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Interaction of oxidative bleach containing detergents with dyes. Part 2: preparation and resistance of hydrazo dyes, derived from aryl diazonium salts and 1-hydroxynaphthalene-4-sulphonic acid, to oxidation by hydrogen peroxide and *meta*-chloroperbenzoic acid

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Abstract

Several variously substituted anilines were diazotised and coupled onto 1-hydroxy naphthalene-4-sulphonic acid. The resulting dyes were treated separately with hydrogen peroxide and *meta*-chloroperbenzoic acid, at 60 °C and pH 9.8, in order to mimic the active bleaching species present in modern detergents, and pseudo first order rate constants for dye destruction were determined. Under the alkaline conditions employed the dyes were largely deprotonated and the pK_a value of each was determined. The peracid was found to be much more effective than hydrogen peroxide in bringing about chromophore destruction: the free peracid, not the derived anion, being the active bleaching species. The introduction of either *ortho*- or *para*- electron withdrawing groups into the diazo component resulted in reduced rates of dye destruction, whereas an electron donating methoxy group in the *para*-position caused an increase in rate. Electron donating *ortho*- alkyl groups had minimal effect on stability towards the peracid.

Keywords: Peroxide; Peracid; Dyes; Azo; Hydrazone; Oxidative bleaching

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1. Introduction

The azo/hydrazo system is the single most widely encountered class of chromophore used in textile dyes [1]. The bulk of direct and reactive greenish, mid and golden yellow, orange, red and violet dyes are either azo or hydrazo derivatives whereas most water soluble navies comprise both an azo and a hydrazo function.

In Part 1 [2] we reported the preparation and resistance to degradation, by peroxide and *meta*-chloroperbenzoic acid, of a series of azo dyes, together with the effect of structural changes on the ease of chromophore degradation by these reagents. We now describe the preparation of a series of related hydrazo dyes and their destruction by peroxide and peracid.

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The continuing introduction by the detergent industry of ever more powerful detergents has placed increasing demands on dyestuff manufacturers to produce dyes with improved resistance to cleansing agents, such as hydrogen peroxide and peracids, components generated by many modern detergents [3]. As part of our continuing study into the interaction of oxidative-bleach containing detergents with dyestuffs, several hydrazo derivatives were prepared, by coupling substituted phenyl diazonium chlorides onto 1-hydroxynaphthalene-4-sulphonic acid, and their rates of degradation, both by peroxide and by *meta*-chloroperbenzoic acid, were determined. Substitution in the diazo component was varied in order to define the structural features associated with good fastness to oxidative-bleaching.

2. Experimental

Elemental microanalyses for carbon, hydrogen, nitrogen and sulphur were carried out on a Carlo Erba 1108 elemental analyzer, at the Department of Chemistry, UMIST. Mass spectra were recorded by two techniques, FAB (fast atom bombardment) and MALDI (matrix assisted laser desorption/ionization). ^{1}H nuclear resonance spectroscopy was conducted using a Bruker DPX300 (300 MHz) spectrophotometer equipped with a proton carbon, z gradient, dual probe with an automatic sample changer. Ultraviolet/visible spectra were recorded using a Phillips PU 8700 spectrophotometer and aqueous solutions of dyes. Reflectance spectra on dyed fabrics were made on a Datacolor Spectraflash 600 spectrophotometer under a D65 lamp.

2.1. Preparation of dyes

The dyes were prepared according to Fig. 1. Substituted phenyl diazonium chlorides were prepared by diazotising the appropriate aniline with nitrous acid in dilute aqueous hydrochloric acid and coupling, in situ, onto 1-hydroxynaphthalene-4-sulphonic acid.

The preparation of 1-hydroxy-2-(2-sulphophenylazo-)naphthalene-4-sulphonic acid was typical. A solution of 1-hydroxynaphthalene-4-sulphonic acid (4.92 g, 0.02 mol, 247.2 gmol^{-1}) in water (50 cm^3) was added dropwise to 2-sulphobenzene diazonium chloride (0.02 mol), prepared as described in Part 1. The mixture was stirred at 0 °C to 5 °C and the pH was maintained at 3 to 4 by the addition of sodium bicarbonate. After 60 min. thin layer chromatography indicated that the reaction was essentially complete; the pH was raised to 6 to give 1-hydroxy-2-(2-sulphophenylazo-)naphthalene-4-sulfonic acid as an orange solid, isolated by filtration. Yield = 8.0 g (88%).

