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Interaction of oxidative bleach containing detergents with dyes. Part 1: Preparation and resistance of 1-amino-2-arylazonaphthalene-4-sulphonic acid dyes to hydrogen peroxide and *m*-chloroperbenzoic acid

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Abstract

A series of red water soluble azo dyes were prepared by coupling variously substituted phenyldiazonium salts onto 1-aminonaphthalene-4-sulphonic acid. In order to mimic the conditions experienced during domestic laundering, in presence of an oxidative-bleach containing detergent, the dyes were then subjected, separately, to treatment with *m*-chloroperbenzoic acid and with hydrogen peroxide. Experiments were conducted under alkaline conditions (pH 9.8) and pseudo first order rate constants were determined for dye destruction. The *m*-chloroperbenzoic acid was much more effective than hydrogen peroxide in bringing about loss of colour. The introduction of electron donating groups into the diazo component of the dyestuff, which would be expected to lead to an increased propensity to undergo attack by electrophilic species, resulted in increased levels of bleaching by the peracid. Additionally reduction in pH caused an increase in the rate of bleaching in presence of peracid, the rate increasing approximately tenfold per unit drop in pH. These observations are consistent with attack by *m*-chloroperbenzoic acid, a highly electrophilic species, rather than *m*-chloroperbenzoate (the major species present at pH 9.8).

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1. Introduction

It has long been recognized that laundering of dyed textiles can result in a loss or change of colour. This can result from simple physical removal of dye by the washing process or by chemical destruction of colour, usually by components present in the detergent. Modern detergents are a complex mixture of chemicals, comprising surfactants, builders, anti-redeposition agents and, usually, bleaching agents. Additional ingredients can include fluorescent brightening agents, enzymes, perfumes, fabric softeners, foam control agents and agents to reduce dye transfer [1].

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Traditionally the bleaching species has been hydrogen peroxide which is generated in situ, usually from sodium percarbonate or sodium perborate. Driven by environmental and commercial pressures, detergent manufacturers have, more recently, produced detergents which cleanse efficiently at lower and lower temperatures. In order to achieve low temperature efficacy modern detergents generally contain a bleach activator [2]. This reacts with hydrogen peroxide, liberated during laundering from the sodium salt of an inorganic peracid, to yield an organic peracid, a very powerful oxidizing agent which exerts a powerful cleansing action at temperatures as low as 30 °C. The most commonly encountered activator, *N*,*N*,*N*′,*N*′-tetraacetyl ethylene diamine, undergoes nucleophilic attack by peroxide anion to yield peracetic acid (Fig. 1).

As detergents have evolved so too have the tests used to predict their effect upon dyed textile substrates. For example the widely used ISO105:CO3 test established in order to study the effect of "soap and soda" at 60 °C, was upgraded to include sodium perborate as part of the ISO 105:CO6 test methodology [3]. In addition to assessing the extent of dye fading this test uses a multi fibre strip, attached to the specimen, to assess the effect of cross staining by loose dye removed from the test specimen. A recently introduced test, ISO105:CO9 [4,5] has been developed to predict the fading, of dyed textiles, during repeated laundering with an activated oxygen bleach detergent. Although this test provides much useful qualitative information on the performance of dyes on textile substrates it is difficult to quantify accurately very small changes in bleach resistance of the chromophore per se: this is because, in addition to oxidative bleaching of the chromophore, colour is sometimes removed physically during the washing process.

In an attempt to study the chemical resistance of different chromophores to oxidative bleaching, a series of experiments were conducted in which dyes were subjected separately to a peracid and to hydrogen peroxide, in homogeneous aqueous solution. Such an experimental protocol obviates any anomalous physical effects associated with testing on fibre or fabric, and thus allows an accurate, readily quantifiable, comparison of the rates of destruction of different chromophores by oxidative-bleaching species. Thereby a ready means of assessing the small effects of minor structural variations is available, which in turn is an essential tool in structure-activity studies aimed at the design of dyes with superior bleach resistance.

Thus a series of substituted phenylazonaphthalene dyes were prepared, by coupling variously substituted phenyl diazonium salts onto 1-aminonaphthalene-4-sulphonic acid. These were then subjected separately to the types of oxidative bleaching species, namely hydrogen peroxide and a peracid, present in modern detergents.

2. Experimental

Ultraviolet/visible spectra of aqueous solutions of the dyes were recorded using a Phillips PU 8700 spectrophotometer and aqueous solutions of dyes.

