, particularly with electron-releasing substituents.

spectrophotometer. Dye concentrations were calculated using the dye purity§ obtained by NMR. Dye solutions were prepared at nominally 50 μM in double distilled water to reduce the likelihood of aggregation. Spectra were recorded at 40 °C using a 10 mm path length quartz cell. Solution pH was adjusted to a value in the region of pH 4 to ensure that the dye was present entirely in its undissociated form.

Dye pK_A values were determined from the pH dependence of electronic absorption spectra in dilute (~50 μM) aqueous solution at 40 °C and at natural ionic strength to preclude dye aggregation. The determination is based upon the principle that, where isosbestic points are present, spectra of dissociated (D^-) and undissociated dye (HD) are additive, *i.e.* absorbance, A, at a given wavelength, is related to the absorbance values of the pure forms of HD and D^- measured at extreme pH values, and to their respective mole fractions, X by the expression:

$$A = X_{HD}A_{HD} + X_{D^-}A_{D^-}$$

and since the mole fractions total unity, then

$$X_{HD} = (A - A_{D^-})/(A_{HD} - A_{D^-})$$

In this way, mole fractions can be determined at a given wavelength as a function of pH and the pK_A can be determined from the point where mole fractions of each species are equal. Experimental error in pK_A values is ±0.1; however, there is additional uncertainty when pK_A values are high due to increase in ionic strength at high pH.

To simplify analysis of data, kinetic measurements were made using absorbance values at the isosbestic points of dyes as the extinction coefficients of the undissociated (HD) and dissociated forms of dye (D^-) are not usually equal. 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. Experiments were conducted under *pseudo* first-order conditions, *i.e.* $[H_2O_2]_T \gg [D]_T$. For the dyes investigated here, logarithmic plots of absorbance with time were linear over a substantial fraction of the reaction, though there were some exceptions, particularly at pH > 12.5. Plots of k_{obs} (obtained from the gradient of lnA/t plots) varied linearly with initial $[H_2O_2]_T$, so the rate law is described by:

$$-d[D]/dt = k_{obs}[D]_T = k_{2obs}[D]_T[H_2O_2]_T = k_2[HD][HO_2^-] \quad (1)$$

All experiments were conducted at pH 11 and 40 °C in the presence of 20 μM EDTA to remove effects due to trace metal impurities. Knowing the pK_A values of the dye and that of peroxide (pK_A = 11.6) allows pH-independent rate constants (k_2) to be calculated from observed rates. Additional details of experimentation have been given earlier.[1,7]

Results and discussion

UV–VIS absorption spectra and pK_A values of dyes

The electronic spectra of both the substituted 2-arylazo-1-naphthol and 1-arylazo-2-naphthol series of dyes in aqueous solution all give maxima around 500 nm (Table 1). The wavelength of absorption maximum for the substituted 1-arylazo-2-naphthol dyes is plotted against the corresponding Hammett σ[11] for the substituent in Fig. 2(a). It is clear that electron-donating substituents produce a bathochromic shift, whilst electron-withdrawing substituents barely influence λ_{max}. This pattern of behaviour, along with the magnitude of λ_{max}, indicates that the undissociated dyes are present predominantly in the hydrazone tautomeric form.[10,12] The observation by ^{1}H NMR of hydrazone *N*–H bands in the region 15–16 ppm and bands in the region 170–180 ppm by ^{13}C NMR (Table 1) confirms this assignment.[13]

