

Kinetic investigations of the oxidation of Methyl Orange and substituted arylazonaphthol dyes by peracids in aqueous solution



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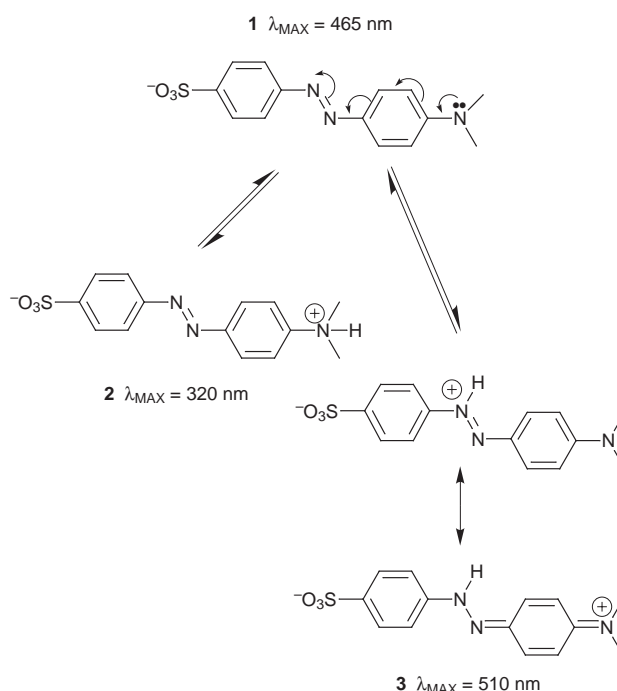
Kinetic and product analyses have been made of the oxidation of an activated azo dye, 4-(4-sulfophenylazo)-*N,N*-dimethylaniline (Methyl Orange, **1**) and a series of tautomeric arylazonaphthol dyes by peracids at 40 °C in alkaline media, particularly peroxosulfate. The arylazonaphthol dyes are readily degraded into fragments ($k_2^E = 10^2\text{--}10^3 \text{ M}^{-1} \text{ s}^{-1}$) whereas the azo link in Methyl Orange is relatively inert ($k_2^E \ll 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$) consistent with the view that dyes that contain the azo or hydrazone link are more resistant to oxidation than the common anion form of arylazonaphthol dyes. Methyl Orange is decolourised by peroxosulfate ($k_2^E = 7.6 \text{ M}^{-1} \text{ s}^{-1}$) simply *via* oxidation of the tertiary amine to amine oxide, resulting in a shift of the spectrum into the UV region. The reaction site in arylazonaphthol dyes has been pinpointed by investigating k_2^E for substituted dyes with the 1-arylazo-2-naphthol and 2-arylazo-1-naphthol structural motifs. In direct contrast to results for oxidation by hydrogen peroxide, the presence of an *ortho*-sulfonate in the aryl ring retards oxidation but an *ortho*-sulfonate in the naphthol ring does not. This suggests oxidation is initiated by electrophilic reaction by the negatively charged peroxosulfate at the nitrogen atom of the common dye anion that is in close proximity to the aryl ring. In contrast to oxidation by hypochlorite, the introduction of an amino group into the 8-position of 2-arylazo-1-naphthol dyes protects the dye against oxidation, *via* its influence upon the dye pK_A .

Introduction

Currently, there is much interest¹ in the oxidation of azo dyes by peracids. Hitherto, the area has attracted little interest despite the use of peracids as low temperature oxidants in detergency for the last two decades. It is known that peracids can oxidise the azo form of dyes to form azoxy compounds² but the current focus of interest is on the oxidation of dyes that adopt the hydrazone tautomeric form, which exhibit much higher oxidation rates. Although it had been assumed^{1,3} that the peracid anion initiates oxidation of such dyes, the earlier paper in this series⁴ showed that the undissociated peracid was the active oxidant, which reacts with the dye common anion; the factors controlling oxidation were also discussed. In contrast, oxidation by peroxide did involve nucleophilic reaction⁴ by the perhydroxyl anion on the hydrazone tautomer and mechanisms of oxidation by hydrogen peroxide⁵ and hypochlorite⁶ were discussed.

This paper extends the investigation by examining the mechanism of peracid oxidation of model, well-characterised⁵ arylazonaphthol dyes that adopt the hydrazone structural motif. In order to place the observations into perspective, oxidation of an azo dye, Methyl Orange, **1**, was also studied. Methyl Orange was selected as it is hydrolytically stable in acidic media, contains no *ortho*-substituents and the presence of the *para*-dimethylamino group activates the *azo* group.[†] This provides a direct comparison of the reactivity of the azo group with the common anion of arylazonaphthol dyes.

