

# Kinetic investigations of the oxidation of arylazonaphthol dyes in hypochlorite solutions as a function of pH

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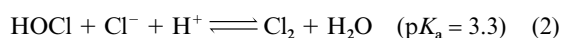
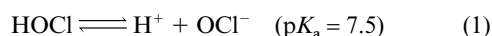
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A kinetic investigation has been made of the oxidation of 4-(4-sulfophenylazo)-1-naphthol (Orange I, **1**), 1-(4-sulfophenylazo)-2-naphthol (Orange II, **2**) and a series of substituted arylazonaphthol dyes in hypochlorite solution as a function of pH. Two chemically distinct reactions occur, one at high pH and the other in acid media (pH < 5), and both involve electrophilic oxidation of the nitrogen atom adjacent to the aryl ring. In acid media, aqueous chlorine reacts with the *N*-H group of the hydrazone tautomer ( $k_2 \approx 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ); in alkaline media, reaction of HOCl with the common anion is much faster ( $k_2 \approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ), due to delocalisation of the negative charge onto the nitrogen atom. *Ortho*- and *para*-substituents influence rate constants for both reactions, producing Hammett plots with slopes of  $-2$  and  $-0.5$  in acid and alkaline media, respectively. A mechanism for dye oxidation in alkaline media is proposed. Overall mechanistic pathways of dye degradation are extremely complex due to degradation of initial reaction products into small fragments. If an amino group is substituted into the dye, *e.g.* at the 8-position of 2-aryloxy-1-naphthol dyes, rate constants for oxidation by aqueous chlorine increase by 500-fold. This indicates that direct reaction with the amino group becomes a precursor to degradation; this pathway is eliminated if an electron-withdrawing triazine group is introduced into the amino group.

## Introduction

In certain countries, *e.g.* USA and Japan, hypochlorite is still the principal disinfectant for treatment of domestic water supplies, due to its low cost and its effectiveness in destroying bacteria at low levels ( $\sim 30 \mu\text{M}$ ).<sup>1</sup> However, contact with coloured garments in domestic washes can give rise to dye fading which, at low temperatures, is primarily a consequence of destruction of dye chromophores rather than breaking of the reactive link between dye and the fabric. An earlier publication<sup>2</sup> on oxidation of azo dyes by a range of oxidants addressed two main issues: (a) the reactive species responsible for initiating oxidation in alkaline media, and (b) the effect of substituents on both dye and oxidant in controlling oxidation. This investigation addresses the oxidation of azo dyes in solution by hypochlorite. The relevant equilibria to consider are<sup>3</sup> (1) and (2). It

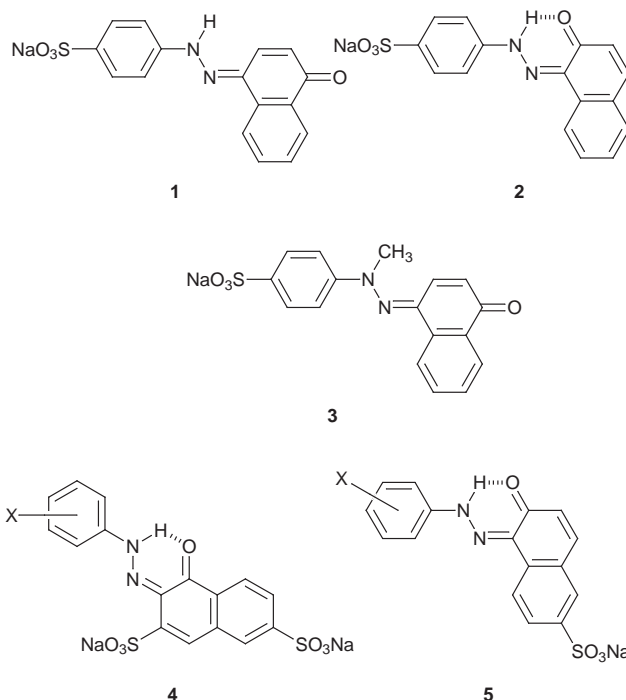


has been shown<sup>2</sup> that HOCl is the active species towards the dye common anion in neutral to alkaline media. However, in acid media equilibrium (2) results in formation of aqueous chlorine, a powerful electrophile, and acid solutions of hypochlorite are frequently used to generate chlorine or to chlorinate organic molecules.<sup>4</sup>