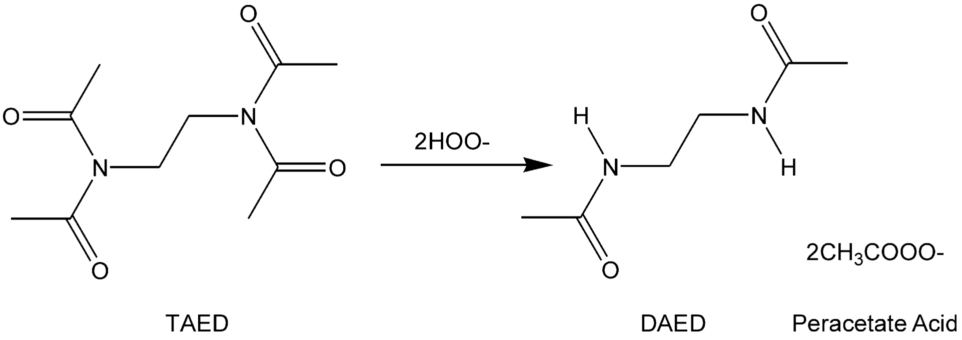

Fig. 1. Generation of peracetic acid from tetra-acetylethylene diamine (TAED) and peroxide.

Reflectance spectra of dyed fabrics were made on a Datacolor Spectraflash 600 spectrophotometer under a D65 lamp.

Thin layer chromatography (t.l.c.) was conducted using aluminum plates coated with silicagel 60 F_{254} (Merck), eluant *iso*-butanol:*n*-propanol:ethyl acetate:water (2:4:1:3). High performance liquid chromatography (h.p.l.c.) was performed using a Hewlett-Packard 1100 instrument with Purospher RP-18 (5 µm) packing and a LiChroCART 125-4 column cartridge. The mobile phases were an aqueous (0.25%) solution of cyclohexylammonium phosphate (solvent A) and acetonitrile (solvent B). All dyes were essentially pure as judged by t.l.c. and h.p.l.c. but contained inorganic salt (usullay sodium chloride) and water. The effective agent content of each dye was determined by titration against a standard solution of titanium^{III} chloride.

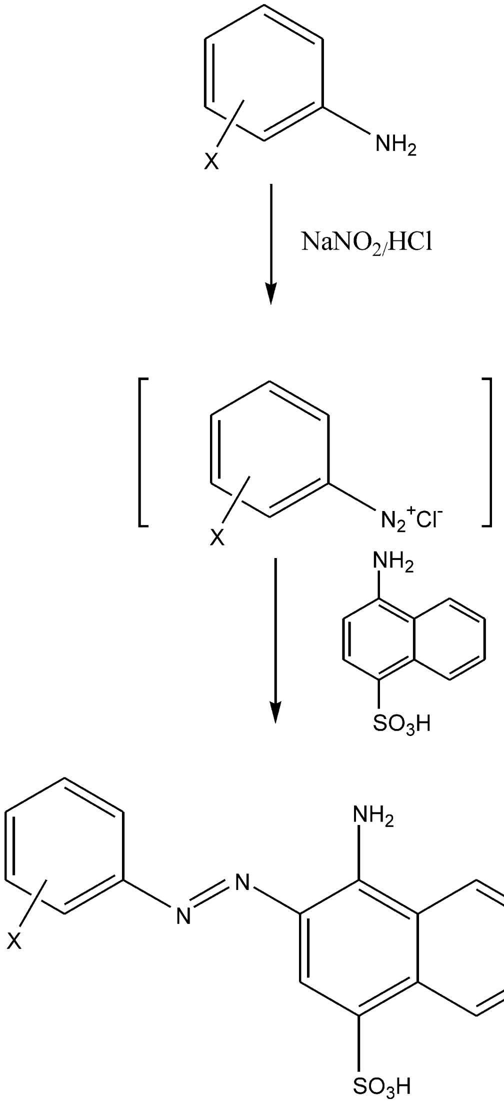

Fig. 2. Synthesis of 1-amino-2-arylazonaphthalene-4-sulphonic acids.

2.1. Preparation of dyes

The dyes were all prepared by a conventional diazotisation–coupling sequence, according to Fig. 2.

The appropriate aniline derivative was diazotised in cold aqueous hydrochloric acid and the resulting diazonium salt was added to a cold aqueous solution of 1-amino-naphthalene-4-sulphonic acid. In this way the dyes listed in Table 1 were prepared.