In acidic media, the dye protonates: either at the dimethylamino group to form an ammonium ion, **2**, or at the *azo* group to form an *azonium* ion, **3**, (Scheme 1). Although there has been



Scheme 1 Species formed on protonation of Methyl Orange.

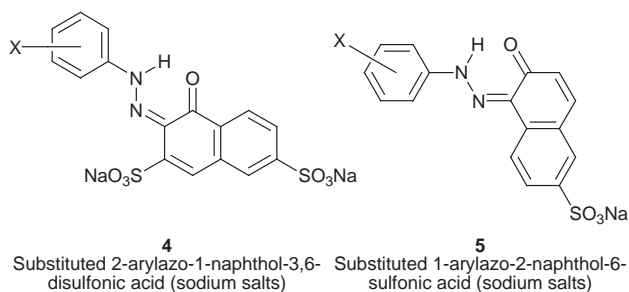
some uncertainty as to which nitrogen atom is the most basic,⁷ studies with dimethylaminoazobenzene suggest⁸ that the *azonium* ion may be the predominant species at pH's as low as 2. Consequently, the reactivity of the *azonium* ion towards peracids is additionally examined.

Although a range of peracids was investigated earlier⁴ and shown to behave similarly, in this study we have concentrated upon peroxosulfate, HSO_5^- , as oxidant for three main reasons; a) it is one of the more reactive peracids, giving a convenient

[†] Although the azo nitrogen atom adjacent to the ring containing the NMe_2 group is anticipated to be the more basic on the basis of inductive effects of the NMe_2 and SO_3^- groups, electromeric delocalisation of the lone pair of the NMe_2 group will tend to favour the other azo nitrogen atom^{2,7,8} as indicated in Scheme 1.

reaction rate and expediting kinetic studies, b) it does not contain organic elements, facilitating analysis of reaction products, particularly NMR, and c) it contains a negative charge in close proximity to the peracid group, making it convenient for studying the influence of the negative charge upon electrophilic reactivity.

Two series of substituted dyes were examined: 2-arylaazo-1-naphthol dyes (4) and 1-arylaazo-2-naphthol dyes (5), both of



which exist predominantly in the hydrazone form. Kinetic investigations—aimed at identifying the active site upon the dye—were supplemented by product analyses to elucidate the mechanism of action.

Experimental

Methyl Orange was obtained from Aldrich and was used without further purification. Arylazonaphthol dyes were prepared and characterised by routes previously described.⁵ Oxidants utilised were described earlier.⁴ These oxidants tend to decompose upon storage, thus they were each assayed by standard iodometric techniques⁹ immediately prior to use. Solutions were prepared in water that was doubly distilled from demineralised water using a Fisons 4BD Still. All other chemicals were of high purity: potassium hydroxide (Fluka Puriss), nitric acid (BDH Analar) and edta (BDH analytical concentrate).

The methodology for kinetic measurements and product analysis has been described elsewhere.^{4,5} Kinetic measurements for oxidation of Methyl Orange were carried out at the absorbance maximum, 465 nm, as a function of time. In alkaline media, arylazonaphthol dyes exist as an equilibrium mixture of undissociated and dissociated dye forms; to simplify analyses, measurements were recorded at the isosbestic point as the extinction coefficients for the two forms are identical. Absorbances were found to obey the Beer–Lambert Law over the experimental range of interest ($<1 \times 10^{-4}$ M). There was no interference from product absorbances. Experiments were conducted under pseudo first order conditions, *i.e.* $[PA]_T \gg [D]_T$, where $[PA]_T$ and $[D]_T$ are the total concentrations of peracid and dye, respectively. Logarithmic plots of absorbance with time were linear over a substantial fraction of the reaction, indicating that the reaction was first-order in $[D]_T$. Similarly, plots of k_{obs} —obtained from the gradient—varied linearly with $[PA]_T$ such that the rate law is described by eqn. (1). All rate constants are quoted at 40 °C unless otherwise stated.

$$-d[D]/dt = k_{obs}[D]_T = k_{2obs}[D]_T[PA]_T \quad (1)$$

The pK_A of Methyl Orange was determined from UV-Vis spectra by monitoring the absorbance at 510 nm as it varied with pH, according to a procedure published elsewhere.⁵

Results and discussion

Oxidation of an azo dye, Methyl Orange

The UV-Vis spectrum of Methyl Orange exhibits a broad peak at 465 nm ($\epsilon = 2.68 \times 10^4$) typical of a substituted azobenzene.⁷