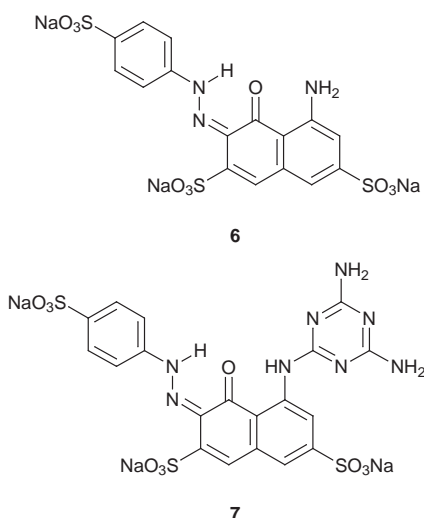
A number of papers have appeared<sup>1,5-7</sup> on the effects of hypochlorite on azo dyes but little is known with certainty about reaction mechanisms, especially in alkaline media. In particular, (a) there is a need to identify which of the three oxidant species, HOCl, ClO<sup>-</sup> and Cl<sub>2</sub> that coexist in equilibria in aqueous solution are reactive towards dyes. (b) Available literature data<sup>1,5-7</sup> is concerned with reactions at pH 7 only, which is generally not the optimum pH for reactivity in aqueous solution. (c) In many cases,<sup>5-7</sup> dye  $\text{p}K_a$  values are unavailable so that analyses are based upon observed rate constants and hence must be treated with extreme caution. (d) Isolation of products<sup>5</sup> was carried out at low pH, where they are more

stable, but kinetic studies were done at pH 7 and involve a different mechanism. (e) Oxidation systems tend to be highly sensitive to trace metal impurities, yet whilst this has been recognised<sup>8</sup> for peracids as oxidants, no previous study has taken steps to eliminate their influence in hypochlorite dye bleaching.

This work focusses on two aspects: (a) an examination of dye oxidation over a wide pH range, and (b) new scientific insights into the reaction mechanism. A series of dye structures have been examined, 4-(4-sulfophenylazo)-1-naphthol (Orange I, **1**), 1-(4-sulfophenylazo)-2-naphthol (Orange II, **2**) and *N*-methylated Orange I (**3**). This has been complemented by a study of two series of substituted dyes (**4** and **5**) having 1-aryloxy-2-



naphthol and 2-aryloxy-1-naphthol structures. These dyes exhibit azo-hydrazone tautomeric equilibria in aqueous solution and were specifically selected as they tend to be more susceptible to oxidation<sup>2</sup> than dyes that exist exclusively in the azo form. Finally, a study has been made of the influence of substituents in the 8-position of 2-aryloxy-1-naphthol dyes (6 and 7). The driving force for this is the observation that introduc-



tion of an amino group at the 8-position markedly reduces its chlorine fastness,<sup>7</sup> whereas an amino triazine group does not. Whilst acyl groups, *e.g.* acetyl and benzoyl, exert the same influence<sup>7</sup> as a triazine group, the latter was selected as it tends to be more commercially significant.

## Experimental

### Materials

Sodium hypochlorite was obtained from BDH in the form of a 12% active chlorine solution. Orange I ( $\lambda_{\max} = 477 \text{ nm}$ ,  $\epsilon = 2.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) was obtained from Fluka and Orange II ( $\lambda_{\max} = 484 \text{ nm}$ ,  $\epsilon = 1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) was obtained from Sigma, both dyes were purified by recrystallisation. The *N*-Me derivative of Orange I was supplied by Peter Gregory (Zeneca). All other dyes were synthesised using standard diazotisation and coupling methods,<sup>9</sup> followed by 'salting out' and purification by recrystallisation from water-ethanol mixtures.<sup>10</sup> Other chemicals used were potassium hydroxide (Fluka Puriss), nitric acid (BDH AnalaR) and disodium ethylenediaminetetraacetic acid (edta, BDH analytical concentrate). Solutions were prepared using water that was double-distilled from demineralised water using a Fisons 'Fi-Stream' 4BD Still.

### Kinetic studies

The rate law for the oxidation of dyes (D) by hypochlorite has been thoroughly examined elsewhere<sup>11</sup> and we concur with their findings. The reaction was shown to be first order in both [D] and [HOCl]; or in [Cl<sub>2</sub>] at low pH. Experimental details have been given previously.<sup>2</sup> Reactions were carried out under pseudo first-order conditions ([HOCl]:[D] ~ 10:1) typically using 200  $\mu\text{M}$  hypochlorite. Use of higher concentrations either gave immeasurably fast rates or gave complex kinetic behaviour with certain dyes, *i.e.* did not exhibit a first-order dependence in [D] over the whole reaction course. This was due to the reaction of primary products with excess oxidant, or autocatalysis by reaction intermediates. If the ratio [HOCl]:[D] was less than 10:1, good first-order plots could still be obtained—but only over the initial phases of the reaction—and sometimes this approach was used to determine rates where it was more experimentally convenient.

