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# Design of Chlorine-fast Reactive Dyes. Part 4: Degradation of Amino-containing Azo Dyes by Sodium Hypochlorite

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## ABSTRACT

*Amino-containing azo dyes were reacted with sodium hypochlorite in water and the rate of decoloration was determined spectrophotometrically. Electrophilic attack at the amino group by a chloronium ion initiates the degradation reaction of the dyes, drastically accelerating the subsequent cleavage of the azo linkage.* o-*Hydroxyazo dyes from aminonaphtholsulphonic acids are more susceptible to decoloration than the corresponding* o-*aminoazo isomers, even when the —NH— N= group of their hydrazone form is sterically protected by two sulphonate groups in the* o,o'-*positions. Effective molecular design for retarding the decoloration can be achieved by acylating the amino group in the* o-*hydroxyazo dyes and by coupling diazotized aniline-2-sulphonic acid to the neighbouring position of the hydroxy group in the* o-*aminoazo isomers.*

## 1 INTRODUCTION

An amino group is the most useful group in dye chemistry; in azo dyes it not only provides access to an azo group, but it is also the most widely used auxochrome. Many azo dyes so obtained have been utilized commercially in most dye classes, resulting in many advantages and some deficiencies. Our continuing studies on chlorine-fast reactive dyes showed that not all azo dyes are resistant to chlorine-based treatments; susceptible azo dyes can undergo quite profound colour change, depending on the proportion of the hydrazone form in the azo–hydrazone tautomerism and on the hydrazone-protecting ability of substituents in the dye molecule.[1-3]

In improving the chlorine resistance of arylazonaphtholsulphonates, which exist predominantly in the hydrazone form, sulphonate ($SO_3^-$) groups play a vital role, particularly when these are positioned in the aryl and naphthol rings so that the —NH—N= group is protected on both sides.[1] A representative example is 2-(2'-sulphonatophenylazo)-1-naphthol-3,6-disulphonate, which is chlorine-fast owing to effective protection by the 2',3-disulphonate groups.

In the course of a recent study into azo dyes derived from H-acid (8-amino-l-naphthol-3,6-disulphonic acid),[3] the unexpected observation was made that 8-amino-2-(2'-sulphonatophenylazo)-1-naphthol-3,6-disulphonate in an aqueous sodium hypochlorite (NaOCl) solution was converted rapidly into colourless compounds. This suggested that the presence of the 8-amino group leads to degradation of a chromogen in which the 2',3-disulphonate groups would still have been expected to protect effectively the —NH—N= group of the hydrazone form.

The present investigation was carried out to examine whether the unexpected degradation is a general one for all amino-containing azo dyes from aminonaphthol- and naphthylamine-sulphonic acids, and to establish countermeasures against the deleterious effect of the amino group on chlorine resistance in the design of chlorine-fast reactive dyes.

## 2 RESULTS AND DISCUSSION

### 2.1 Synthesis and structure of amino-containing azo dyes

Amino-containing azo dyes tested were *o*-aminoazo and/or *o*-hydroxyazo dyes derived from aminonaphtholsulphonic acids such as H-acid, γ-acid (7-amino-1-naphthol-3-sulphonic acid), 2R-acid (7-amino-1-naphthol-3,6-disulphonic acid), J-acid (6-amino-1-naphthol-3-sulphonic acid), sulpho J-acid (6-amino-1-naphthol-3,5-disulphonic acid), *N*-methyl J-acid (6-methylamino-1-naphthol-3-sulphonic acid) and M-acid (5-amino-1-naphthol-3-sulphonic acid) and their related monoazo and disazo dyes.

Figure 1 gives the reaction scheme used to prepare monoazo and disazo dyes derived from J-acid (**I**). Essentially, the *o*-aminoazo dyes (**II**) were prepared by coupling diazotized anilinesulphonic acids with **I** at pH 1 to 3, and the *o*-hydroxyazo dye (**V**) was prepared by coupling diazotized aniline-2-sulphonic acid with *N*-acetyl J-acid (**IV**) at pH 6 to 8. Subsequent hydrolysis of the acetylamino group gave the *o*-hydroxyazo dye (**VI**). *o*-Aminoazo and *o*-hydroxyazo dyes from the other aminonaphtholsulphonic acids, and their related monoazo dyes, were prepared similarly, except for *o*-aminoazo dyes from sulpho J-acid and M-acid, both of