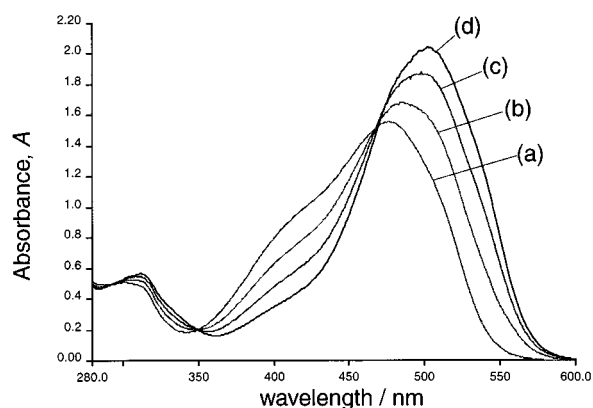


Fig. 1 UV-Vis absorption spectrum of Methyl Orange at 40 °C. Spectra (a) to (d) at pH = 9.6, 3.6, 3.0 and 1.9 respectively.

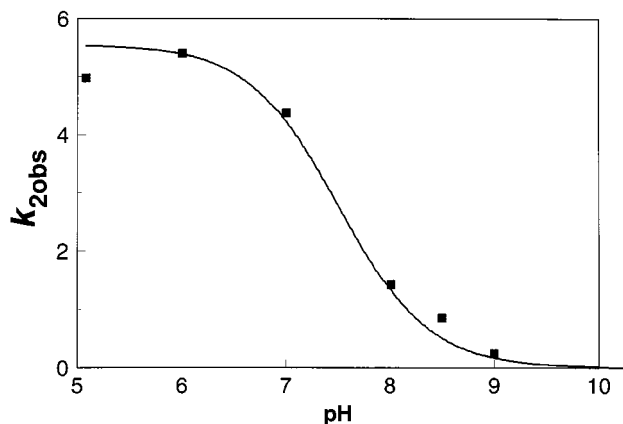


Fig. 2 Plot of k_{2obs} versus pH for reaction of Methyl Orange with *m*-chloroperbenzoic acid at 40 °C. The smooth curve is the theoretical fit to experimental points.

This peak is independent of pH from pH 11 down to pH 5 (Fig. 1a). As the pH is reduced below pH 5, the dye protonates and the spectrum shifts to longer wavelength (Fig. 1 b–d) via an isosbestic point (470 nm). This represents a simple equilibrium with $pK_A = 3.35$ at 40 °C. The new peak is centred at 510 nm. By analogy with dyes that exist in the hydrazone form, this is attributed to protonation at the azo group to form the azonium ion. The dimethylamino group has a lower affinity for protons ($pK_A \sim 2$); formation of the ammonium ion results in a weaker absorption peak centred at 320 nm at lower pH. Di-protonation becomes important^{7,8} at still lower pH.

Above pH 5, where Methyl Orange exists in the azo form, its reaction with peracids is found to depend strongly upon the solution pH. Indeed, measured second-order rate constants were found to decrease with increasing pH and closely match the undissociated peracid speciation profile, suggesting that the rate-determining step involves undissociated peracid as oxidant. A typical example using *m*-chloroperbenzoic acid (MCPBA) as oxidant is illustrated in Fig. 2. This suggests that reaction is initiated by electrophilic reaction by the peracid upon an electron-rich site on the dye, implicating the amino group or one of the azo nitrogen atoms [eqn. (2)]. The



pH-independent second-order rate constant, k_2^E , determined from the pH profiles for peroxosulfate was $7.6 \text{ m}^{-1} \text{ s}^{-1}$; those for other peracids,⁴ *p*-nitroperbenzoic acid (PNPBA), (*sec*-butyl-imido)peroxytrimellitic acid (BIPTA), MCPBA and 6-phthalimidoperoxyacetic acid (PAP) are 10.7, 5.2, 5.4 and $0.4 \text{ m}^{-1} \text{ s}^{-1}$, respectively.