1-Amino-2-(2-sulphophenylazo-)naphthalene-4-sulphonic acid (Dye 5) was prepared as detailed below: other dyes were prepared in similar manner.

2.1.1. Preparation of 1-amino-2-(2-sulphophenylazo-)naphthalene-4-sulphonic acid

2.1.1.1. Diazotisation of 2-aminobenzenesulphonic acid (orthanilic acid). Orthanilic acid (4.10 g, 0.021 mol, 195.2 gmol^{-1}) was dissolved in water (50 cm^3). Hydrochloric acid (36%; 10 cm^3) was added and the solution was stirred at 0–5 °C. After 10 min. sodium nitrite (1.45 g, 0.021 mol) was added and the resulting red-brown solution stirred for 15 min. Thin layer chromatography confirmed that all of the orthanilic acid had been

Table 1
Dyes prepared in the present

Dye	Substituent
1	H
2	*p*-Nitro
3	*p*-Methoxy
4	2,4,6-Trichloro
5	*o*-Sulfo
6	*o*-Bromo

consumed. Excess nitrous acid was destroyed by the addition of a small quantity of sulfamic acid, and the solution was filtered.

2.1.1.2. Coupling of 2 - sulphophenyldiazonium chloride with 1-aminonaphthalene-4-sulfonic acid. 1-Aminonaphthalene-4-sulfonic acid (4.90 g, 0.02 mol, 245.2 g mol^{-1}) was dissolved in water (50 cm^3) and then added dropwise to the diazonium salt solution prepared above. The reaction mixture was stirred in an ice-bath and the pH was maintained at 4 by the addition of further sodium bicarbonate. After 30 min thin layer chromatography indicated that the reaction was complete; the pH was raised to 6 by the addition of sodium bicarbonate. Sodium chloride was added (13% w/v) to precipitate 1-amino-2-(2-sulphophenylazo-)-naphthalene-4-sulfonic acid as an orange solid, isolated by filtration. Yield = 8.3 g (92%).

2.2. *Characterisation of dyes*

2.2.1. *Measurement of effective agent strength by titration against titanous chloride*

The strengths of the dyes prepared above were measured by titration against titanium^{III} chloride ($TiCl_3$) solution. Ti^{III} salts readily reduce azo derivatives to amino species whilst at the same time being oxidized to Ti^{IV} salts, see Fig. 3 [5,6]. Solutions of titanium^{III} chloride are also readily oxidized by atmospheric oxygen and are therefore conveniently stored under an inert atmosphere, such as carbon dioxide.

Hence a monoazo dye is reduced by four molar equivalents of titanium^{III} chloride. The strength of a dye of unknown purity is conveniently expressed as Mol In, which is defined by Eq. (A1), and is the weight, in grams, that contains one mole of dye. The effective agent strength (EA) of a dye is then given by Eq. (A2) (For Eqs. (1)–(5) see Appendix A).

2.2.2. *Experimental determination of the Mol In of synthetised dyes*

An accurately measured quantity of CI Acid Blue 54 (0.2 g, Mol In = 1041.7) was dissolved in water (80 cm^3) and buffered by sodium tartrate buffer solution (20 cm^3, 0.2M, pH 8.0). The solution was heated to boiling and then titrated against titanium^{III} chloride solution; the end-point was determined by the addition of a few drops of a dilute aqueous solution of Lyssamine Green, which was destroyed more slowly than the dye under evaluation and hence left a bright green solution when all of the CI Acid Blue 54 had been destroyed. The strength of the titanium^{III} chloride solution, i.e. the titre factor (T_f) was calculated using Eq. (A3). T_f was taken as the mean of three determinations (equal to 0.789).

Two accurately measured samples (ca. 0.1 g) of each dye were dissolved in water, buffered and titrated against titanium^{III} chloride as described above. [NB: the solubility of some dyes was improved by the addition of ethanol (50 cm^3)]. The Mol In and effective strength (EA) values were calculated using Eqs. (A1) and (A2); the results are shown in Table 2.

$$4\,Ti^{3+} + R\text{-}N{=}N\text{-}R' + 4\,H^{+} \longrightarrow 4\,Ti^{4+} + R\text{-}NH_2 + R'\text{-}NH_2$$

Fig. 3. Reduction of azo dyes with titanous salts.