Other dyes prepared by a similar procedure, but using alternative diazo components in place of orthanilic acid, are listed in Table 1.

2.2. Characterisation of dyes

All the dyes were essentially pure organically, as judged by TLC and HPLC, but contained varying amounts of water and inorganic salts. The effective agent contents were determined by titration against a freshly standardized solution of titanous chloride [2,4].

2.2.1. Determination of the wavelength of maximum absorbance, λ_{max}, and molar extinction coefficient, ϵ_{max}, of dyes

Ultraviolet/visible spectra were recorded using a Philips 8720 Scanning Spectrophotometer as described in Part 1 [2].

Table 1
Dyes synthesised to investigate oxidative bleaching

Dye	Substituent X (Fig. 1)
1	H
2	*p*-nitro
3	*p*-methoxy
4	2,4,6-trichloro
5	*o*-sulfo
6	*o*-bromo
7	*o*-iodo
8	*o*-chloro
9	*o*-fluoro
10	*o*-methyl
11	*o*-isopropyl
12	*o*-trifluoro-methyl

2.3. Determination of dye pK_a values

The determination of dissociation constants by ultra-violet or visible spectrophotometry depends upon the direct determination of the ratio of molecular (neutral) species to ionised species in a series of non-absorbing buffer solutions of known pH [5]. Hence, absorption spectra of the two species involved in the equilibrium were first obtained. A wavelength was then chosen corresponding to a peak in absorbance of only one of the species being studied; the absorbance of this peak was then measured over a pH range encompassing an approximate pK_a value as determined by a 'sighting' reading (as described below).

A sample of a given dye (0.1 g) was dissolved in water (100 cm^3): 20 cm^3 of this solution was made up to 100 cm^3 (i.e. 0.2 g l^{-1}). Stock solutions of 0.1 M phosphate, borate and carbonate buffers, suitable non-absorbing species, as described by Albert and Serjeant [6], were made by dissolving 0.05 mol of potassium di-hydrogen phosphate, sodium tetraborate and sodium hydrogen carbonate respectively in 500 cm^3 H_2O. In addition, 0.01 M $HCl_{(aq)}$ and 0.01 M $NaOH_{(aq)}$ stock solutions were prepared. Using the buffer stock solutions, 100 cm^3 of 0.01 M buffers were prepared at 0.2 pH unit intervals, from pH 6.40 to 10.00 (±0.01) using either dilute $HCl_{(aq)}$ and dilute $NaOH_{(aq)}$.

After making an approximate estimate of the pK_a of a given dye by observing the colour change of the solution as the pH was slowly increased, 12 buffers were chosen (6 above the pK_a estimate and 6 below) and 10 cm^3 of each buffer pipetted into a separate vial. Two further vials containing 10 cm^3 0.01M $HCl_{(aq)}$ and 10 cm^3 0.01M $NaOH_{(aq)}$ were also prepared. To each of the 14 vials was added 2 cm^3 of the dye stock solution (0.2 g l^{-1}). The absorbance of each sample was measured at the wavelength (λ_A) corresponding to the peak present in acidic, and not basic solution, (usually 350–380 nm).

2.4. Oxidative degradation of dyes

The unsubstituted parent, Dye 1 (Table 1), was treated separately with a large excess of both