The reaction products for the peroxosulfate oxidation of Methyl Orange were studied at 40 °C by UV-Vis and ¹H NMR

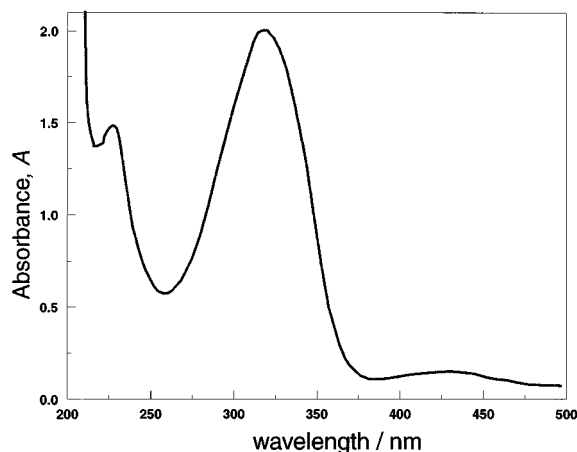
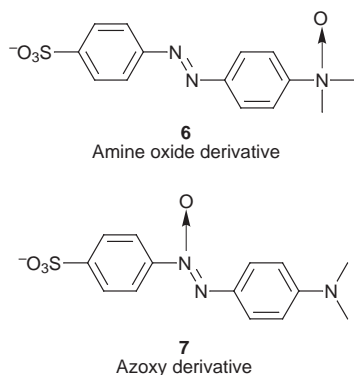


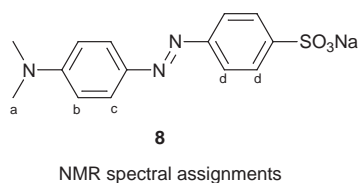
Fig. 3 UV-Vis spectrum of reaction product from oxidation of Methyl Orange with peroxosulfate in alkaline media at 40 °C.

spectroscopy. The intensity of the 465 nm peak decreased with time and a new peak emerged at 320 nm, *via* an isosbestic point. This suggests direct conversion into a reaction product, with no evidence of a long-lived intermediate. The spectrum of the reaction product is illustrated in Fig. 3. This spectrum is virtually identical to that known⁷ for the amine oxide derivative of dimethylaminoazobenzene. It is quite unlikely that for the azoxy derivative or where both azo and amino functions have been oxidised.⁷ Furthermore, the absorption band at 435 nm indicates that the azo group retains its integrity. The visible absorption spectra provide good evidence that oxidative attack occurs on the amine nitrogen atom to form **6** rather than at the azo group to form **7**. Thus the loss of colour simply results from



a shift of the spectrum into the UV, rather than degradation of the molecule into smaller fragments.

This interpretation is corroborated by ¹H NMR studies. The NMR spectrum of Methyl Orange in D₂O exhibits a singlet at high field 3.0 ppm characteristic of the *N*-methyl protons (a) and three groups of aromatic proton resonances, a pair of doublets at 6.8 ppm (b) and 7.92 ppm (c) and a quartet (d) centred at 7.74 ppm; peak assignments are shown in **8**. The



relative intensities of the four groups of signals are 3:1:1:2, respectively. The two doublets at 7.92 and 6.8 ppm are attributed to aromatic protons *meta* and *ortho* to the dimethylamino group and the quartet at 7.74 ppm is assigned to aromatic protons in the ring carrying the sulfonate group. Upon oxidation,

all the proton resonances shift to lower field. The *N*-methyl resonance (a) shifts from 3.0 to 3.65 ppm and the aromatic protons in the ring carrying the sulfonate group (d) show the smallest shift—from 7.74 to 8.05 ppm—but the quartet fine structure becomes better resolved. The resonances in the other ring (b) and (c) exhibit the largest shifts—from 7.92 to 8.45 ppm and from 6.8 to 8.1 ppm—so that the protons *ortho* to the amino group give the largest shift. The relative intensities of the signals remain at 3:1:1:2, indicating there is no loss of protons upon oxidation. These studies are consistent with the formation of the *N*-oxide, *i.e.* shift of the *N*-methyl protons from 3.0 to 3.65 ppm, large shift of the attached ring proton resonances—with the *ortho* protons most affected—and very little shift for those protons in the ring to which the sulfonate is attached.‡ This result is consistent with the view that oxidation in aqueous media occurs *via* electrophilic reaction by peracid at the amine nitrogen.

There is no evidence for oxidation of the azo group with peracids under the conditions studied, indicating the reaction has 1:1 stoichiometry. However, literature investigations of substituted azobenzene derivatives suggest that azoxy derivatives can be formed under more extreme conditions.² Furthermore, oxidation of similar molecules in organic solvents⁷ initially occurs at the amino group, followed by subsequent reaction at the azo group to form the azoxy compound. Oxidation of Methyl Orange still occurs at low pH when it becomes protonated (pH < 5). The second-order rate constant decreases for peroxosulfate oxidation from 7.6 at pH 6 to 4 M⁻¹ s⁻¹ at pH = 3. Speciation calculations show that the reduction in rate can be explained by conversion of around half of the Methyl Orange to the protonated form, *i.e.* when the *azo* group becomes protonated the rate of oxidation becomes insignificant.§ Evidently, protonation of the *azo* group reduces the electron density of the dimethylamino group by virtue of formation of the azonium ion (Scheme 1).