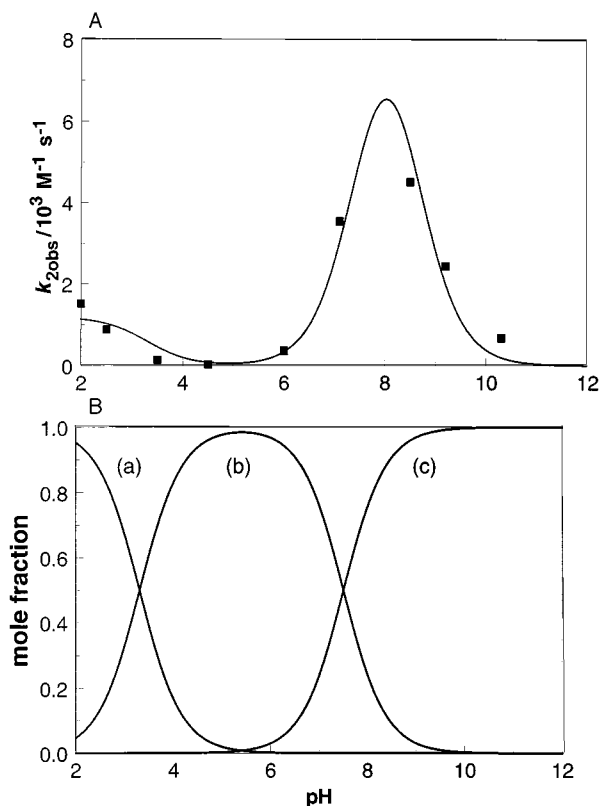
Kinetic measurements at pH 2 were carried out by monitoring the absorption maximum of the dye as a function of time. At other pH's, kinetic measurements were made<sup>2</sup> at the dye isosbestic points, to simplify data analysis. Initial absorbance (*A*) invariably obeyed the Beer-Lambert law over the experimental range of interest (up to  $10^{-4} \text{ M}$  dye). There was usually no interference from product absorbances. To eliminate trace metal impurities all experiments were conducted in the presence of 20  $\mu\text{M}$  edta. To preclude dye aggregation, addition of electrolyte was avoided. The pH was controlled in the absence of buffers by automatic addition of HNO<sub>3</sub> or KOH(aq) from a pH stat. Initial experiments were carried out at 15 °C to minimise loss of hypochlorite *via* self decomposition; it was found that oxidant self-decomposition was slow relative to dye oxidation and that reliable data could be achieved at temperatures as high as 40 °C. Generally, observed second order rate constants,  $k_{2\text{obs}}$ , for the oxidation of most dyes by hypochlorite exhibit broad maxima in alkaline media, in line with earlier observations.<sup>2</sup> Speciation profiles of both dye and oxidant were utilised to determine pH-independent rate constants ( $k_2$ ).

### Product analysis

Product analysis was found to be extremely complex due to the degradation of initial reaction products into small, highly water-soluble fragments. Although a number of analytical approaches were utilised, *e.g.* electrospray mass spectrometry, HPLC or TLC analyses, the following techniques yielded the most valuable mechanistic information.

Volatile organics were identified by GC and GC-mass spectral analysis *via* comparison of their retention times and mass spectral fragmentation patterns with standards. GC analyses were performed on buffered dye-bleach solutions using a Perkin Elmer HS101 headspace autosampler linked to an 8500 gas chromatograph fitted with a 2 m  $\times$  1/8" od stainless steel column packed with 20% Carbowax 20M on Chromosorb WHP 80-100 mesh. The instrument parameters were initial temperature of 80 °C, heated to 200 °C (held 4 min) at 5 °C min<sup>-1</sup>, sample temperature 60 °C, injector at 180 °C, detector at 250 °C; carrier gas helium at 25 psi head pressure. For GC-mass spectral analysis, headspace extractions were taken using a Supelco® Solid Phase Micro Extraction (SPME) sampler with a non-polar phase adsorbent. A pre-conditioned probe was exposed to dye-bleach headspace for 2 min, followed by desorption at 240 °C into a Hewlett Packard GCD (GC-mass selective detector) fitted with a 0.25 mm id 30 metre HP.5 column, 0.25  $\mu\text{m}$  film thickness. The instrument parameters were oven initial temperature 50 °C (held 0.5 min) to 230 °C (held 20 min) at 10 °C min<sup>-1</sup>. The detector was heated to 280 °C and the carrier gas flow (helium) was electronically controlled at 1.0 ml min<sup>-1</sup>.

Organic solvent extractable products were also analysed by GC-mass spectral analysis, using solutions extracted with diethyl ether (2 ml). The ether layer was removed and the volume of solvent reduced by air-drying. Two microlitres of concentrated ether extract was injected onto the column. The samples were simultaneously acquired using a Perkin Elmer ITD mass spectrometer and a Perkin Elmer GC with flame ionisation detection. The GC was operated using splitless injection with a BPX5 (non-polar, 25 m, 0.25) column and a temperature programme of 50 to 300 °C with a 10 °C min<sup>-1</sup> temperature ramp. The mass spectrometer was operated in electron impact mode collecting a mass range of 50-400 amu at a scan rate of 1 scan per second. Products of the reaction in alkaline media were found to be extremely soluble in water, with little extraction into organic solvents. Consequently, the strategy adopted was two-fold: (i) direct injection of aqueous solutions onto the column, and (ii) NMR investigations of extracts of freeze- or air-dried samples in deuterated DMSO and/or D<sub>2</sub>O. NMR spectra were obtained using a Bruker



**Fig. 1A** Variation of observed rate constant  $k_{2\text{obs}}$  for the oxidation of Orange I in hypochlorite solution at 25 °C as a function of pH. **B** Speciation profiles for hypochlorite as a function of pH. (a)  $\text{Cl}_2$ , (b)  $\text{HOCl}$ , (c)  $\text{ClO}^-$ .