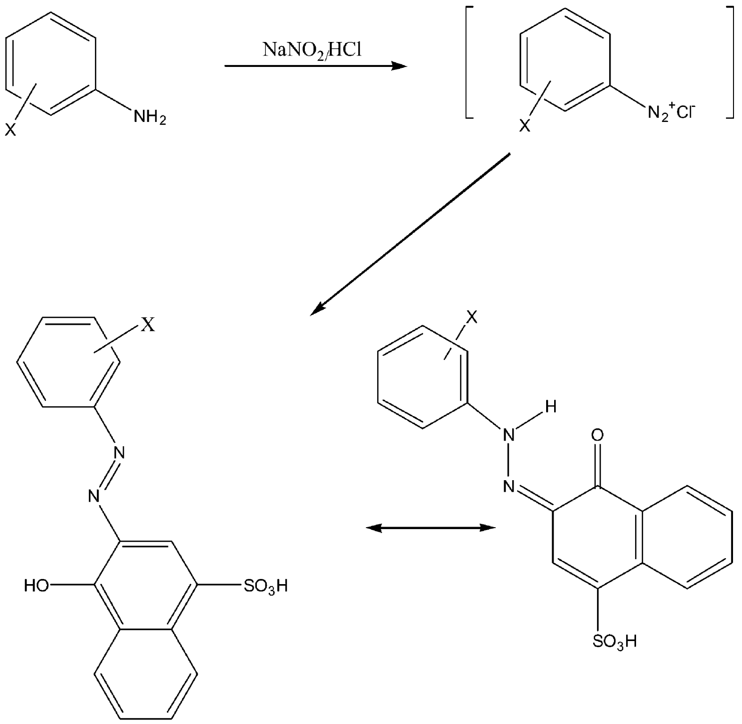

Fig. 1. Preparation of dyes.

meta-chloroperbenzoic acid and of hydrogen peroxide. The former was chosen as a more convenient model for the peracetic acid produced in the ISO 105:CO9 (UK-TO) test [7,8].

The pH was maintained at 9.80±0.02 with a carbonate buffer and the temperature at 60 °C±0.5 °C with a thermostatically controlled water-bath. A dye concentration was 1×10^{-4} M was selected. The equivalent of 1 g l^{-1} ethylene-diamine-tetra-acetic acid (EDTA) was added to eliminate the effects of metal ions. Samples were taken from each reaction at regular intervals and excess peracid quenched with sodium thiosulfate solution. The optical density of each sample was recorded.

Table 2
Effective agent contents of dyes, by titration against titanous chloride

Dye	Mol(In)/ g mol^{-1}	Molecular mass/g mol^{-1}	EA strength/%
1	391.5	350.0	89.4
2	508.6	373.3	73.4
3	453.4	380.4	83.9
4	589.2	453.7	77.0
5	580.0	452.4	78.0
6	503.2	429.2	85.3
7	609.0	476.2	78.2
8	440.3	384.8	87.4
9	403.4	368.3	91.3
10	386.0	364.4	94.4
11	595.4	392.4	65.9
12	452.8	418.0	92.3

3. Results and discussion

The hydrazo derivatives of the present study were prepared by coupling variously substituted phenyldiazonium chlorides onto 1-hydroxy-naphthalene-4-sulphonic acid. All the dyes were prepared in high yield: in all cases the dyes were readily collected by filtration, some after salting out with common salt. They were essentially pure organically, as judged by HPLC and TLC, but contained inorganic electrolyte and moisture. The molecular weights and effective agent (EA) strengths of the dyes are listed in Table 2

Adherence to Beer Lambert's Law was checked by ensuring that absorbance was proportional to concentration, see Fig. 2 for Dye 1. The dyes were generally orange in shade with absorption maxima in the range 460–490 nm, except for the red nitro derivative, λ_{max} 534 nm. Details are shown in Table 3.

Having recorded the optical density of each dye at various times after the addition of hydrogen peroxide or *meta*-chloroperbenzoic acid (*m*.CPBA), a graph was plotted of Absorption against Time, from which the half life of the dye, under these respective conditions, was calculated. Fig. 3 shows data for the degradation of Dye 1 in *m*.PCBA. Apparent rate constants for the destruction of Dye 1 by *meta*-chloroperbenzoic acid hydrogen peroxide were also determined. Thus a graph of ln[$Abs_{initial}$/ Abs_{time}] versus time gave a straight line of slope equal to the rate constant: Fig. 4 shows these data

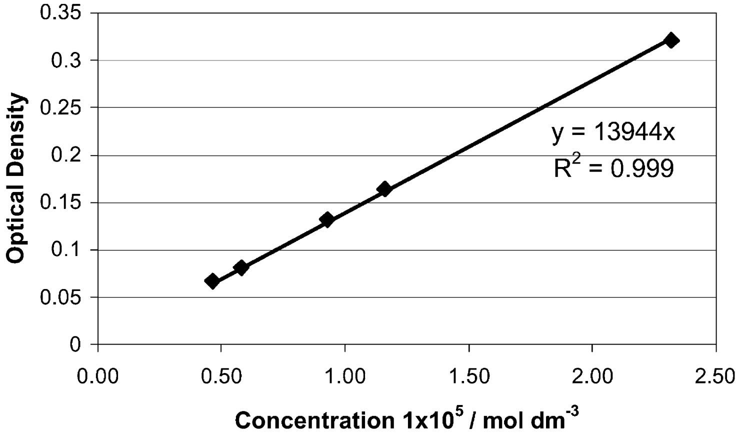

Fig. 2. Concentration versus optical density (at 453.6 nm) of Dye 1.