Table 2
Effective agent strength of dyes

Dye	Mol(In) (gmol^{-1})	Molecular mass (gmol^{-1})	EA strength (%)
1	443.4	350.3	79.0
2	665.4	372.6	56.0
3	541.2	379.4	70.1
4	1088.2	452.7	41.6
5	626.1	451.4	72.1
6	560.5	428.2	76.4

2.2.3. Optical properties of dyes (wavelength of maximum absorbance, λ_{max}, and molar extinction coefficient, ε_{max})

An accurately measured quantity of each dye was dissolved in water (1 g l^{-1}) then diluted 25× to give a stock solution. Five samples were taken from each stock solution and further diluted to give five test solutions viz. 2:1, 4:1, 5:1, 8:1, 10:1. The optical density, at λ_{max}, of each test solution was measured using a Philips 8720 UV/visible Scanning Spectrophotometer and plotted against the molar concentration of dye. In each case a linear relationship between optical density and concentration signified adherence to Beer–Lambert's Law. Table 3 lists the absorption characteristics, i.e.wavelength of maximum absorbance, λ_{max}, and molar extinction coefficient, ε_{max}, of each dye.

2.3. Oxidative degradation of dyes

2.3.1. At pH 9.8

The dyes were each treated separately with a large excess (100 fold) of *m*-chloroperbenzoic acid and of hydrogen peroxide. The former was chosen as a convenient model for the peracetic acid produced in the ISO105:CO9 test. The pH was maintained at 9.80±0.02 with a carbonate buffer and the temperature at 60±0.5 °C with the aid of a thermostatically controlled water-bath. A dye concentration of 1×10^{-4} M was chosen to yield convenient optical density (OD) values. 1 gl^{-1} Ethylenediamine-tetra-acetic acid (EDTA), 1 gl^{-1}, was added to eliminate the effects of metal ions. Samples were taken from each reaction at regular intervals and excess oxidant quenched with sodium thiosulfate solution. The optical density of each sample was measured and plotted against time.

Table 3
Absorbance of aqueous solutions of dyes

Dye	Substituent	λ_{max} (nm)	ε_{max} (m^2 mol^{-1})
1	H	453.6	13,900
2	*p*-Nitro	497.9	19,800
3	*p*-Methoxy	460.8	17,200
4	2,4,6-Trichloro	454.4	6100
5	*o*-Sulfo	468.5	16,200
6	*o*-Bromo	464.3	15,000

2.3.2. At variable pH

In order to ascertain whether the dissociated or undissociated peracid was responsible for chromophore destruction, the degradation of Dye 1, with *m*-chloroperbenzoic acid, was conducted at a range of pH values selected such that the concentration of Dye 1 remains constant (because under these conditions it does not undergo either protonation or deprotonation) and the concentation of peracid varies with changing pH. Oxidation was carried out at decreasing pH until the reaction rate became so rapid that it could not be accurately determined with the equipment being used.

3. Results and discussion

3.1. Preparation and properties of dyes

All the dyes were readily prepared according the same general method as that described for Dye 5. In each case diazotisation was effected in dilute aqueous hydrochloric acid and the partially soluble dyes precipitated by the careful addition of salt to the reaction mixture. All dyes were essentially pure organically, as judged by h.p.l.c. and t.l.c., but contained varying quantities of water and inorganic salts, largely sodium chloride. The Mol. In of each dye was determined by titration against titanous chloride.

The molar extinction coefficients of the dyes varied from 6100 to 19,800 m^2 mol^{-1}. As expected, the most pronounced bathochromic shift in the wavelength of maximum absorbance, λ_{max}, resulted from the introduction of the strongly electron withdrawing *para*-nitro group (Dye 2): also this was chromophorically the strongest dye. Conversely the introduction of three chlorine atoms in the 2,4,6 positions of the diazo component resulted in substantial steric hindrance around the azo linkage leading to a reduction in extinction coefficient. It is interesting to note that both the *p*-nitro and the *p*-methoxy groups cause large increases in the intensity of absorption, relative to the unsubstitued parent dye, despite the latter being electron-donating. The *o*-sulfonate, Dye 5, and *o*-bromo substituents, Dye 6, are weakly electron-withdrawing: both causing a bathochromic shift in absorbance relative to Dye 1 but to a lesser extent than the nitro group.

3.2. Oxidative degradation of dyes

3.2.1. Peroxide versus peracid degradation

The unsubstituted parent Dye 1, (Table 1) was treated separately with a large (100-fold) excess of *m*-chloroperbenzoic acid and of hydrogen peroxide. The former was chosen as a convenient model for the peracetic acid produced in the ISO105:CO9 test.