DRX500 FTNMR spectrometer and products were identified using standards.

## Results and discussion

### Reactivity profile with pH

A plot of the observed second-order rate constants,  $k_{2\text{obs}}$ , for the oxidation of Orange I is given over a wide pH range at 25 °C in Fig. 1A. Corresponding plots for Orange II—or other dyes examined—are similar, the main exception being that the maxima are broader and centred at higher pH's due to higher dye  $\text{p}K_{\text{a}}$  values. The speciation profile of hypochlorite over this pH range—calculated from eqns. (1) and (2)—is depicted in Fig. 1B. The determination of reactivity over a wide pH profile is extremely important as it can be demonstrated that two separate reactions occur, involving different reactants and mechanisms. The observed maximum in  $k_{2\text{obs}}$  in alkaline media has been explained previously<sup>2</sup> and the reactants identified as  $\text{HOCl}$  and the dye common anion. The rate profile in Fig. 1A was simulated assuming reaction of  $\text{HOCl}$  with the dye common anion with  $k_2 = 1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and reaction of  $\text{Cl}_2(\text{aq})$  with undissociated dye,  $k_2 = 1.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and the fit is illustrated in Fig. 1A. As the reaction between ionised dye and hypochlorite is insignificant at pH 2, measurements of observed second order rate constants for the oxidation of dye by aqueous chlorine were recorded at this pH at 25 °C and converted to  $k_2$ . In the next section, attention is focussed upon oxidation by aqueous chlorine in acidic media.

### Reaction with chlorine in acidic media

In the following, it will be shown that the reaction in acidic media involves initial attack by the electrophilic chlorine molecule on the nitrogen atom containing the highest electron density, *i.e.* upon the  $N\text{-H}$  nitrogen atom of the hydrazone tautomer of the dye. The mechanism is likely to involve nucleo-

**Table 1** Rate constants for reaction of  $\text{Cl}_2$  and  $\text{HOCl}$  with dyes **1**, **2** and **3**

Dye	$\text{p}K_{\text{a}}$	$k_2(\text{Cl}_2)^a$	$k_2(\text{HOCl})$
Orange I ( <b>1</b> )	8.2	1200	110 000
<i>N</i> -Me derivative ( <b>3</b> )	—	90	0.05 <sup>b</sup>
Orange II ( <b>2</b> )	11.4	60	130 000

<sup>a</sup> Units of  $k_2 = \text{M}^{-1} \text{ s}^{-1}$ . <sup>b</sup> Reaction with  $\text{ClO}^-$ .

**Table 2** Influence of the substituent on the rate of reaction of  $\text{Cl}_2$  with substituted 1-arylo-2-naphthol dyes (**5**)

Dye substituent	Hammett $\sigma$	$\text{p}K_{\text{a}}$		$k_2^a$	
		<i>para</i>	<i>ortho</i>	<i>para</i>	<i>ortho</i>
-H	0	10.8	10.8	320	320
- $\text{CH}_3$	-0.17	10.9	11.4	830	97
-Cl	0.23	10.5	11.3	330	5
- $\text{OCH}_3$	-0.27	10.8	11.7	7600	150
- $\text{NO}_2$	0.78	10.7	11.6	5	0.30
- $\text{CO}_2\text{H}$	0.43	11.2	12.2	34	13
- $\text{SO}_3^-$	0.37	10.8	12.1	97	15

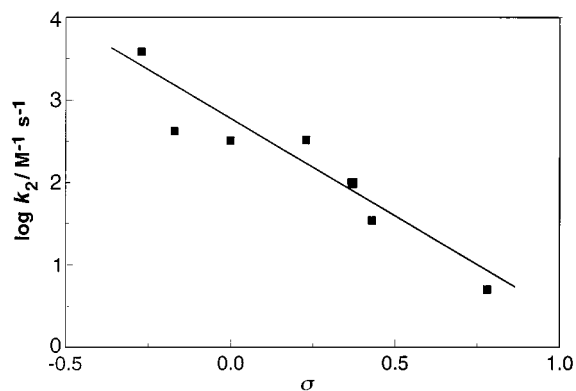
<sup>a</sup> Units of  $k_2 = \text{M}^{-1} \text{ s}^{-1}$ .

philic attack by the nitrogen lone-pair upon the chlorine molecule—resulting in heterolytic scission of the  $\text{Cl-Cl}$  bond—with expulsion of chloride and concomitant loss of a proton from the nitrogen atom. If this is correct, this mechanism should be eliminated by *N*-methylation. Although the *N*-Me derivative (**3**) is unreactive<sup>2</sup> at  $\text{pH} > 5$ , it does react with chlorine in acid media. However, it is an order of magnitude less reactive<sup>†</sup> than Orange I, supporting the view that the nitrogen atom of the  $N\text{-H}$  fragment of the hydrazone is the site for initial attack. The rate constants are compared in Table 1 and the results for Orange II are included. Orange II is a structural isomer of Orange I, they both exist exclusively in the hydrazone form but Orange II has a much higher  $\text{p}K_{\text{a}}$  (11.4 *cf.* 8.2). The rate constant is a factor of twenty lower than Orange I (Table 1). Evidently, the  $N\text{-H}$  bond is involved in strong intramolecular H-bonding in Orange II—resulting in the higher  $\text{p}K_{\text{a}}$ —which could lower its effectiveness as a nucleophile. Indeed, basicities can be measured from protonation equilibria in organic solvents and it can be shown<sup>10</sup> that Orange II is less basic than Orange I. This will be reflected in reduced electron density at the nitrogen atom and is likely to be a key factor in reducing the rate.