for the destruction of Dye 1 by *meta*-chloroperbenzoic acid. It can be seen from Table 4 that the *meta*-chloroperbenzoic acid is much more effective in destroying colour than is hydrogen peroxide

Earlier studies [2] had shown that free *meta*-chloroperbenzoic acid (a highly electrophilic reagent) and not the anionic perbenzoate, is the active bleaching species responsible for the destruction of 1-amino-2-arylazonaphthalene-4-sulphonic acids. A study of the rates of oxidation of the hydrazones of the present study is further complicated by the fact that they are capable of undergoing loss of a proton, under sufficiently alkaline conditions. Dyes derived from a naphthol coupling component exist essentially as the hydrazo tautomer at low pH values; as the pH increases, de-protonation occurs as shown (Fig. 5). As the active dye species is involved in a pH-dependent equilibrium, the observed rate depends on the concentration of dissociated dye and hence on the pK_a of the dye. Corrections must therefore be applied when comparing the rates of destruction of different dyes at a given pH. The rate constant ($k_{observed}$) must be adjusted (becomes k_{true}) to take account of the actual concentration of active dye species present. It was therefore necessary to determine the pK_a of all the dyes.

Using the absorbance of a series of buffered dye solutions at the wavelength of maximum absorbance of the protonated species a value of the pK_a was of each dye was calculated using Eq. (1) [5], where A represents the absorbance at λ_A at a particular pH, $A_{[base]}$ the absorbance at the same

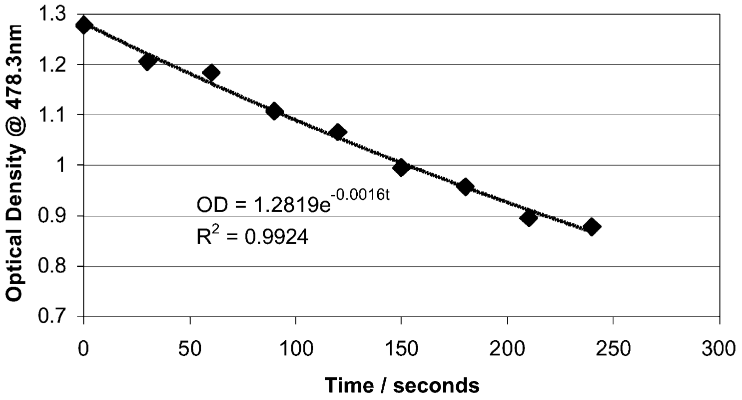

Fig. 3. Degradation of Dye 1 using mCPBA. Half-life = 432 seconds [Dye 1, X = H; $C_{16}H_{11}N_2SO_4Na$ M.W. = 350 g mol^{-1}].

Table 3
Absorption characteristics of dyes

Dye	Substituent	λ_{max}/nm	ϵ_{max}/m^2 mol^{-1}
1	H	479.0	15,400
2	*p*-nitro	533.6	15,100
3	*p*-methoxy	482.3	20,500
4	2,4,6-trichloro	466.0	14,300
5	*o*-sulfo	473.3	15,000
6	*o*-bromo	486.3	19,500
7	*o*-iodo	484.6	18,000
8	*o*-chloro	486.7	17,300
9	*o*-fluoro	487.4	20,200
10	*o*-methyl	472.7	17,500
11	*o*-isopropyl	461.7	11,000
12	*o*-trifluoro-methyl	479.7	18,100

wavelength in 0.01M $NaOH_{(aq)}$ and $A_{[acid]}$ the absorbance in 0.01M $HCl_{(aq)}$. An average pK_a and the associated standard deviation were then calculated from at least 8 pH values. The results are shown in Table 5.