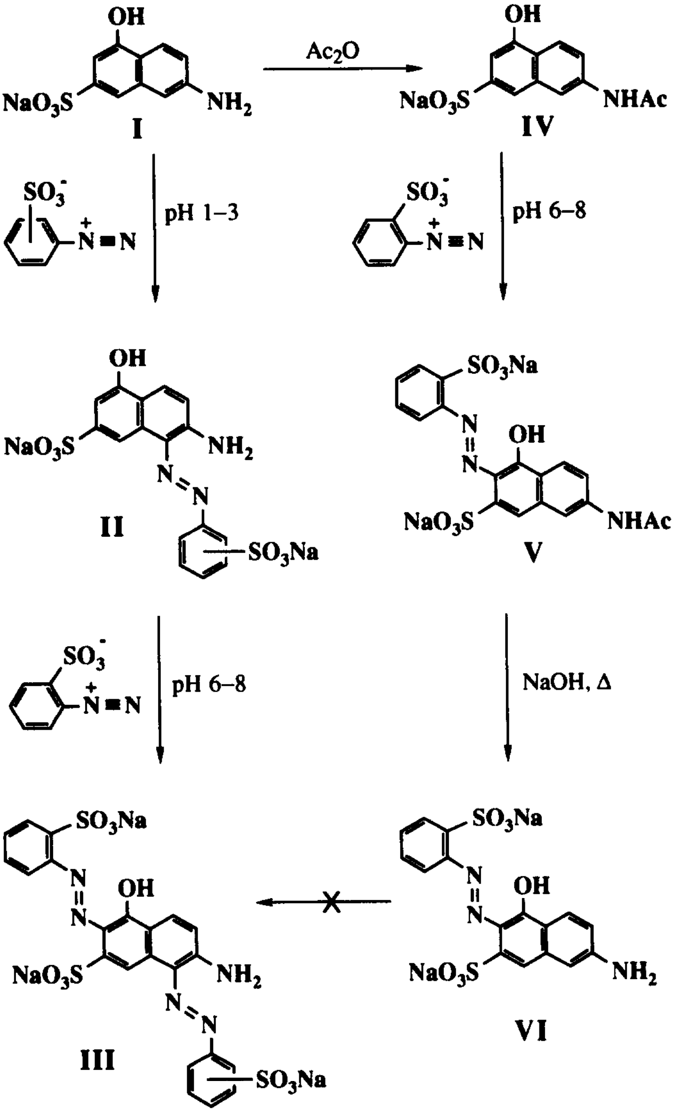


Fig. 1. *o*-Aminoazo dyes II, *o*-hydroxyazo dyes V and VI, and disazo dyes III derived from J-acid I, and reaction sequence used to synthesize these dyes.

which could not be obtained owing to the presence of a 5-sulphonate group and the dominance of *p*-coupling, respectively.

Disazo dyes (III) were prepared by further coupling of II with diazonium salts at pH 6 to 8. Since, however, ionization of the hydroxy group of the *o*-aminoazo dyes obtained from γ- and 2R-acids and the *p* aminoazo dyes from M-acid is difficult under the coupling conditions used, owing to a strong intramolecular hydrogen bond with the neighbouring azo group,[4] the desired disazo dyes could not be obtained. Such twice-coupled dyes are prepared exclusively by stepwise couplings at low pH first and then at high pH; thus, **III** cannot be derived from **VI**. As a result, the disazo dyes obtained were those from H-acid, J-acid and *N*-methyl J-acid.

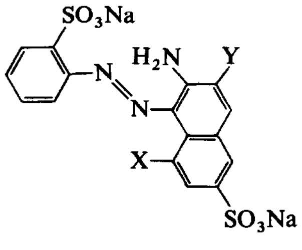
## 2.2 *o*-Aminoazo dyes from $\gamma$-acid

In order to examine structure–reactivity relationships for these dyes, dyes **1–5**, having systematically varied substituents and orientation (Table 1), were allowed to react with NaOCl in an aqueous pH 7·0 buffer solution at 24°C (initial concentration of dye $2.0 \times 10^{-5}$ M and NaOCl $2.0 \times 10^{-3}$ M). Decoloration observed in all dyes suggests that the reaction involves cleavage of the azo linkage. Judging from the many colourless compounds obtained, the degradation mechanism is very complex. The nature of the basic chemical reactions involved is, therefore, not yet clear.

The rate of decoloration was followed spectrophotometrically. Figure 2 shows the plots of $\ln A_0/A_t$ against time, where $A_0$ and $A_t$ are the absorbance at $\lambda_{max}$ of each dye at times 0 and $t$ (in seconds), respectively. The plots gave a straight line passing through the origin for all dyes, indicating that, in spite of the complexity of the degradation, the decoloration reaction is first order with respect to dye concentration for the time shown. The rate constants $k$ calculated from the equation $\ln A_0/A_t =$

**TABLE 1**

Visible Absorption Maxima and Rate Constants of Decoloration for *o*-Aminoazo Dyes[a]



| *Dye no.* | *X* | *Y* | $\lambda_{max}$ *(nm)* | $\varepsilon_{max} \times 10^{-4}$ [b] | k *(s⁻¹)* |
|---|---|---|---|---|---|
| **1** | H | H | 460 | 1·35 | $4·0 \times 10^{-2}$ |
| **2** | $SO_3Na$ | H | 442 | 1·36 | $1·0 \times 10^{-1}$ |
| **3** | H | $SO_3Na$ | 457 | 1·49 | $1·5 \times 10^{-2}$ |
| **4** | OH | H | 504 | 1·78 | $2·7 \times 10^{-2}$ |
| **5** | OH | $SO_3Na$ | 509 | 1·82 | $3·6 \times 10^{-3}$ |

[a] Initial concentration of dye $2·0 \times 10^{-5}$ M and NaOCl $2·0 \times 10^{-3}$ M, pH 7·0 and 24°C.
[b] In $dm^3/(mol\ cm)$.