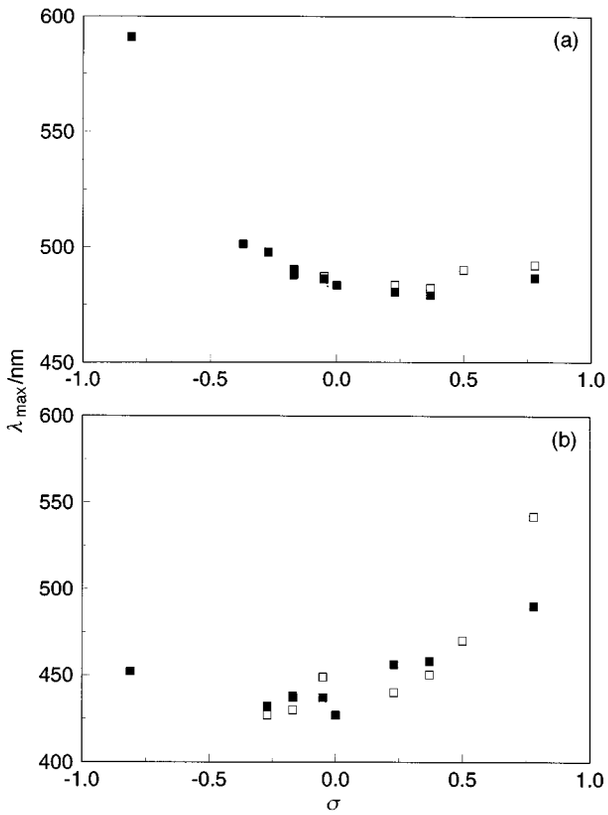


Fig. 2 (a) Variation of λ_{max} for undissociated 1-arylazo-2-naphthol dyes with Hammett σ (■ *o*-substituents, □ *p*-substituents); (b) Variation of λ_{max} for ionised 1-arylazo-2-naphthol dyes with Hammett σ (■ *o*-substituents, □ *p*-substituents).

Under alkaline conditions, the substituted arylazonaphthol dyes ionise to form the common anion[10] so that the observed spectrum becomes successively replaced by that of the anion with increase in pH, *via* an isosbestic point.[1] In particular, upon ionisation of 1-arylazo-2-naphthol dyes, the main absorption band in the visible spectrum undergoes a hypsochromic shift, *e.g.* for 1-(4-sulfophenylazo)-2-naphthol (Orange II) the main absorption band (λ_{max} = 484 nm, $\varepsilon_{max} = 1.57 \times 10^4$) splits into a doublet, the main peak appearing at λ_{max} = 456 nm, $\varepsilon_{max} = 0.82 \times 10^4$, with a weaker band appearing at higher wavelength (505 nm). The corresponding plot of λ_{max} *versus* Hammett σ for the substituent is illustrated in Fig. 2(b). In this particular case, the trend is opposite to that for undissociated dyes, *i.e.* electron-withdrawing substituents yield a bathochromic shift, with electron-donating substituents having little effect.¶ Although the ionised dye exists as a common ion in which there is electron delocalisation over the whole molecule, the present results for arylazonaphthol dyes are consistent with earlier conclusions[10,12] and with NMR data[13] which indicate that it has predominantly azo character (*i.e.* electron density is concentrated upon the hydroxy O atom). In either case, it is seen that analogous dyes, differing only in position of substitution (*ortho*- or *para*-) give near-identical λ_{max} values. Data for 2-arylazo-1-naphthol dyes are less complete (Table 1), but the same trends can be discerned.

Dye pK_A values are given in Table 1 for both series of substituted arylazo naphthol dyes. These were determined primarily for the purpose of calculating absolute rate constants.

§ Dye purity estimated by analytical NMR—by comparison with trioxan—is considered to be a more accurate assay than that by HPLC.

¶ Strictly speaking, since the main absorption band tends to be split into a doublet[1] due to vibrational fine structure, a weighted averaged band position should be plotted; however, the longer wavelength component tends in some cases to be very weak and λ_{max} yields a more convenient and more reliable measurement.

In general, pK_A values for the dyes investigated are much higher than corresponding values for naphthols (9.34, 9.51 for 1- and 2-naphthols, respectively[14]) or their substituted counterparts. For hydrazone tautomers, this is generally accepted to arise from intramolecular hydrogen bonding between the oxygen atom of the naphthol ring and the *N*–H proton of the hydrazone group.[10,15] Unlike λ_{max} or second-order rate constants,[1] k_2, there is no correlation between pK_A values and the corresponding Hammett σ for either the *ortho*- or the *para*-substituted arylazonaphthol dyes. A number of interesting observations can be made and these are summarised and discussed below:-

a) Substitution in the *ortho*-position causes a pronounced increase in dye pK_A (Table 1).

b) The dye pK_A is relatively insensitive to *para*-substitution (Table 1), indicating that intramolecular hydrogen bonding is a key determinant.

c) For the *ortho*-substituted series of dyes, the presence of a charged substituent appears to play a major role in controlling the pK_A but uncharged substituents still have an effect, no matter whether they are electron-withdrawing or -releasing. The order‖ of effects in increasing the pK_A is as follows:

$$O^- \sim SO_3^- \sim CO_2^- > OCH_3 > NO_2 > CH(CH_3)_2 \sim CH_3 \sim Cl > H$$