There are two interesting facets of the oxidation: a) The azo and azonium groups are much less readily oxidised by peracids ($k_2^E \ll 0.1 \text{ M}^{-1} \text{ s}^{-1}$), compared to the common anion of aryl-azonaphthol dyes⁴ ($k_2^E = 10^3 \text{ M}^{-1} \text{ s}^{-1}$). As the azo group in Methyl Orange is activated to electrophilic attack by the electron-donating dimethylamino group, it seems likely that other simple azo functionalities will be up to five orders of magnitude less reactive than the common anion.¶ b) Although protonation most readily occurs at the azo group to form the azonium ion, in marked contrast, oxidation—which would normally have been expected to occur at the more basic azo site to form an azoxy compound—actually occurs exclusively at the amine nitrogen atom to form the *N*-oxide.

This apparent paradox simply arises because oxidation is kinetic in origin, whereas protonation is a thermodynamic phenomenon. The most easily oxidised nitrogen is normally the one with greater electron density and this often is the sole factor in controlling the rate of oxidation. However, the nitrogen that is preferentially protonated in dilute acidic solutions is the most basic, not necessarily the most electron-rich, and it is this particular lone pair of electrons that will coordinate the proton.

‡ Oxidation of Methyl Orange has been carried out¹⁰ in 0.1 M borax (pH 9.2) at ambient temperature; the NMR spectrum (recorded in deuterated DMSO and methanol) gave similar constants to those recorded here in D₂O.

§ In contrast, protonation of Methyl Orange activates reaction with aqueous chlorine ($k_2 = 100 \text{ M}^{-1} \text{ s}^{-1}$), by facilitating reaction at the *N*-H site.

¶ Similar conclusions hold for the series of dyes existing predominantly in the hydrazone form. Unlike Methyl Orange, these do not protonate in aqueous media, *i.e.* the *N*-H group is less basic, probably due to electron donation into the neighbouring imine group.¹¹ Thus we estimate that the hydrazone form will be no more reactive towards electrophilic oxidants than the azo group and is insignificant under experimental conditions employed, *i.e.* the rate profile remains symmetrical.

Table 1 Influence of substituents on second-order rate constants ($\text{M}^{-1} \text{s}^{-1}$) for the oxidation of 1-arylozo-2-naphthol dyes by peroxosulfate (1 mM) and MCPBA (1 mM) at 40 °C

Dye substituent	$\text{p}K_{\text{A}}$		$k_{2\text{obs}}(\text{HSO}_5^-)^a$		$k_2^{\text{E}}(\text{HSO}_5^-)$		MCPBA ^b	
	<i>para</i>	<i>ortho</i>	<i>para</i>	<i>ortho</i>	<i>para</i>	<i>ortho</i>	$k_{2\text{obs}}$	k_2^{E}
-CH ₃	10.9	11.4	10.8	1.6	480	201	—	—
-H	10.8	10.8	7.2	7.2	235	235	0.5	410
-CH(CH ₃) ₂	10.9	11.4	11.2	1.4	510	195	0.087	132
-Cl	10.5	11.3	9.6	0.42	215	42	0.044	100
-OCH ₃	10.8	11.7	16.5	0.29	545	65	—	—
-COCH ₃	10.9	—	6.5	—	290	—	—	—
-NO ₂	10.7	11.6	8.9	0.28	265	55	—	—
-CO ₂ ⁻	11.2	12.2	3.2	0.20	240	108	—	—
-SO ₃ ⁻	10.8	12.1	4.9	0.053	180	28	0.011	350

^a pH 10.5. ^b pH 11.**Table 2** Influence of substituents on second-order rate constants ($\text{M}^{-1} \text{s}^{-1}$) for the oxidation of 2-arylozo-1-naphthol dyes by peroxosulfate (1 mM) and MCPBA (1 mM) at 40 °C

Substituent	$\text{p}K_{\text{A}}$	$k_{2\text{obs}}(\text{HSO}_5^-)^a$	$k_2^{\text{E}}(\text{HSO}_5^-)$	$k_{2\text{obs}}(\text{MCPBA})^b$	$k_2^{\text{E}}(\text{MCPBA})$
-H	11.5	4.2	540	—	—
<i>p</i> -SO ₃ ⁻	11.3	2.3	279	0.22	1205
<i>o</i> -CH ₃	12.0	0.49	180	—	—
<i>o</i> -CH(CH ₃) ₂	12.0	0.30	141	0.038	1030
<i>o</i> -Cl	11.7	0.14	35	—	—
<i>o</i> -OCH ₃	12.5	0.53	50	—	—
<i>o</i> -CO ₂ ⁻	13.2	0.052	35	—	—
<i>o</i> -SO ₃ ⁻	13.2	0.005	20	0.00072	250

^a pH 10.5. ^b pH 10.