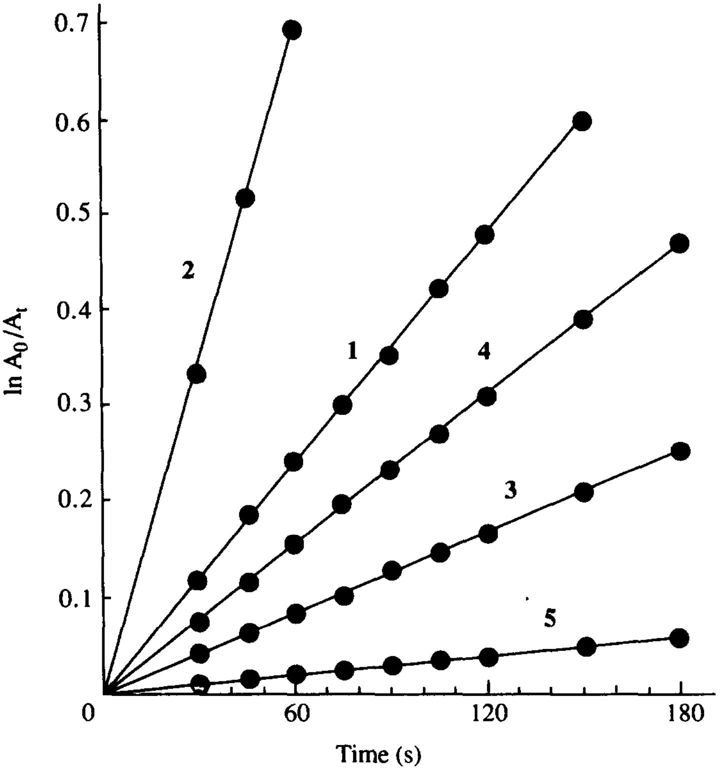


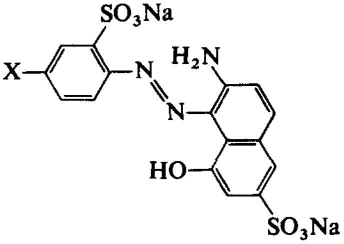
**Fig. 2.** Plots of ln $A_0/A_t$ against time for decoloration reactions of dyes **1–5** with NaOCl. $A_0$ and $A_t$ are the absorbance at $\lambda_{max}$ of each dye at times 0 and $t$ (in seconds), respectively. (Initial concentration of dye $2.0 \times 10^{-5}$ M and NaOCl $2.0 \times 10^{-3}$ M, pH 7.0 and 24°C.)

*kt* are also given in Table 1; they can be used to compare the degrees of resistance of the dyes to decoloration.

In such *o*-aminoazo dyes, the azo form is favoured, as was shown both in solution and in the crystalline state.[5] The visible absorption maxima in the table support this view. Substituents on the naphthalene ring markedly affect the reactivities of the dyes with NaOCl; the importance of an $SO_3Na$ group is evident from the decrease in rate produced by that in the Y position (dyes **3** and **5**). In contrast, the $SO_3Na$ group in the X position acts to make dye **2** more susceptible to decoloration, whereas it (i.e. 8-$SO_3Na$) plays an important role in imparting high chlorine resistance to 1-(2'-sulphonatophenylazo)-2-naphthol-6,8-disulphonates, which exist predominantly in the hydrazone form.[1] The differences in contributions of the $SO_3Na$ group arise primarily from differences in the azo–hydrazone tautomerism of these dyes. Considering the retarding effect revealed by the $SO_3Na$ group in the Y position, the degradation of

### TABLE 2

Effect of Substituent X on Visible Absorption Maxima and Rate Constants of Decoloration for *o*-Aminoazo-γ-acid Dyes



| *Dye no.* | *X* | $\lambda_{max}$ *(nm)* | $\varepsilon_{max} \times 10^{-4}$ [a] | k $(s^{-1})$ [b] |
|---|---|---|---|---|
| **6** | $NO_2$ | 554 | 2·50 | 2·5 × $10^{-3}$ |
| **7** | $SO_3Na$ | 512 | 1·95 | 5·7 × $10^{-3}$ |
| **4** | H | 504 | 1·78 | 5·7 × $10^{-3}$ |
| **8** | $CH_3$ | 502 | 1·90 | 6·7 × $10^{-3}$ |
| **9** | $OCH_3$ | 506 | 2·17 | 6·0 × $10^{-3}$ |
| **10** | $NH_2$ | 515 | 2·57 | 9·9 × $10^{-2}$ |

[a] In $dm^3$/(mol cm).

[b] Initial concentration of dye 2·0 × $10^{-5}$ M and NaOCl 6·0 × $10^{-4}$ M. pH 6·0 and 20°C.

the *o*-aminoazo dyes is suggested to initiate at the amino group by electrophilic attack of a chloronium ion generated in the aqueous NaOCl solution. The additional resistance of dyes **4** and **5**, having the hydroxy group in the X position, is attributable to an intramolecular hydrogen bond with the azo group.