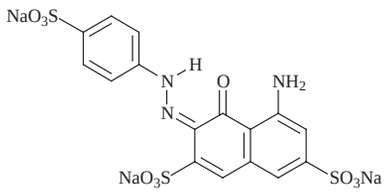
d) The unsubstituted representative of the 1-arylazo-2-naphthol series, dye **2** (X = H), has a lower pK_A (10.8) than that (11.5) for the corresponding representative of the 2-arylazo-1-naphthol series, dye **1** (X = H). This is lower than that (12.1) for the *o*-sulfonated 1-arylazo-2-naphthol dye, dye **2** (X = SO_3^-), which, in turn, is less than that (13.2) for the *o*-sulfonated 2-arylazo-1-naphthol dye, dye **1** (X = SO_3^-) *i.e.* an *o*,*o*′-disulfonated dye.

e) 4-(4-Sulfophenylazo)-1-naphthol (Orange I), which is present in the hydrazone form in aqueous media, has a pK_A = 8.2. The low value of its pK_A is anticipated as the *N*-H proton cannot be involved in hydrogen bonding.

f) 2-Arylazo-1-naphthol dyes (**3** and **4**) that do not contain substituents in the naphthol ring *ortho* to the azo functionality also have extremely low pK_A values. The low pK_A are particularly surprising since λ_{max} values in both DMSO and water suggest that both dyes primarily adopt the hydrazone tautomeric form and intramolecular hydrogen bonding is expected. ^{13}C NMR spectra for **3** are consistent with this assignment, since a peak is observed at 173.4 ppm, which is typical of a carbonyl group. Although the *N*–H proton shift at 14.94 ppm is the lowest observed so far, its magnitude still suggests extensive hydrogen bonding.

g) If position 8 of the 2-arylazo-1-naphthol dyes is substituted with an amino group (dye **5**) the pK_A is increased from 11.3 to 12.7; a key factor is likely to be hydrogen bonding interactions with the neighbouring oxygen in position 1. Replacing one H atom of the amino group with a triazine group (dye **6**) to produce the electron-withdrawing amino-triazine group prevents the increase in pK_A and actually reduces it from 11.5 to 11.35.

A reasonable correlation is obtained between *N*–^{1}H chemical shifts in DMSO and pK_A for dyes for the substituted 1-arylazo-2-naphthol series (Fig. 3). The proton shift to low fields with increasing pK_A suggests that intramolecular hydrogen bonding is a key factor in controlling pK_A values. The main deviation that occurs is with *p*-methoxy and the *o*-sulfonate substituents; the low value of the shift for *p*-methoxy can be explained in terms of there being a greater proportion of the dye existing in the azo tautomeric form in DMSO. Examination of UV–VIS



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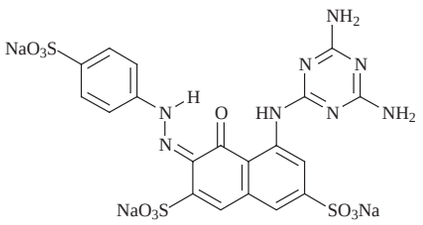
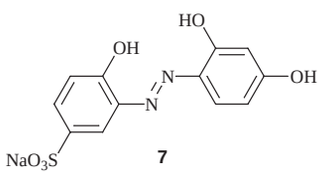
pK_A = 12.7, λ_{max} = 534 nm



6

pK_A = 11.35, λ_{max} = 536 nm



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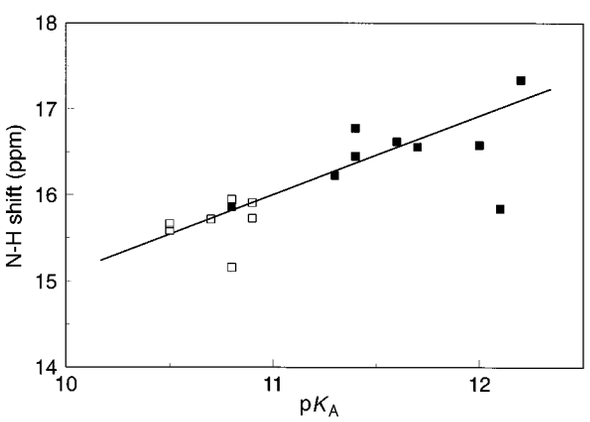