$$pK_a = pH + \log\frac{A - A[\text{base}]}{A[\text{acid}] - A} \tag{1}$$

Substituents in the diazo component exert a dramatic effect on the pK_a of the resulting hydrazone dye and its resistance to oxidative degradation by peracids. These might operate by both steric and electronic effects. For substituents in the para position the effects would be expected to be exclusively electronic. For example, the introduction of a powerfully electron withdrawing nitro group into the para position leads, as expected, to a reduction in the pK_a of the hydrazone dye, i.e. pK_a 7.91 versus 8.26 for the unsubstituted material. Less obviously, a para methoxy group also causes a drop in the pK_a (8.13); presumably the net result of electron withdrawing inductive and electron donating electromeric effects. If the peracid destroys colour by electrophilic attack on dye, as was demonstrated in the case of related dyes derived from 1-aminonaphthalene-4-sulphonic acid [2], it seems reasonable to postulate that the active species undergoing attack is the deprotonated form of the dye: this is in keeping with other workers' findings [13]. However, of the dyes prepared, the methoxy derivative, Dye 3, is by far the most sensitive to destruction by peracid (see Fig. 6), possibly by virtue of the lone electron pair on the methoxy group leading to enhanced susceptibility of the deprotonated dye to electrophilic attack by peracid.

In the case of substituents *ortho*- to the hydrazo group it is necessary to consider steric, as well as electronic, effects. For example the introduction of a highly electron withdrawing group, such as trifluoromethyl or fluorine, causes an expected reduction in the pK_a of the hydrazo dye, to pK_a 7.91 and 8.00 respectively, versus 8.26 for the unsubstituted Dye 1, see Table 5. Other less powerful electron withdrawing substituents, such as chlorine, bromine and iodine, lead to an increase in pK_a, 8.63, 8.54 and 8.51 respectively. These are sterically more demanding than the fluorine atom but probably less so than the trifluoromethyl group. The largest increase in pK_a is observed

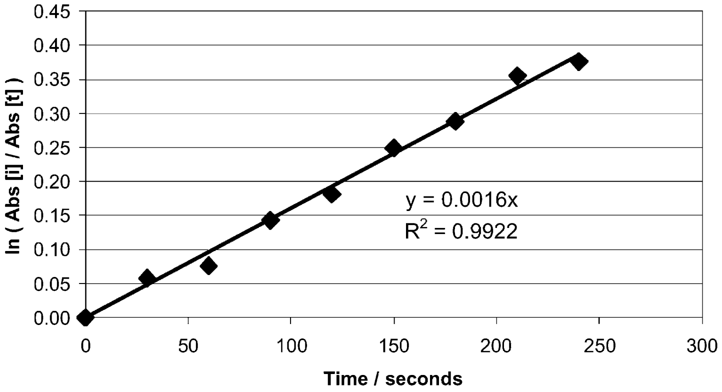

Fig. 4. Degradation of Dye 1 by *meta*-chloroperbenzoic acid.

Table 4
Rates of oxidative destruction of Dye 1 using hydrogen peroxide and mCPBA

Dye	Oxidising species	Rate constant k/s^{-1}
1	mCPBA	0.00161
1	H_2O_2	0

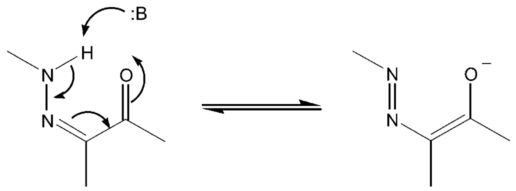

Fig. 5. Hydrazone ionisation at increased pH.

when a sulfonic acid residue, Dye 5, is incorporated in the diazo component, *ortho* to the hydrazo group. Aryl sulphonic acids are strong acids [9] and under alkaline conditions will exist essentially in the ionized sulphonate form. The negative charge associated with this group would be exected to hinder removal of an additional proton from the nearby nitrogen of the hydrazone, leading to an increase in pK_a.

Introduction of an *ortho*-methyl or *ortho*-isopropyl group, Dyes 10 and 11, both of which are weakly electron-donating, but sterically bulky, result in a significant increase in pK_a, to 8.92 and 8.64 respectively.