Since most commercial *o*-aminoazo dyes for synthetic and natural polyamides have been derived from γ-acid[6] and because of the favourable retarding effect on the rate of decoloration observed in previous series when γ-acid is used as a coupling component, a further series of *o*-aminoazo-γ-acid dyes, with a *p*'-substituent on the disazo component residue, was examined. The rate constants obtained for the dyes are recorded in Table 2. In order to estimate precise differences in substituent effects on the decoloration, the degradation reactions were carried out under milder conditions (initial concentration of dye 2.0 × $10^{-5}$ M and NaOCl 6.0 × $10^{-4}$ M, pH 6.0 and 20°C). As a result, for example, the rate of dye **4** obtained here was about one-fifth of that under the previous conditions. The plots of ln $A_0/A_t$ against time also gave a straight line passing through the origin for all dyes tested.

An electron-withdrawing substituent in the X position reduces the rate of decoloration, and an electron-donating substituent increases it. Figure 3

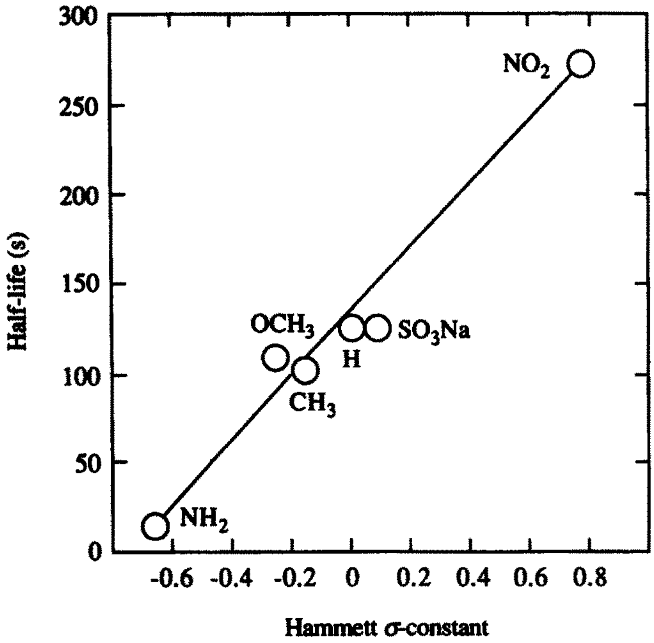


**Fig. 3.** Hammett plots for half-life of decoloration for 4'-substituted 2'-sulphonatophenylazo-γ-acid dyes in an aqueous NaOCl solution: (Initial concentration of dye $2.0 \times 10^{-5}$ M and NaOCl $6.0 \times 10^{-4}$ M, pH 6.0 and 20°C); $NO_2$ (**6**), $SO_3Na$ (**7**), H (**4**), $CH_3$ (**8**), $OCH_3$ (**9**), $NH_2$ (**10**).

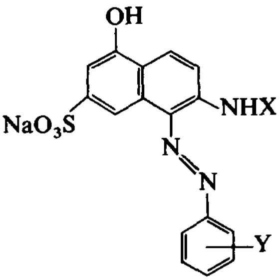
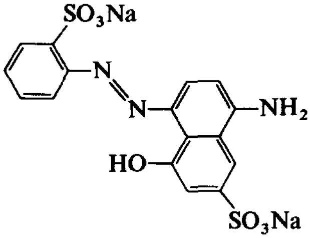
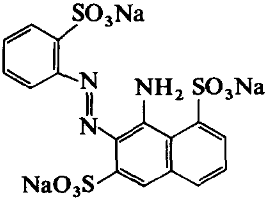
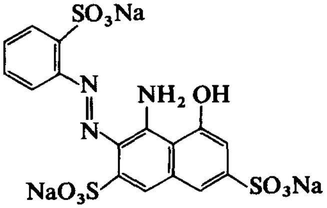
indicates a linear relationship between half-lives of the decoloration and Hammett σ-constants of the substituents.

## 2.3 *o*-Aminoazo dyes from J-acid and their analogues

Comparison of the rate constants of decoloration in Table 3 clearly shows that the position of the amino group is functionally important for chlorine-resistant arylazonaphthylamine systems. The higher resistance of dye **11** compared with dye **14** is due to intramolecular hydrogen-bonding formation between the amino-hydrogen and the azo-nitrogen.[4] A similar result was noted above for the isomeric γ-acid dye **4**. Dye **14**, which can not form such a hydrogen bond, is much more susceptible to decoloration by a factor of about 10. The great susceptibility is not surprising since it is well documented that *N*-triazinylated derivatives of its analogous dyes are very susceptible to decoloration, despite the reduced electron density of the amino-nitrogen induced by this substituent.[2] However, this hydrogen bond is not so stable to electrophilic attack of a chloronium ion, because the *N*-methylated dye **12** shows a slight decrease