Fig. 3 Correlationof N–H proton shift of 1-arylazo-2-naphthol dyes with dye pK_A (■ *o*-substituents, □ *p*-substituents).

spectra (Fig. 1) shows that the hydrazone form dominates the spectrum in water but the azo tautomeric form is present in significant amounts in DMSO. Similar UV–VIS observations in acetonitrile (the HPLC solvent system) show that the azo–hydrazone equilibrium is more displaced towards the hydrazone form for *ortho*-substituents, compared to corresponding *para*-substituents and the effect is particularly noticeable with electron-releasing substituents. Indeed, the same trend is evident in measured *N*–^{1}H or ^{13}C carbonyl shifts in DMSO, so they may additionally reflect a shift in position of the azo–hydrazone equilibrium with change of substituent and/or the presence of water inextricably associated with dye. Although data points are limited, the correlation for the substituted 2-arylazo-1-naphthol series is less good and highlights the fact that there are other contributing factors.

In addition to increased hydrogen bonding in the hydrazone tautomer, the influence of negative charge on the substituent may increase the pK_A by destabilising the anion—*via* electrostatic repulsion. There may also be steric effects of the substituents, which could also destabilise the anion by twisting the molecule out of the plane—thereby resulting in partial loss of conjugation. Loss of conjugation *via* steric effects is likely to play a significant role in the stability of the dye anion and is less

‖ This order for the arylazonaphthol dyes studied here differs from that found earlier[4] for 2-arylazo-1-naphthol dyes substituted at the 8-position by an aminotriazine group; this difference may arise from additional hydrogen bonding involving the *N*–H group in position 8.

Table 2 Influence of substituents upon reactivity of 1-arylazo-2-naphthol dyes towards hydrogen peroxide at 40 °C

		pK_A		$k_{2obs}/M^{-1}\,s^{-1}$ [a]		$k_2^N/M^{-1}\,s^{-1}$		$k_2^E/M^{-1}\,s^{-1}$	
Dye substituent	Hammett σ	*para*-	*ortho*-	*para*-	*ortho*-	*para*-	*ortho*-	*para*-	*ortho*-
H	0	10.8	10.8	0.002	0.002	0.028	0.028	0.004	0.004
CH_3	−0.17	10.9	11.4	0.0017	0.0077	0.019	0.054	0.0038	0.030
$CH(CH_3)_2$	−0.17	10.9	11.4	0.0018	0.0079	0.021	0.053	0.0041	0.033
Cl	0.23	10.5	11.3	0.00061	0.026	0.013	0.20	0.001	0.098
OCH_3	−0.27	10.8	11.7	0.00084	0.0061	0.011	0.36	0.0018	0.046
$COCH_3$	0.50	10.9	—	0.022	—	0.15	—	0.12	—
NO_2	0.78	10.7	11.6	0.058	0.42	0.86	2.60	0.11	2.6
CO_2^-	−0.05	11.2	12.2	0.0019	0.0074	0.016	0.04	0.0061	0.13
SO_3^-	0.37	10.8	12.1	0.0046	0.03	0.059	0.16	0.0093	0.50
OH	−0.27	—	8.5	—	0.0001	—	0.02	—	—
O^-	−0.81	—	12.6	—	0.0001	—	0.002	—	0.02

[a] Rate constants ±50%.

Table 3 Influence of substituents upon reactivity of 2-arylazo-1-naphthol dyes towards hydrogen peroxide at 40 °C

Substituent	pK_A	$k_{2obs}/M^{-1}\,s^{-1}$ [a]	$k_2^E/M^{-1}\,s^{-1}$	$k_2^N/M^{-1}\,s^{-1}$
H	11.5	6.8×10^{-4}	3.6×10^{-3}	4.5×10^{-3}
p-SO_3^-	11.3	1.2×10^{-3}	4.5×10^{-3}	9.0×10^{-3}
o-CH_3	12.0	9.8×10^{-5}	1.4×10^{-3}	5.4×10^{-4}
o-Cl	11.7	2.6×10^{-4}	4.1×10^{-3}	1.5×10^{-3}
o-OCH_3	12.5	4.8×10^{-5}	2.0×10^{-3}	2.5×10^{-4}
o-CO_2^-	13.2	1.0×10^{-5}	2.0×10^{-3}	5.0×10^{-5}
o-SO_3^-	13.2	5.6×10^{-5}	1.1×10^{-2}	2.7×10^{-4}

[a] Rate constants ±50%.

important for undissociated dye, which, being in the hydrazone form, is not conjugated to the phenyl ring; however, there may be sterically-induced loss of interactions with the solvent in the hydrazone tautomer.