To provide confirmation that the lower susceptibility of Orange II towards  $\text{Cl}_2$  reflects its lower nucleophilicity, a number of *para*- and *ortho*-substituted 1-arylo-2-naphthol dyes were examined. The results are presented in Table 2. Inspection of Table 2 shows that the rate constants within the *para*-series of substituents vary with the nature of the substituent: electron-releasing substituents increasing the rate and electron-withdrawing substituents causing a corresponding decrease in rate.<sup>‡</sup> Indeed, rate constants for reaction of  $\text{Cl}_2$  with the *para*-substituted dyes exhibit a good correlation with the Hammett  $\sigma^{12}$  value and the plot is illustrated in Fig. 2. The slope of Fig. 2 is found to be  $-2$ . The negative sign is consistent with electrophilic reaction with aqueous chlorine and its magnitude suggests that attack occurs at a site close to the source of electronic perturbation, namely on the neighbouring nitrogen atom,

<sup>†</sup> The reaction that does occur yields an apple green product ( $\lambda_{\text{max}} = 448 \text{ nm}$ ). The hypsochromic shift and retention of colour, *i.e.* conjugation, suggests chlorination of the aryl ring, as occurs in *N,N*-dimethylaniline<sup>4</sup>).

<sup>‡</sup> Although examples of multi-substitution in the present work are limited, the effects of *ortho*- and *para*-substituents appear to be additive.



**Fig. 2** Variation of rate constant,  $k_2$ , for the oxidation of *para*-substituted arylazo-2-naphthol dyes with  $\text{Cl}_2$  as a function of the Hammett  $\sigma$  at 25 °C.

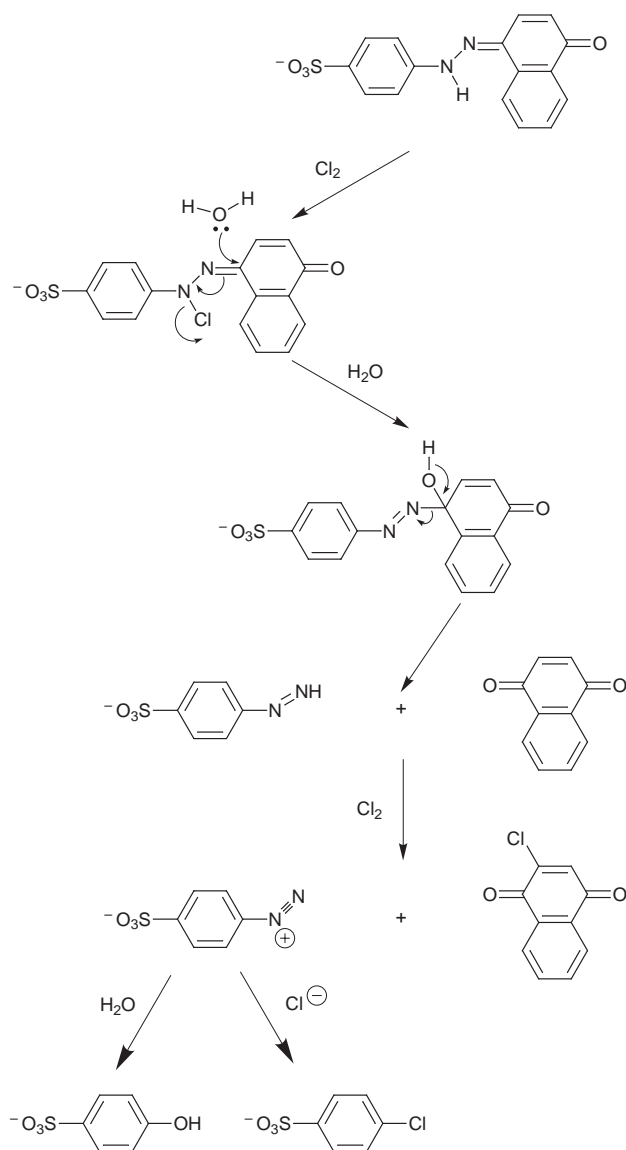
*i.e.* *N*-H site. Thus electron-withdrawing substituents tend to reduce electron density at the nitrogen atom, rendering the lone-pair less available for reaction with  $\text{Cl}_2$ . For the same reason, electron-releasing substituents increase the rate by increasing electron density upon the nitrogen.