## TABLE 3

Visible Absorption Maxima and Rate Constants of Decoloration[a] for Aminoazo Dyes Other Than *o*-Aminoazo-γ-acid Dyes

| *Structure* | *Dye no.* | $\lambda_{max}$ (*nm*)<br>($\varepsilon_{max} \times 10^{-4}$) | k ($s^{-1}$) |
|---|---|---|---|
|  | **11** (X = H, Y = *o*-$SO_3Na$) | 481<br>(1·49) | $1{\cdot}9 \times 10^{-2}$ |
| | **12** (X = $CH_3$, Y = *o*-$SO_3Na$) | 516<br>(1·74) | $1{\cdot}5 \times 10^{-2}$ |
| | **13** (X = $CH_3$, Y = *p*-$SO_3Na$) | 503<br>(1·91) | $1{\cdot}6 \times 10^{-2}$ |
|  | **14** | 505<br>(2·52) | $1{\cdot}9 \times 10^{-1}$ |
|  | **15** | 487<br>(1·73) | $7{\cdot}5 \times 10^{-2}$ |
|  | **16**[b] | 521<br>(2·49) | $8{\cdot}2 \times 10^{-2}$ |

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[a] Initial concentration of dye $2{\cdot}0 \times 10^{-5}$ M and NaOCl $2{\cdot}0 \times 10^{-3}$ M, pH 7·0 and 24°C.
[b] Data cited from Ref. 3.

in rate. This suggests that one of the two amino-hydrogens participates in the decoloration. On the other hand, the $SO_3Na$ group in the diazo component residue has little significant effect (dye **13** relative to dye **12**).

Other notable trends are that dyes **15** and **16** derived from 1-naphthylaminesulphonates are more susceptible to decoloration than dyes derived from 2-naphthylaminesulphonates (dyes **1**, **3–5** and **11–13**), the only exception being dye **2**. Therefore, it may be concluded that the resistance to decoloration increases in passing from 1-phenylazo-4-naphthylamine dyes by way of 2-phenylazo-1-naphthylamine dyes to 1-phenylazo-2-naphthylamine dyes.

## 2.4 *o*-Hydroxyazo dyes from aminonaphtholsulphonic acids

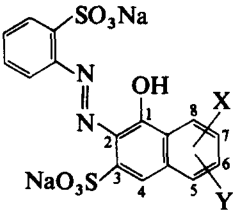
Compared to the *o*-aminoazo dyes, *o*-hydroxyazo dyes derived from aminonaphtholsulphonic acids have found more extensive use for cellulosic fibres. Despite their technical importance, there has been little information as to how well such dyes meet recently increased demands for chlorine resistance.

The *o*-hydroxyazo dyes examined comprised a series of 2-(2'-sulphonatophenylazo)-1-naphthol-3-sulphonates in which substituents were varied in a systematic fashion (Table 4). Dyes **17** and **18** are also given for comparison. In general, such dyes exist predominantly in the hydrazone form, both in solution and in the solid state.[1,7] The visible absorption maxima of dyes **17–25**, **29** and **30** support this view. Doubt concerning the predominance of the hydrazone form in dyes **26–28** arises because of a double maximum, *c.* 100 nm apart, and a much lower $\varepsilon_{max}$ than that of the other dyes.[1]

The free amino and substituted amino groups on the naphthalene ring affect the $\lambda_{max}$ and $\varepsilon_{max}$ of these dyes; both groups in the 5- and 8-positions cause bathochromic and hyperchromic shifts compared to those of dyes **17** and **18**, respectively. In contrast, the groups in the 6-position cause slight hypsochromic and markedly hyperchromic shifts. The most striking feature in this series is the extremely beneficial effect of an acetylamino group in increasing the colour depth of the dyes. Therefore, *N*-acetyl J-acid is very useful as a coupling component in *o*-hydroxyazo dyes ranging in shade from orange to scarlet; for red dyes, *N*-acetyl H-acid suits this purpose.

Dyes **17–30** were allowed to react with NaOCl under the same conditions as above to yield colourless compounds. The rate constants obtained are also summarized in Table 4. These are strongly dependent on electrochemical characters and positional factors of the substituents on the naphthalene ring. Firstly, dyes **17** and **18**, lacking an amino group,

TABLE 4
Substituent Effect on Visible Absorption Maxima and Rate Constants of Decoloration for *o*-Hydroxyazo Dyes[a]