This arises because the basicity of a nitrogen atom not only depends upon the electron density on the nitrogen atom but also on the relative stability of the cation formed from proton addition. Clearly, in the case of Methyl Orange, the electronic charge is extensively distributed across atoms in the molecule and delicately balanced between nitrogen atoms. Consequently, there may be sufficient difference in electron density among nitrogen atoms to lead to only one particular nitrogen being oxidised preferentially, *i.e.* the amino nitrogen, whereas the basicity of the other nitrogen may be higher because it forms a more stable cation.

Oxidation of tautomeric arylazonaphthol dye series

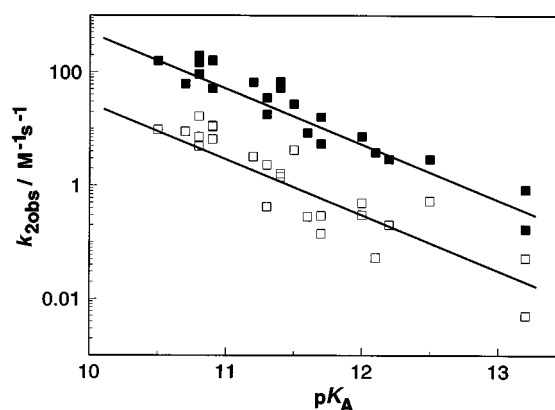
Unlike Methyl Orange, where bleach-induced decolourisation simply arises from a shift of the spectrum into the UV without destroying the azo linkage, oxidation of the tautomeric arylazonaphthol dyes results in chromophore destruction. Another difference was that in all cases, the observed rate constants exhibited maxima at pH values midway between the $\text{p}K_{\text{A}}$ values of the peracid and dye. Typical results have been illustrated earlier.⁴

The rate is described by eqn. (3), where the common anion,

$$-\text{d}[\text{D}]/\text{d}t = k_2^{\text{E}}[\text{D}^-][\text{PA}] \quad (3)$$

D^- , is the relevant dye species for arylazonaphthol dyes.⁴ Rate constants recorded at the maximum (pH 10.5) for the reaction of peroxosulfate (1 mM) with a range of arylazonaphthol dyes are given in Tables 1 and 2.

Also shown are some data for MCPBA (1 mM), measured at the maximum, pH 10. Examination of Tables 1 and 2 indicates that observed second-order rate constants for peroxosulfate generally follow the same trend⁴ with substituent as hypochlorite. This is illustrated in Fig. 4, which shows a good correlation with dye $\text{p}K_{\text{A}}$ over several orders of magnitude for both oxidants. This arises because the dye $\text{p}K_{\text{A}}$ controls the concentration of the reactive dye species—the common anion—and

**Fig. 4** Observed rate constants for the oxidation of substituted arylazonaphthol dyes as a function of dye $\text{p}K_{\text{A}}$ at 40 °C. (■ = 0.2 mM HOCl, pH 10 and □ = 1 mM HSO_5^- , pH 10.5).

indicates that the reaction mechanism of peracid and hypochlorite initiated oxidation of dyes is similar, namely, the active species are the respective undissociated oxidants.⁴ It also follows that any contribution from nucleophilic reaction of peroxosulfate with the hydrazone tautomer is negligible; a point further reinforced from observation of the comparatively low rate constants for nucleophilic reaction of a range of oxidants with the hydrazone molecule.⁴

Observed rate constants were converted to pH-independent electrophilic second-order rate constants, k_2^{E} , from speciation profiles and are also given in the Tables 1 and 2. Earlier, it was shown that the influence of substituents upon k_2^{E} for hypochlorite can be explained simply by their electron releasing or withdrawing capacities.⁴ However, examination of Tables 1 and 2 indicates that the rate constants for 1-arylozo-2-naphthol dyes are suppressed by *ortho*-substituents in the aryl ring more than can be explained by electronic effects alone. Although peroxosulfate is more bulky than HOCl, the main deviation occurs