One particularly interesting finding is the extremely low values for the pK_A values for dyes **3** and **4** compared to dyes **1** and **2**, comparable to simple naphthols. This suggests i) that the sulfonate in the naphthol ring *ortho* to the azo group in dye **1**, and ii) the adjacent ring—particularly the carbon atom in position 8—of dye **2**, may provide steric hindrance and may restrict conformations that the dye can adopt.

It is concluded that substituents may influence dye pK_A values in three main ways: i) changes in hydrogen bonding, ii) influencing the stability of the anion, and iii) steric factors that may impose conformational restrictions. In principle, molecular modelling could provide insight into the relative importance of these factors, but current packages do not yet have the level of sophistication to predict pK_A values or electron density distributions in azo, hydrazone and common ion forms.

Peroxide oxidation

Influence of substituents upon rates. Observed second order rate constants for the hydrogen peroxide oxidation of all the dyes examined were found to pass through a maximum with change in solution pH. The main differences from other oxidants[1] are that rate constants are lower, necessitating higher hydrogen peroxide concentrations (0.2 M) and that the maxima occur at higher pH, *i.e.* ~pH = 11. Typical pH profiles for reactivity towards 4-(4-sulfophenylazo)-1-naphthol (Orange I) and 1-(4-sulfophenylazo)-2-naphthol (Orange II) have been illustrated in the literature.[2,3] The maxima observed are centred[1] at a pH equal to $\{pK_A^{(H_2O_2)} + pK_A^{(HD)}\}/2$ but are relatively sharp due to the close proximity of the pK_A values. Observed rate constants, k_{2obs} for the influence of dye substituents on oxidation of 1-arylazo-2-naphthol and 2-arylazo-1-naphthol dyes at 40 °C and pH 11 are given in Tables 2 and 3, respectively.

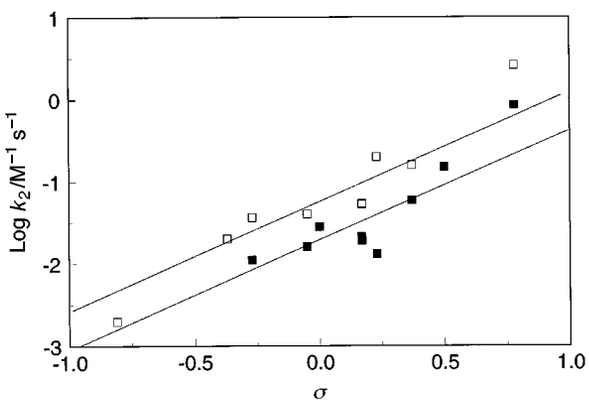


Fig. 4 Variation of second-order rate constant, k_2^N for oxidation of substituted 1-arylazo-2-naphthol dyes with Hammett sigma constant of substituent at 40 °C (■ *p*-substituents, □ *o*-substituents).

Inspection of observed rate constants, k_{2obs}, for *ortho*- and *para*-substituted 1-arylazo-2-naphthol dyes by hydrogen peroxide (Table 2) reveals interesting differences from corresponding data when oxidation is by hypochlorite[7] or peracids.[1] In particular, whereas *ortho*-substituents tend to give *lower* rate constants than corresponding *para*-substituents for hypochlorite or peracid oxidation, in the case of hydrogen peroxide the rate constants are actually *higher*. Another difference is that observed rates do not become suppressed as the substituent increases in size or becomes charged.[1] Nor is there any apparent correlation with dye pK_A. Second-order rate constants for nucleophilic and electrophilic reaction (k_2^N and k_2^E respectively) were calculated from speciation profiles and the results are included in Table 2. Evidently, rates for *ortho*- and *para*-substituted dyes are similar only when k_2^N is considered, consistent with the view[1] that reaction occurs between the perhydroxy anion and the hydrazone tautomer. Plots of k_2^N for *ortho*- and *para*-substituted dyes *versus* Hammett σ are illustrated in Fig. 4. Accordingly, k_2^N is found to increase with increasing electron-withdrawing capability of the substituent and it is shown that a positive correlation with slope ~1 is obtained. Since charged substituents in the *ortho*-position of the aryl ring do not suppress reaction rates, this suggests that reaction does not occur at a site immediately adjacent to the aryl ring. Nevertheless, the slope of Fig. 4 suggests that the site of attack must still be in close proximity, implicating the imine functionality.