Table 5
Experimentally determined pK_a values of dyes

Dye		Wavelength/nm	pK_a	Std deviation
1	aniline	363.4	8.26	0.03
2	*p*-nitro	370.1	7.91	0.15
3	*p*-methoxy	360.9	8.13	0.04
4	2,4,6-trichloro	379.9	6.90	0.04
5	*o*-sulfo	375.1	9.40	0.06
6	*o*-bromo	359.7	8.54	0.11
7	*o*-iodo	359.2	8.51	0.12
8	*o*-chloro	370.2	8.63	0.03
9	*o*-fluoro	366.9	8.00	0.02
10	*o*-methyl	368.4	8.92	0.02
11	*o*-isopropyl	368.4	8.64	0.06
12	*o*-trifluoro-methyl	362.1	7.91	0.09

Table 6
Ionisation properties of dyes based on 2-arylazo-1-naphthol-4-sulfonic acid at pH 9.8

		pK_a	pK_a−9.80	% ionised
1	(H)	8.26	−1.54	97.2
2	(*p*-nitro)	7.91	−1.89	98.7
3	(*p*-methoxy)	8.63	−1.17	93.7
4	(2,4,6-trichloro)	6.90	−2.90	99.9
5	(*o*-sulfo)	9.40	−0.40	71.5
6	(*o*-bromo)	8.54	−1.26	94.8
7	(*o*-iodo)	8.51	−1.29	95.1
8	(*o*-chloro)	8.63	−1.17	93.7
9	(*o*-fluoro)	8.00	−1.80	98.4
10	(*o*-methyl)	8.92	−0.88	88.4
11	(*o*-isopropyl)	8.64	−1.16	93.5
12	(*o*-trifluoro methyl)	7.91	−1.89	98.7

3.1. Influence of dye pK_a on apparent rate constants

The equation linking pK_a to the proportion of ionised dye present in solution (% ionised) at pH 9.8 is given in Eq. (2). The extent of ionisation for each dye at this pH, is listed in Table 6 and demonstrates that treatment with peracid is carried out at a pH (9.8) where the dyes exist almost exclusively in de-protonated, anionic, form. Consequently, a correction needs to be applied to the observed rate constants, k_{observed}, taking into account the extent of de-protonation of dye (assuming that it is the de-protonated dye which is the active species undergoing electrophilic attack by peracid). Fig. 6 depicts the true rate constants (k_{true}) and observed rate constants (k_{observed}) for the destruction of the de-protonated forms of Dyes 1 to 12 by *m*-chloroperbenzoic acid. The difference in true and observed reaction rates is

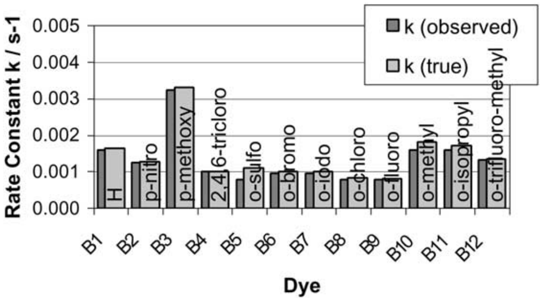

Fig. 6. Rates (observed and true) of oxidative degradation of Dyes 1 to 12 by mCPBA.

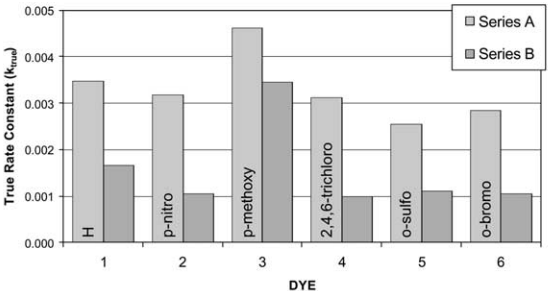

Fig. 7. Rate constants for oxidative degradation of 2-arylazonaphthylamines (Series A) and 2-arylazonaphthols (Series B) by *meta*-chloroperbenzoic acid.

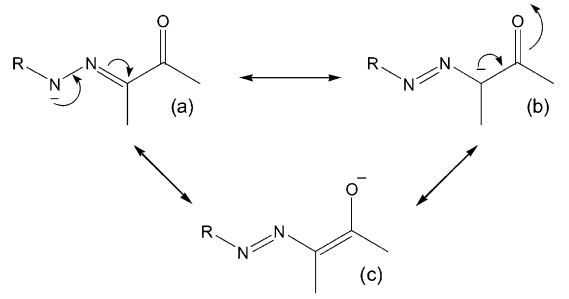

Fig. 8. Resonance structures of hydrazone anion.

small, however the greater pK_a of the *ortho*-sulfo derivative means that, although experimental observations suggest it is the most resistant to oxidation, the dissociated structure is more susceptible to peracid than those dyes containing a halogen residue.