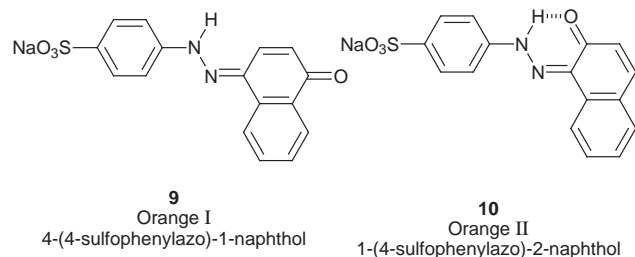
Table 3 Second-order rate constants ($\text{M}^{-1} \text{s}^{-1}$) for the oxidation of Orange I and Orange II by different oxidants at 25 °C

	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}	$k_2^{\text{N}^a}$	k_2^{E}
Orange I	—	1.0×10^5	—	1.5	—	1.4	3.0×10^{-1}	—
Orange II	—	1.3×10^5	—	1.8×10^2	—	4.2×10^2	4.5×10^{-2}	—

^a k_2^{N} is rate constant for nucleophilic attack by oxidant anion.

with the charged substituents, particularly with the sulfonate group. As peroxosulfate contains a nearby negative charge, the contrast with HOCl suggests that charge–charge interactions may be a key factor in reducing k_2^{E} . On the other hand, the presence of a sulfonate group in the naphthol ring adjacent to the azo functionality does not inhibit reactivity towards peroxosulfate. These observations are the reverse of those found for oxidation by the perhydroxyl anion.⁵ Indeed, the fact that a charged *ortho*-substituent in the aryl ring suppresses rates, but a charged sulfonate in the *ortho*-position of the naphthol ring does not, is suggestive of attack on the negatively charged nitrogen atom of the common anion adjacent to the aryl ring. A further point to note is that *ortho*-substituents in the aryl ring have a much more pronounced effect on suppressing rate constants in 2-arylaazo-1-naphthol dyes (Table 2). Indeed, the second-order rate constant $\log k_2^{\text{E}}$ correlates well with the $\text{p}K_{\text{A}}$ for such dyes, suggesting they are influenced by similar factors. The result parallels that for oxidation by the perhydroxyl anion⁵ and implicates direct charge–charge interactions due to influence of the substituent and/or steric overcrowding in the activated complex as the driving force for inhibition.

Identification of the nitrogen atom adjacent to the aryl ring as the reactive site is supported by: a) observations that, although *ortho*-substituents suppress $k_{2\text{obs}}$ (Tables 1 and 2) for reaction with MCPBA, k_2^{E} is much less influenced as it is uncharged^{||} and b) Orange II (**10**, $\text{p}K_{\text{A}} = 11.4$) produces higher rate constants, k_2^{E} (Table 3) with peracids than Orange I (**9**, $\text{p}K_{\text{A}}$