*Ortho*-substituents produce a similar Hammett plot with slope  $-2$ , although more scatter is observed, perhaps due to some contribution from steric hindrance from the *ortho* group in the hydrazone tautomer. Nevertheless, there are two important facets, (i) the strong correlation with the Hammett  $\sigma$  suggests that electronic effects of *ortho* substituents predominate, and (ii) the lower rate constants observed for *ortho* substituents compared to corresponding *para* substituents, may be due to lower basicities as reflected in their higher  $\text{p}K_a$  values.

Earlier work<sup>5</sup> indicated that products of the reaction with Orange I are the diazonium salt, diazotised sulfanilic acid (originally used to synthesise Orange I) and 2-chloro-1,4-naphthoquinone. The overall stoichiometry of reaction was found to be  $2\text{Cl}_2 = 2\text{HOCl}$  per dye molecule. If these are the only products for dyes containing the hydrazone structural motif, then a plausible reaction scheme based upon kinetic and product analyses is illustrated in Scheme 1 and is adapted from that outlined earlier.<sup>5</sup> In essence,  $\text{Cl}_2$  delivers a chlorine atom as  $\text{Cl}^+$  which, upon subsequent hydrolysis, leaves as  $\text{Cl}^-$ , a net two-electron reduction of  $\text{Cl}_2$ . The second molecule of  $\text{Cl}_2$  may be utilised by rapid oxidation of the diazene intermediate to the diazonium salt by a similar mechanism; otherwise, the diazene will oxidise in air initially to form the diazene radical, which in turn will liberate nitrogen (see later, Scheme 3). Excess chlorine may be consumed by chlorination of the quinone ring. Further aspects of the mechanism will be discussed in the next section.

### Reaction with hypochlorite in alkaline media

Earlier,<sup>2</sup> it was shown that substituents affect the reactivity ( $k_{2\text{obs}}$ ) of  $\text{HOCl}$  towards dyes in the alkaline region by two different routes. The main effect is to increase the dye  $\text{p}K_a$  which, in turn, controls rates by reducing the equilibrium concentration of the reactive dye species, the common anion. Secondly, substituents influence the nucleophilicity of the common anion: electron-donating substituents increasing the reaction rate and electron-withdrawing substituents decreasing the reaction rate. The corresponding Hammett plot for reaction of undissociated  $\text{HOCl}$  with 1-arylaazo-2-naphthol dyes was illustrated earlier<sup>2</sup> and it was shown that both *ortho*- and *para*-substituents give comparable rates. This suggests that the rate is not influenced by steric or charge factors associated with the substituent and that the electronic effect of a given substituent on the anion (whether it be *para*- or *ortho*-) is similar. The slope of the Hammett plot is  $-0.5$ . The negative sign is anticipated as  $\text{HOCl}$  acts as an electrophile, but the magnitude of the slope deserves further discussion. Although the negative charge upon

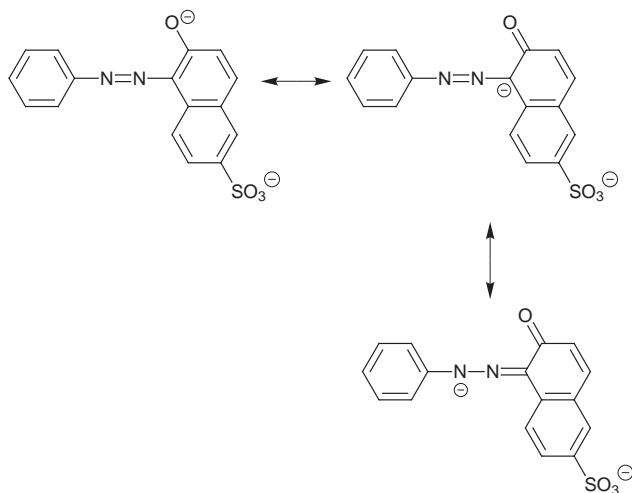


**Scheme 1** Postulated reaction pathway for oxidation by  $\text{Cl}_2$  in acid media.

the anion is mainly centred<sup>13</sup> upon the naphtholate oxygen atom, nevertheless, it is still extensively delocalised within the anion. Thus there are three potential sites (Scheme 2) for attack: (i) at the naphtholate oxygen atom, (ii) the imine carbon or (iii) the nitrogen atom ( $\text{N}^-$ ) and we have used a 1-arylaazo-2-naphthol dye for illustrative purposes. Of these options, the first may be eliminated as it is a less effective nucleophile<sup>9</sup> than simple naphtholates. Although attack could occur at the imine carbon with certain oxidants, it seems likely that electrophilic reaction with hypochlorite occurs at the nitrogen atom adjacent to the aryl ring for two reasons: (i) the presence of the lone pair makes the nitrogen atom a good nucleophile towards oxygen transfer oxidants and delocalisation of the negative charge will make  $\text{N}^-$  an even more powerful nucleophile, and (ii) the imine carbon<sup>§</sup> has been considered as the reactive centre<sup>10</sup> in oxidation by peracids but the nitrogen atom was identified as the reactive site.