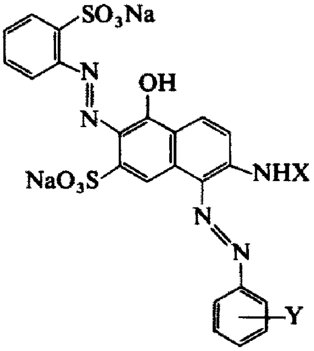
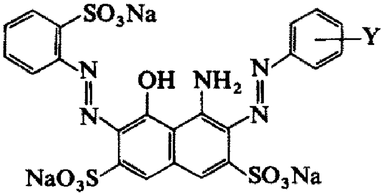
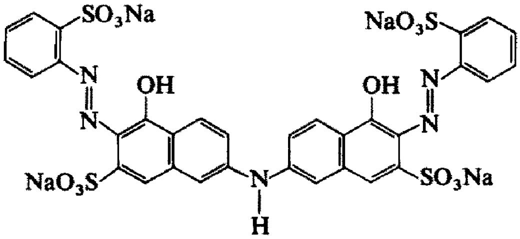
| *Dye no.* | *X* | *Y* | $\lambda_{max}$ *(nm)* | $\varepsilon_{max} \times 10^{-4}$ [b] | k $(s^{-1})$ |
|---|---|---|---|---|---|
| **17** | H | H | 485 | 2·16 | $3{\cdot}8 \times 10^{-4}$ |
| **18**[c] | H | 6-$SO_3Na$ | 489 | 2·52 | $5{\cdot}5 \times 10^{-4}$ |
| **19** | 5-$NH_2$ | H | 496 | 2·25 | $1{\cdot}3 \times 10^{-2}$ |
| **20** | 5-NHAc | H | 487 | 2·48 | $3{\cdot}2 \times 10^{-4}$ |
| **21** | 6-$NH_2$ | H | 473 | 3·80 | $8{\cdot}9 \times 10^{-2}$ |
| **22** | 6-$NH_2$ | 5-$SO_3Na$ | 473 | 3·63 | $8{\cdot}8 \times 10^{-2}$ |
| **23** | 6-NHAc | H | 482 | 2·92 | $4{\cdot}8 \times 10^{-4}$ |
| **24** | 6-$NHCH_3$ | H | 482 | 4·09 | $4{\cdot}2 \times 10^{-2}$ |
| **25** | 6-$N(CH_3)Ac$ | H | 484 | 2·73 | $1{\cdot}6 \times 10^{-4}$ |
| **26** | 7-$NH_2$ | H | 514 | 1·41 | $4{\cdot}4 \times 10^{-2}$ |
| | | | 403 | 1·50 | |
| **27** | 7-$NH_2$ | 6-$SO_3Na$ | 525 | 1·41 | $1{\cdot}2 \times 10^{-1}$ |
| | | | 406 | 1·39 | |
| **28** | 7-NHAc | H | 496 | 2·20 | —[d] |
| | | | 387 | 1·09 | |
| **29**[c] | 8-$NH_2$ | 6-$SO_3Na$ | 528 | 2·92 | $9{\cdot}5 \times 10^{-2}$ |
| **30** | 8-NHAc | 6-$SO_3Na$ | 524 | 2·94 | $2{\cdot}6 \times 10^{-4}$ |
| | | | 506 | 3·00 | |

[a] Initial concentration of dye $2{\cdot}0 \times 10^{-5}$ M and NaOCl $2{\cdot}0 \times 10^{-3}$ M, pH 7·0 and 24°C.
[b] In $dm^3/(mol\ cm)$.
[c] Data cited from Ref. 3.
[d] Could not be determined owing to abnormal discoloration.

are less reactive owing to the 2',3-disulphonate groups.[1] Secondly, the amino group drastically accelerates the rate, depending on its position in the following order: 5- < 7- < 6- ≤ 8- (dyes **19**, **26**, **21** and **29**). Thirdly, monomethylation of the amino group is effective for decrease in the rate (dye **24**). Finally, acetylation of it is more effective; the resulting acetylamino dyes **20**, **23**, **25** and **30** have reactivities similar to those of dyes **17** and **18**.

The susceptibility to decoloration of the amino-containing dyes is obviously attributed to the presence of an electron-rich –NH– group,

**TABLE 5**
Combined Effect of Two Sulphonatophenylazo Groups in Disazo Dyes from J-acid, *N*-methyl J-acid and H-acid

| *Structure* | *Dye no.* | $\lambda_{max}$ *(nm)* $(\varepsilon_{max} \times 10^{-4})^a$ | k $(s^{-1})^b$ |
|---|---|---|---|
|  | **31** (X = H, Y = *o*-SO$_3$Na) | 501<br>(4·70) | 9·8 × $10^{-3}$ |
| | **32** (X = CH$_3$, Y = *o*-SO$_3$Na) | 515<br>(4·61) | 5·8 × $10^{-3}$ |
| | **33** (X = CH$_3$, Y = *p*-SO$_3$Na) | 512<br>(4·73) | 6·2 × $10^{-3}$ |
|  | **34**[c] (Y = *o*-SO$_3$Na) | 601<br>(4·36) | 3·6 × $10^{-3}$ |
| | **35**[c] (Y = *p*-SO$_3$Na) | 596<br>(4·76) | 5·4 × $10^{-3}$ |
|  | **36** | 528<br>(9·80) | 4·2 × $10^{-3}$ |

[a] In dm$^3$/(mol cm).
[b] Initial concentration of dye 2·0 × $10^{-5}$ M and NaOCl 2·0 × $10^{-3}$ M, pH 7·0 and 24°C.
[c] Data cited from Ref. 3.

which is the most highly nucleophilic site in the molecule. Electrophilic attack at the nitrogen atom by a chloronium ion, to form a reactive *N*-chloro compound, initiates the decoloration, resulting in the cleavage of the azo linkage of the dyes.[8,9] An electron-withdrawing group substituted at the amino-nitrogen can make the parent dye more resistant to decoloration, provided that the substituent is intrinsically stable to the attack of a chloronium ion. An SO$_3$Na group does not always exert a chlorine resistance-improving effect, this being dependent on its position. For this series, the presence of the $SO_3Na$ group at the 3-position always shows improvement,[1] at the 5-position it does not when the 6-$NH_2$ group is present (dye **22**), and at the 6-position the effects worsened when the 7-$NH_2$ group is present (dye **27**); correlations of chlorine resistance with $SO_3Na$-positions are inconclusive.