It is illustrative to compare this Hammett plot with those obtained previously[1,7] for oxidation by Cl_2 and HOCl, which both give negative slopes due to electrophilic reaction. Good Hammett plots are obtained for reaction between Cl_2 and the hydrazone tautomer, but differences in basicity at the nitrogen of the *N*–H group result in the *para*-substituted dye having the higher rate constant, k_2^E. Reaction of the dye common

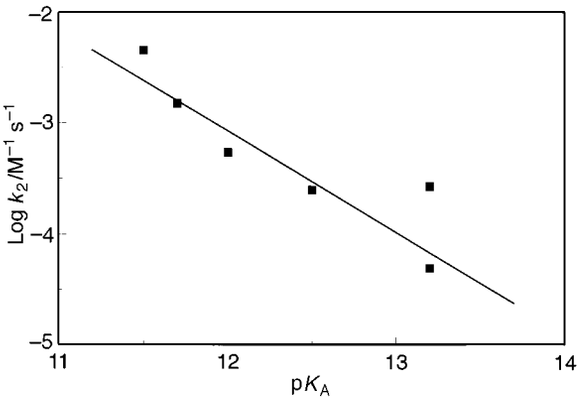


Fig. 5 Variation of second-order rate constant, k_2^N, for oxidation of substituted 2-arylazo-1-naphthol dyes with dye pK_A at 40 °C.

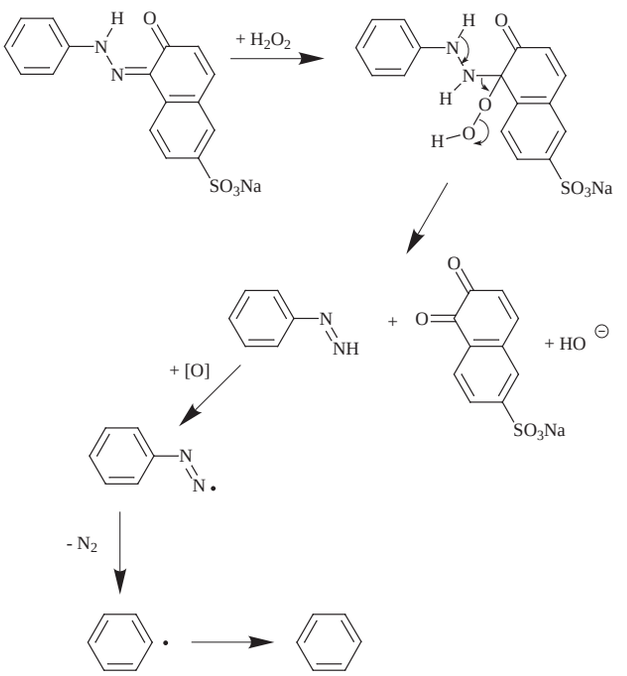
anion with HOCl also produces a good Hammett plot, but *ortho*- and corresponding *para*-substituents yield the same rate, demonstrating[1,7] that neither steric nor charge effects of the substituent control dye reactivity. The magnitudes of k_2^N for reaction of *para*-substituted dyes with hydrogen peroxide are consistently lower than for the corresponding *ortho*-substituents (Table 2), a trend which is statistically significant. This is believed to be due to small differences in the electropositive character of the hydrazone tautomer at a site more remote from the aryl ring than the *N*–H, again implicating the imine functionality.