The rate of oxidation was assumed to be proportional to the concentrations of both dye and oxidant at the specified temperature. However, since oxidation was carried out using a 1×10^{-2} M solution of oxidant, a hundred-fold excess, thus making the concentration of oxidant effectively constant [Eq. (A4)], the kinetics simplified to *pseudo*-first order.

Measuring the optical density of the reaction mixture provided the most convenient method of determining dye concentration. Hence samples were taken from each reaction at regular intervals and excess peracid quenched with sodium thiosulfate solution. The absorption of each sample was measured and plotted against time. From the resulting graph, the equation of the line of best fit gave the relationship between optical density and time. By choosing suitable OD values, the reaction half-life i.e. the time for the concentration of dye to fall to half its initial value, could be calculated.

A first order reaction can be described by Eq. (A5).

The rates of oxidative degradation of Dye 1 by *m*-chloroperbenzoic acid and hydrogen peroxide, at pH 9.8, are listed in Table 4.

Two conclusions can be drawn from Table 4. First, hydrogen peroxide has little or no effect on Dye 1 at pH 9.8 and 60 °C, resulting in essentially negligible chromophore degradation under the conditions and timescale employed. Second, the rate of chromophore degradation by *m*.-perbenzoic acid under similar conditions is very much more rapid than that by hydrogen peroxide.

Table 4
Rates of degradation of Dye 1 in with hydrogen peroxide and mCPBA

Derivative	Oxidising species	Rate constant (k/s^{-1})
1	MCPBA	0.00347
1	H_2O_2	$<10^{-5}$

Although peracetic acid has long been associated with the loss of colour from dyed substrates during domestic laundering, it had been assumed that the species causing degradation was the peracetate anion, pK_a ca. 8 [7], as the peracetic acid will be largely (~99%) dissociated in the wash liquor, typically of pH ca. 10.2. There is however no evidence to substantiate this claim.

In order to ascertain whether the dissociated or undissociated peracid is responsible for chromophore destruction, the degradation of Dye 1 with *m*-chloroperbenzoic acid was conducted over a range of pH conditions. Since Dye 1 cannot be ionised over the range of pH used, its concentration remains constant. The only factor that can change is the concentration of free peracid. Oxidation was therefore conducted at decreasing pH until the reaction rate became so rapid that it could not readily be ascertained with the equipment available.

The rate of dye destruction was found to increase as the pH was decreased i.e. as the proportion of free acid increases, so does the rate of dye destruction. Indeed, any attempt to measure the rate of reaction below pH ca. 8.4 proved difficult because the rate of decolourisation became too rapid to monitor accurately with the equipment available (see Fig. 4). This suggests that it is the relatively small quantity of free acid, a powerful electrophile, which is the active oxidizing species rather than the anionic *m*-chloroperbenzoate anion; this is in accord with other findings by Oakes and Gratton [8] concerning the oxidation of hydrazo dyes by peracid. This interpretation is also consistent with the observation (see Fig. 5) that the introduction of electron withdrawing substituents, such as a 4-nitro group, into the diazo component of the dye reduce susceptibility to oxidation whereas an electron donating group such as methoxy in the *para*-position results in an increased rate of oxidation. Dyes 4, 5 and 6, all of which possess at least one weakly electron withdrawing group *o*- to the azo bond, were also more resistant to oxidation by peracid that the parent Dye 1.