### 2.5 Disazo dyes from J-acid, *N*-methyl J-acid and H-acid

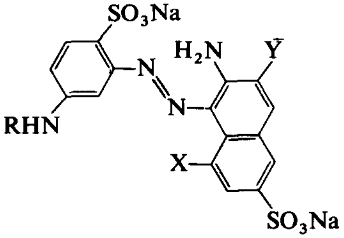
Table 5 shows that chlorine-sensitive *o*-aminoazo dyes can be converted into chlorine-resistant dyes by coupling diazotized aniline-2-sulphonic acid with them (dyes **31–35** versus dyes **11–13** and **16** in Table 3). A symmetrical J-acid dye (**36**) is also chlorine-fast.

### 2.6 Design of chlorine-fast reactive dyes

For designing chlorine-fast reactive dyes containing a free amino group and/or substituted amino groups, the question remains as to how well the

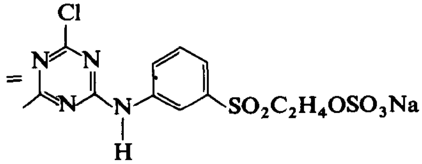
TABLE 6

Visible Absorption Maxima and Chlorine Fastness for *o*-Aminoazo Reactive Dyes with an NHR Group in the Diazo Component Residue



| *Dye no.* | *X* | *Y* | $\lambda_{max}$ *(nm)* | *Chlorine fastness* |
|---|---|---|---|---|
| **37** | H | H | 474 | 2 |
| **38** | $SO_3Na$ | H | 444 | 1 |
| **39** | H | $SO_3Na$ | 465 | 2–3 |
| **40** | OH | H | 515 | 2–3 |
| **41** | OH | $SO_3Na$ | 520 | 3 |

R is a heterobifunctional reactive system as follows:



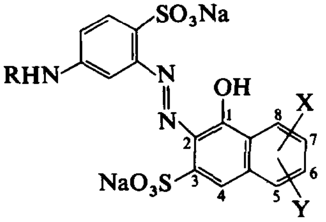
**VII**

structure–resistance relationships obtained above for the nonreactive dyes in water apply to the corresponding reactive dyes on cellulosic fibres. The constraints on mobility imposed by the dye–fibre interaction, including the dye–fibre bond formation, are certainly different from those imposed by the dye–water interaction, and, further, the position of the azo–hydrazone tautomeric equilibrium of these dyes may vary with differences in the media in which they are present. Nevertheless, when a fibre-reactive component NHR (R is a heterobifunctional reactive system comprising two different reactive groups, a $\beta$-sulphatoethylsulphone group and a monochlorotriazine group, as shown in formula **VII** of Table 6) is incorporated into the nonreactive dyes, the resulting reactive dyes, can exhibit in the dyed state on cellulosic fibres, the same structure–resistance relationships as the nonreactive dyes in water. Two sets of examples shown in Tables 6 and 7, in conjunction with Tables 1 and 4, respectively, present unambiguous evidence supporting this conclusion.

The two reactive groups in the NHR system of such reactive dyes may react with cellulosic fibres under mild alkaline conditions to form one or two covalent bonds, partially accompanied by the hydrolysis of these

TABLE 7

Chlorine Fastness of *o*-Hydroxyazo Reactive Dyes with an NHR Group in the Diazo Component Residue

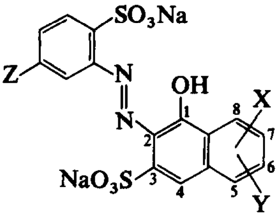


| *Dye no.* | *X* | *Y* | *Chlorine fastness* |
|---|---|---|---|
| **42** | H | H | 3–4 |
| **43** | H | 6-$SO_3Na$ | 3–4 |
| **44** | 6-$NH_2$ | H | 1 |
| **45** | 6-$NH_2$ | 5-$SO_3Na$ | 1 |
| **46** | 6-NHAc | H | 3–4 |
| **47** | 7-$NH_2$ | H | 1 |
| **48** | 7-$NH_2$ | 6-$SO_3Na$ | 1 |
| **49** | 7-NHAc | H | 2 |
| **50** | 8-$NH_2$ | 6-$SO_3Na$ | 1 |
| **51** | 8-NHAc | 6-$SO_3Na$ | 3–4 |

R = heterobifunctional reactive system **VII**.