$$\%\text{Ionised} = \frac{100}{1 + 10^{(\mathrm{p}K_a - 9.8)}} \quad (2)$$

It is interesting to compare the relative rates at which dyes derived from 1-hydroxynaphthalene-4-sulphonic acid and 1-aminonaphthalene-4-sulphonic acid are destroyed by *meta*-chloroperbenzoic acid. Without exception, dyes of the present study, which are derived from a naphthol coupling component, are more resistant to attack by *meta*-chloroperbenzoic acid than the analogous naphthylamine derivatives described in Part 1 (Fig. 7). This might seem at variance with the concept of a dye behaving nucleophilically towards peracid, as the 2-arylazo-1-naphthol dyes are almost completely ionised at the reaction pH and therefore might be expected to be particularly nucleophilic ini nature. However ionisation of the dyes based on 2-arylazo-1-naphthol produces three possible resonance forms (Fig. 8). Structure 8(c) will be the major contributor, oxygen being the most electronegative element and therefore more capable of supporting a negative charge. Phenols are known to be stable in the presence of peracid; indeed, in combination with ferrous sulphate this reagent is used synthetically to bring about the oxidation of aryl compounds to phenols [10]. It seems logical therefore that, by analogy with the known stability of phenols, the naphthoxide component, 8(c), will not be readily susceptible to attack by peracid. The most likely site for peracid attack on the 2-arylazo-1-naphthol system is the nitrogen closest to the diazo component as substituents on this ring can affect the rate of oxidation both electronically and sterically. This is consistent with the known ability of peracids to oxidize azo compounds to azoxy derivatives [11]. Thus electron withdrawing groups such as *para*-nitro would be expected to reduce the amount of electronic charge present at the reactive site, thereby reducing the rate of oxidation. Additionally steric effects appear to be operative, despite nitro groups being very deactivating, the introduction of a much less powerfully electron withdrawing/activating chlorine atom at a position *ortho* to the hydrazone nitrogen results in a dye that is less sensitive to peracid degradation. In the case case of the corresponding dyes derived from 1-aminonaphthalene-4-sulphonic acid a similar mode of attack by peracid would involve attack of peracid at the azo linkage. However, it is feasible that reaction of peracid with such aminoazo dyes also takes place at the primary amino group, since peracids have been reported to react with primary amines [12]. Thus both series of dyes, those derived from aminonaphthalene and naphthol coupling components probably undergo attack by peracid at the azo linkage: additionally the former class can also be attacked at the primary amino, resulting in less overall stability to peracids.

4. Conclusions

1. Twelve dyes were prepared by coupling variously substituted phenyldiazonium chlorides onto 1-hydroxynaphthalene-4-sulphonic acid.
2. The molar extinction coefficients were generally of the order of 15,000 to 20,000 m^2 mol^{-1} but introduction of bulky *ortho* substituents such as 2,6-dichloro and *ortho*-*iso*-propyl resulted in a reduction in extinction coefficient (chromophoric strength).
3. All of the dyes, with the exception of the para nitro derivative, Dye 2, were orange in shade, with λ_{max} values in the range 460 to 490 nm: Dye 2 was a bluish red λ_{max} 534 nm.

4. Under the alkaline conditions employed (pH 9.8) for reaction with *meta*-chloroperbenzoic acid or hydrogen peroxide, the dyes were largely deprotonated: the most acidic being Dye 4, derived from 2,4,6-trichloroaniline and the least acidic being that derived from 2-aminobenzene sulphonic acid (Dye 5).
5. All of the dyes underwent facile destruction by *meta*-chloroperbenzoic acid but were much more resistant to attack by hydrogen peroxide. Dyes 8 and 9, derived from *ortho*-chloroanline and *ortho*-fluoroaniline were the most resisitant to attack by the peracid. The beneficial effect of an *ortho*- halogen in conferring increased resistance to peracid appears not to have been noted previously.
6. Dyes derived from 1-aminonaphthalene-4-sulphonic acid as coupling component less stable to *meta*-chloroperbenzoic acid than the corresponding dyes derived from naphthol coupling components. This may arise because the former series possess two sites which are attacked, the azo and amino groups, whereas the latter dyes are attacked only at the azo group.

Acknowledgements

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