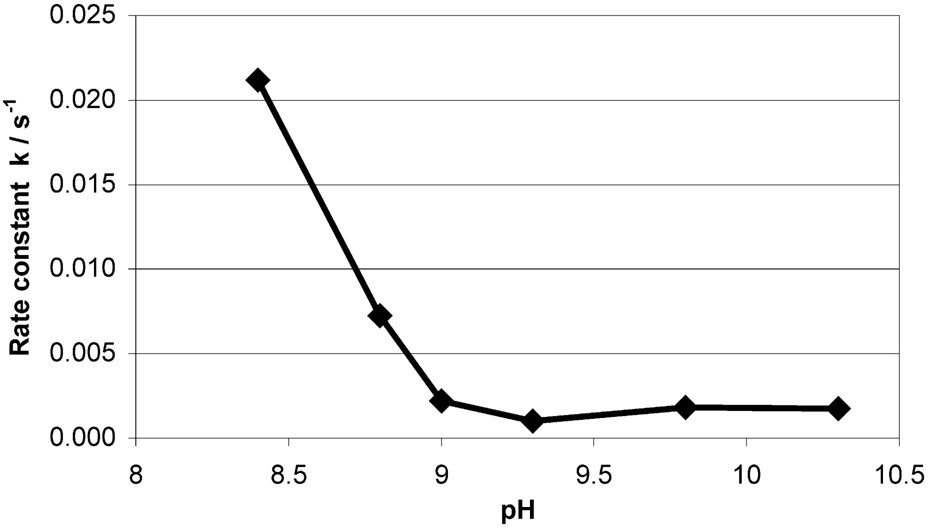

Fig. 4. Degradation of dye 1 by *m*-chloroperbenzoic acid over a range of pH.

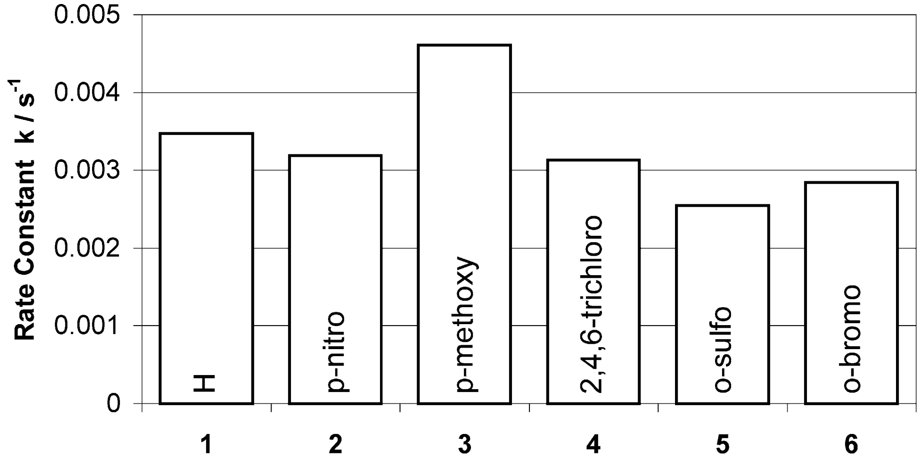

Fig. 5. Rates of destruction of substituted 2-arylazo-1-aminonaphthalene-4-sulphonic acids.

The initial attack of peracid is likely to take place at a nitrogen atom. This is in keeping with the known ability of peracids to oxidize both azo derivatives [9], to azoxy compounds, and primary ammines [10] to nitroso derivatives.

4. Conclusions

1. At 60 °C and pH 9.8 destruction of dye by *m*-chloroperbenzoic acid is much faster than by hydrogen peroxide.
2. The active species involved in peracid attack is the undissociated *m*-chloroperbenzoic acid, not the prebenzoate anion.
3. The introduction of electron withdrawing substituents into the *ortho*- or *para*-position of the diazo component of 1-amino-2-arylazonaphthalene-4-sulphonic acids, which would render the dye less susceptible to attack by electrophlic species, confers increased resistance to *meta*-chloroperbenzoic acid.

4. The chromophoric strength of the parent Dye 1 was enhanced by the introduction into the *para*-position of either an electron withdrawing (nitro) or an electron donating methoxy substituent.

Acknowledgements

We are grateful to Procter and Gamble for financial support (D.A.).

Appendix A

$$Mol\ In = \frac{Mass \times Hydrogen\ \ Factor \times 10000}{TitreFactor \times Volume} \tag{A1}$$

where

Mass: the mass of dye (in grams) of unknown Mol In, to undergo evaluation;
Hydrogen Factor (H_f): the total number of hydrogen atoms needed to completely reduce the dye molecule (i.e. 4 for each azo bond, 6 for each nitro- group etc.);
Tire Factor (T_f): a measure of the strength of the titanous chloride solution, as determined by titration against a standard of known Mol In;
Volume: the quantity of titanous chloride solution (in cm^3) required to decolourise the solution containing the dye of unknown Mol In.

$$EA = \frac{Molecular\ \ Mass}{MolIn} \times 100\% \tag{A2}$$

$$Tf = \frac{Mass \times Hf \times 10000}{1041.7 \times Volume} \tag{A3}$$

$$Rate = k'.[Dye] \tag{A4}$$

$$kt = \ln\left(\frac{Ao}{A}\right) \tag{A5}$$

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