Thus the site of attack is identical to that for reaction of dyes with  $\text{Cl}_2$  but the magnitude of the slope of the Hammett plot is lower ( $0.5$  *cf.*  $2$ ); however, substituents may have less influence as the active site is negatively charged and the gradient may be related to the probability of finding a negative charge upon the

<sup>§</sup> Indeed, the initial product formed *via* reaction at the imine carbon occurs as a step in Scheme 3.



**Scheme 2** Resonance structures, showing potential reactive sites.

nitrogen atom. Two potential reaction mechanisms could be considered (Scheme 3), involving symmetric or asymmetric cleavage of the azo dye, which can be distinguished by product analysis. Both mechanisms assume nucleophilic attack by  $N^-$  upon HOCl and, since this reaction occurs with peracids, it is further assumed that  $Cl^-$  is expelled as the leaving group.¶

The isolation and characterisation of reaction products is extremely complex and represents a major challenge, particularly as reaction intermediates tend to react further and as dye concentrations are low with oxidant, electrolyte and/or sequesterant levels relatively high. A number of research groups<sup>14–17</sup> have attempted to isolate dye reaction products but have met with varying degrees of success and there is some disagreement between workers.<sup>14–16</sup> They have tended to use high dye concentrations, but this leads to dye aggregation and formation of coupled products. Quantitative conversion into reaction products has not been achieved. Lack of mass balance reflects the complexity of the reaction—a multiplicity of reaction products have been observed<sup>16</sup> indicating that more than one mechanism may be operating simultaneously. The most successful studies have been done<sup>5,15</sup> at low pH and the problems tend to be more acute in neutral or alkaline media, where: (a) reaction intermediates/products tend to be unstable, and (b) there is a reservoir of conjugate oxidant which, although inert to native dye, may be reactive towards primary degradation products.

Nevertheless, we have been able to produce evidence in favour of one of the two illustrated reaction pathways. For example, using dye **5** ( $X = H$ ), benzene, chlorobenzene and traces of azobenzene were detected as volatile organics. Such species can be understood in terms of the mechanism involving asymmetric cleavage of the dye. On the other hand, there was no evidence of nitrobenzene formation *via* headspace GC–MS or GC–MS on solution extracts; nor was there evidence of ammonium ions (NMR). This argues against symmetrical cleavage of the dye in alkaline media.¶

To date we have been unable to detect the naphthoquinone, probably due to its involvement in further reaction. Indeed,

¶ We cannot completely rule out the possibility that the initial step in asymmetric cleavage may involve  $OH^-$  rather than  $Cl^-$  as leaving group since similar reaction products are anticipated.

¶ Support has been provided for Scheme 1 with dye **5** ( $X = H$ ) in acid media, *e.g.* observation of phenol, chlorobenzene with no indication of benzene. Also, reaction products dissolved completely in DMSO with only trace levels of acetate or formate, suggesting little breakdown of the naphthol ring. However, other data suggest the reaction may be more complicated, with detection of significant quantities of ammonium ions—indicating scission of the N–N bond—together with unidentified aromatics. Indeed, scission of the N–N bond is more likely in acidic media due to protonation of symmetrically cleaved intermediates.

**Table 3** Influence of 8-substitution on the reaction of  $Cl_2$  and HOCl with 2-arylamino-1-naphthol dyes (**4**) at 40 °C

Dye <b>4</b>	8-Substituent	$pK_a$	$k_2 (Cl_2)^a$	$k_2 (HOCl)$
$p-SO_3^-$	H	11.3	13	$1.3 \times 10^5$
$o-SO_3^-$	H	13.2	13	$9.6 \times 10^4$
$p-SO_3^-$	$NH_2$	12.7	8000	$\sim 5.0 \times 10^5$ <sup>b</sup>
$p-SO_3^-$	NH-Tr	11.4	10	$1.5 \times 10^5$

<sup>a</sup> Units of  $k_2 = M^{-1} s^{-1}$ . <sup>b</sup> There is additional reaction with  $-NH_2$  group of dye, having  $k_2 = 1.0 \times 10^2$ .