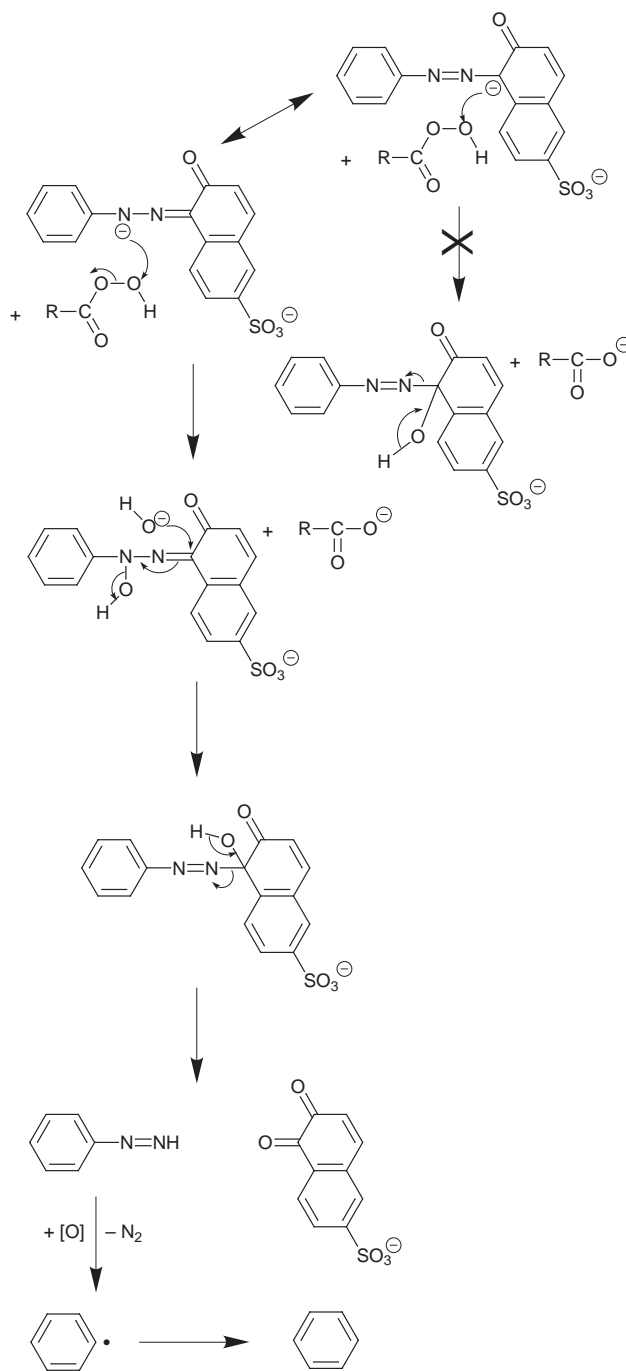


8.2) due to the higher basicity of the common anion, *i.e.* electron density on nitrogen adjacent to the aryl ring.**

Earlier investigations outlined the product analysis strategy and ways of distinguishing asymmetric cleavage of the dye from symmetric cleavage.^{5,6} Using dye **5** ($\text{X} = \text{H}$), the main reaction product with peroxosulfate was found to be benzene (GC-MS headspace analysis), with no evidence of formation of nitrobenzene, phenol or ammonia. Again, this parallels observations⁶ with HOCl that the dye is cleaved asymmetrically and a similar mechanism is envisaged, *i.e.* benzene is produced by hydrogen atom abstraction by phenyl radicals, formed from decomposition of a diazene intermediate. Two possible reaction pathways are outlined in Scheme 2, which differ simply in the

^{||} There is some scatter in the data; this arises from steric effects or simply because calculated rate constants depend strongly upon the accuracy of measured $\text{p}K_{\text{A}}$, *e.g.* if $\text{p}K_{\text{A}}$ is in error by 0.1, the calculated rate constant could change by a factor of two.

** The reverse is true for the perhydroxyl anion—and the magnitude of the effect is less—due to the electrophilic site on the dye being more distant.

**Scheme 2**

site of attack. As illustrated, one of the pathways—involving reaction at the nitrogen site—is strongly suggested in the light of kinetic evidence and its known nucleophilic properties.

An initial hydroxylated intermediate is postulated, which undergoes rearrangement prior to decomposition (in effect the hydroxyl group enters as OH^+ and leaves as OH^-) analogous to reaction with aqueous chlorine.⁶ We have been unable to detect the naphthoquinone reaction product due, we believe, to its

Table 4 Effect of 8-substituents on the second-order rate constants for oxidation of 2-aryloxy-1-naphthol dyes towards peroxosulfate (1 mM) at 40 °C

Naphthol Dye	8-Substituent	pK _A	k _{2obs} ^a	k ₂ ^E
-H	H	11.5	4.2	540
<i>p</i> -SO ₃ ⁻	H	11.3	2.3	270
<i>p</i> -SO ₃ ⁻	-NH ₂	12.7	0.3	595
<i>p</i> -SO ₃ ⁻	<i>N</i> -H-Triazine	11.4	2.6	290

^a pH 10.5.

further reaction with the peracid anion that is invariably present in excess under reaction conditions.†† However, the reaction with the peroxosulfate anion, SO₅²⁻, is less aggressive than with the perhydroxyl anion or chlorite anion as NMR evidence suggests less formate/acetate is produced and less extensive degradation of the naphthoquinone ring occurs.

Influence of substituents in the 8-position of 2-aryloxy-1-naphthol dyes towards oxidation with peroxosulfate at 40 °C

An examination has been made of the influence of introduction of an amino group into the 8-position of 2-aryloxy-1-naphthol dyes. Earlier,⁶ it was shown that this led to enhanced reactivity to both chlorine and hypochlorite as it created a new site to initiate dye degradation. However, this did not stimulate reactivity towards peracids; conversely, introduction of the amino group actually leads to protection against oxidation (Table 4). The observed rate constant towards peroxosulfate is reduced by approximately 10-fold upon introduction of an 8-amino group. The observed rate constants exhibit a maximum at a pH equal to the midpoint of the peracid and dye pK_A values. This is anticipated for electrophilic attack by undissociated peracid on the dye common anion and it demonstrates that

†† Naphthoquinone reaction products have been reported¹² in reaction with aqueous chlorine, *i.e.* under conditions where there is no excess nucleophilic oxidant.

oxidation of the amino group by peracids is relatively slow. Furthermore, examination of k₂^E (Table 4) shows that the influence of the amino group is primarily due to increasing the dye pK_A. It can also be seen that substitution of an amino group proton with a triazine group removes its protecting effect.

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