Effect of dye type. Examination of Table 3 shows that the unsubstituted 2-arylazo-1-naphthol dye and the *para* derivative yield rate constants (k_2^N) that are an order of magnitude lower than those for the corresponding 1-arylazo-2-naphthol dyes. Evidently, the presence of the negatively charged *ortho*-sulfonate upon the naphthol ring plays a key role in suppressing rates. This does not happen for HOCl as it is uncharged[1,7] or, as we have seen, when negatively charged substituents are placed in the aryl ring of 1-arylazo-2-naphthol dyes. As the perhydroxy anion is negatively charged, this suggests that the imine carbon atom is the most likely site of attack. Furthermore, the effect with 2-arylazo-1-naphthol dyes is much more pronounced when there are additional *ortho*-substituents upon the aryl ring (Table 3). The rate suppression is largest for dyes where the additional *ortho*-substituents in the aryl ring are charged. The rate constants, k_2^N, for oxidation of 2-arylazo-1-naphthol dyes are plotted *versus* dye pK_A in Fig. 5. The good correlation of k_2^N with dye pK_A suggests that the rate is controlled by the same factors that control the pK_A, namely steric over-crowding—hindering development of the activated complex—and charge–charge interactions.

In summary, a number of observations support the view that reaction of the perhydroxy anion with the hydrazone tautomer occurs at the imine carbon: a) the sensitivity of rates in 1-arylazo-2-naphthol dyes to Hammett σ; b) higher rates, k_2^N, observed for *ortho*-substituted 1-arylazo-2-naphthol dyes compared to the corresponding *para*-isomers; c) the insensitivity of rates in 1-arylazo-2-naphthol dyes to charged *ortho*-substituents in the aryl ring; d) the oxidative resistance of 2-arylazo-1-naphthol dyes containing a sulfonate group on the naphthol ring adjacent to the azo-site; e) the powerful retarding influence of *ortho*-substituents in the 2-arylazo-1-naphthol series.

Furthermore, there is evidence that hydrolysis of hydrazones—formed by reaction of hydrazine with *ortho*-quinones—occurs[16] *via* nucleophilic attack at the imine carbon atom. This reinforces the view that the imine carbon atom is the site for reaction with the perhydroxy anion.

Postulated reaction mechanism. Like the reaction[7] with HOCl, the reaction between the perhydroxy anion and arylazonaphthol dyes in alkaline media is extremely complex, with initial reaction products degrading still further to smaller fragments. The overall strategy for isolating reaction products has been outlined earlier[7] and trapping of volatile organics was found to be instrumental in providing mechanistic insights. Reaction of hydrogen peroxide with dye **2** (X = H) produces benzene, detectable by headspace analysis. Based upon the observation of benzene, in conjunction with identification of the active site by kinetic studies, a mechanism can be proposed for the reaction, and is illustrated in Scheme 1. This mechanism



Scheme 1 Postulated reaction pathway for oxidation by hydrogen peroxide.

bears similarities to proposals in the literature based upon studies of dye breakdown by peroxide systems catalysed[17] by metal species—where benzene was detected as a key reaction product—or by peroxidases.[16,18] Although the quinone was not detected,** significant evidence was obtained for acetate and formate, together with phthalic acid/phthalic anhydride derivatives, suggesting it reacts further with the perhydroxy anion. Owing to the complexity of the reaction, we cannot rule out the possibility that reaction can occur at the carbonyl carbon or at electropositive sites in the ring—resulting in ring scission. There is evidence that this can happen with certain dyes that are present in the azo form, *e.g.* Superchrome Garnet Y, dye **7**. Separation of oxidation products by TLC shows that oxidation by hydrogen peroxide gives rise to aliphatic dicarboxylic acid oxidation products,[19] *e.g.* succinic/maleic, from the dihydroxylated phenyl ring,†† together with *p*-hydroxybenzenesulfonate, the major reaction product. Monohydroxylated *azo* dyes, *e.g.* 4-(4-sulfophenylazo)-2,6-difluorophenol, tend to be inert‡‡ to oxidation, but the rate of oxidation is enhanced by introduction of a second hydroxy group into the phenyl ring,[3], *e.g.* 4-(4-sulfophenylazo)-3-hydroxyphenol (Acid Orange 6). This suggests that oxidation is initiated by reaction

** It could be detected by electrospray mass spectrometry under certain conditions, *e.g.* where excess peroxide was minimised by the presence of metal catalysts.

†† These are also the main reaction products from the hydrogen peroxide oxidation of resorcinal.

‡‡ Azo compounds can undergo oxidation by peracids under more forcing conditions to form azoxy linkages.[22]

of the perhydroxy anion with the dihydroxylic phenyl ring, ultimately yielding an alkyl–aryl azo intermediate. These are unstable[21] and decompose, liberating nitrogen, to form the corresponding phenyl radical derivative and, ultimately, *p*-phenol sulfonate.

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