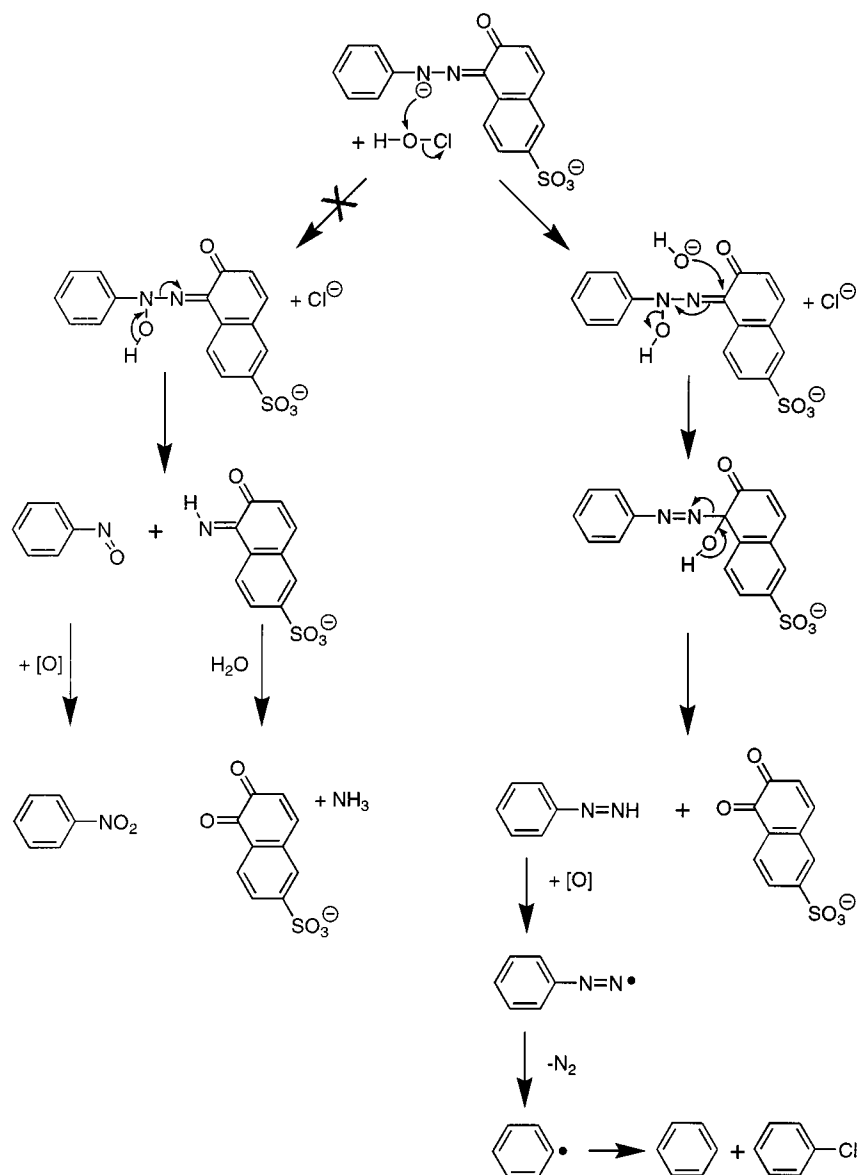
substitution of the dye **5** ( $X = H$ ) by dye **2** (Orange II) where there are no substituents upon the potential 1,2-naphthoquinone reaction product, failed to promote its detection by GC–MS. Indeed, examination of reaction products in DMSO or  $D_2O$  gave evidence of further breakdown products, *e.g.* acetate, formate, phthalic acid derivatives and other unidentified aromatic products. Obviously, initial reaction products are degraded further *via* a complex set of reaction pathways which are too complex to unravel, even if products were trapped or derivatised. Pathways involving radical species—formed from breakdown of diazene radicals—are implicated, together with reactions involving nucleophilic attack by  $ClO^-$  on potential quinone-like derivatives so that quantification of reaction products becomes an impossible task.

#### Influence of substituents in the 8-position of 2-arylamino-1-naphthol dyes

Finally, a number of 2-arylamino-1-naphthol dyes have been examined primarily to probe the influence of substituents in the 8-position. Such dyes behave similarly to their 1-arylamino-2-naphthol counterparts in that (i) observed rates in alkaline media are suppressed as the dye  $pK_a$  is raised,<sup>2</sup> and (ii) rate constants in acid media are similar to *ortho*-sulfonated 1-arylamino-2-naphthol derivatives (Table 2). Measured rate constants for reaction with  $Cl_2$  and HOCl are given in Table 3. However, a notable exception occurs when an amino group is substituted at the 8-position (**6**): in this case the rate is greatly enhanced with aqueous chlorine (acidic media). The high rate suggests that (i) chlorination now occurs at the amino nitrogen atom and it evidently leads to rapid degradation of the dye, and (ii) the amino group is a much better nucleophile than the N–H of a hydrazone. A further difference is that an additional electrophilic reaction occurs in the neutral pH region, with  $k_2 = 100 M^{-1} s^{-1}$ ; this reaction is far less effective than with the nitrogen atom in the ionised dye. This observation suggests that HOCl can also oxidise the amino group, leading to rapid degradation and the observed rate profile can be fitted with rate constants given in Table 3. Electrophilic reaction of the amino group does not occur with peracids;<sup>10</sup> this suggests that reaction with HOCl proceeds *via* *N*-chlorination, with expulsion of  $OH^-$ . Both these reactions are eliminated if one of the protons of the amino group is substituted by a triazine group (**7**). The reactivity returns to approximately that for the non-8-substituted dye (Table 3). Evidently, incorporation of the electron-withdrawing triazine group deactivates the amino group—by reducing its basicity—to attack by both  $Cl_2$  and HOCl; however, we cannot rule out the possibility in this particular case that two amino protons are required in the degradation step. This finding is corroborated by observations that an acetyl or benzoyl group has the same effect<sup>7</sup> as a triazine group.

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**Scheme 3** Potential reaction pathways for oxidation by HOCl in alkaline media.

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