## TABLE 8

Comparative Visible Absorption Maxima, $\lambda_{max}$ in nm ($\varepsilon_{max}$ in dm$^3$/(mol cm) × $10^{-4}$), of 2-(2'-Sulphonatophenylazo)-1-naphthol-3-sulphonates with and without an NHR Group in the Diazo Component Residue



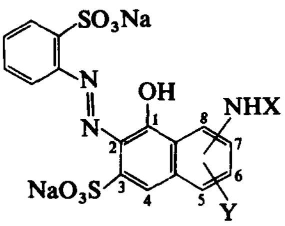
| *X* | *Y* | *Z*<br>*H* | <br>*NHR* |
|---|---|---|---|
| H | H | 485 (2·16) | 487 (2·34) |
| H | 6-SO$_3$Na | 489 (2·52) | 491 (2·43) |
| 6-NHAc | H | 482 (2·92) | 484 (2·78) |
| 7-NHAc | H | 496 (2·20) | 499 (2·06) |
|  |  | 387 (1·09) | 389 (0·91) |
| 8-NHAc | 6-SO$_3$Na | 524 (2·94) | 526 (2·82) |
|  |  | 506 (3·00) | 510 (2·84) |

*R* = heterobifunctional reactive system **VII**.
The data of *Z* = *NHR* are cited from Ref. 1.

groups. The resulting structural changes in the NHR unit have hardly any effect on the delocalized π-electron system of the chromogens, because these are chemically insulated from the changed parts by two or more single bonds. A prerequisite for the structure–resistance relationships to be valid is, therefore, that an NHR group is incorporated into nonreactive dyes so as not to change the electronic state of the dyes.

A suitable position for it to be incorporated is the 5'-position in 1-(2'-sulphonatophenylazo)-2-naphthylamine-6-sulphonates (Table 6 compared to Table 1) and in 2-(2'-sulphonatophenylazo)-l-naphthol-3-sulphonates (Table 8); in both series the presence of the 5'-NHR group has little effect on the visible absorption maxima of the dyes, irrespective of whether they exist as the azo or hydrazone form. When the NHR group is present in the 4'-position, the corresponding dyes have undesirable bathochromic shifts. Incorporation of it into the 3'- and 6'-positions is somewhat difficult to effect, and the resulting dyes would be less valuable practically because of their low affinities to cellulosic fibres due to steric crowding.

TABLE 9
Comparative Visible Absorption Maxima, $\lambda_{max}$ in nm ($\varepsilon_{max}$ in dm$^3$/(mol cm) × $10^{-4}$), of 2-(2'-Sulphonatophenylazo)-1-naphthol-3-sulphonates with and without an NHR Group in the Coupling Component Residue



| *Orientation of NHX* | *Y* | *X* | | |
|---|---|---|---|---|
| | | *H* | *Ac* | *R* |
| 6- | H | 473 (3·80) | 482 (2·92) | 483 (3·20) |
| 7- | H | 514 (1·41) | 496 (2·20) | 500 (2·01) |
| | | 403 (1·50) | 387 (1·09) | 394 (1·06) |
| 8- | 6-SO$_3$Na | 528 (2·92) | 524 (2·94) | 534 (3·29) |
| | | | 506 (3·00) | 514 (3·26) |

*R* = heterobifunctional reactive system **VII**.
The data of *X* = *R* are cited from Ref. 1.

Table 9 shows that when an NHR group is present on the coupling component residue, the $\lambda_{max}$ and $\varepsilon_{max}$ of these dyes are almost the same as those of the dyes containing an NHAc group in place of the NHR group. Therefore, the NHR-containing dyes are relatable by way of the NHAc-containing dyes, to the corresponding nonreactive dyes.

In the amino-containing azo dyes examined, the *o*-aminoazo dyes are generally more resistant to chlorine than the amino-containing *o*-hydroxyazo dyes. Since the former dyes exist predominantly in the azo form, it is essential, for an increase in the chlorine resistance, to protect the amino group, which is the most active site in the dye molecule, against electrophilic attack of a chloronium ion. The amino group could not, however, undergo acylation such as acetylation and triazinylation; an approach to this problem is limited to incorporation of a sulphonate group into the neighbouring position to it (dye **5** in Table 1 and dye **41** in Table 6).

The lower $\varepsilon_{max}$ of *o*-aminoazo dyes of this type compared to analogous *o*-hydroxyazo dyes, however, makes these dyes unsuitable for meeting commercial requirements of reactive dyes for cellulose. In contrast, the disazo dyes derived from the *o*-aminoazo dyes comprising J-acid, *N*-

methyl J-acid and H-acid (Table 5) give much higher $\varepsilon_{max}$ and better chlorine resistance. These results are exclusively applicable to the design of chlorine-fast reactive dyes with deep shade.

Amino-containing *o*-hydroxyazo dyes are widely applicable for this purpose, since replacement of an amino-hydrogen by an electron-withdrawing substituent such as acetyl, benzoyl and triazinyl is readily achievable. It is noteworthy that such replacement not only imparts high chlorine resistance, but also ensures that both or either of the hue and the deep shade are similar to those of the original dyes (Table 9). Thus, the deleterious amino group can be converted into a useful imino linkage connecting a chromogenic system to a strong electron-withdrawing N-heterocyclic reactive system such as halogenated triazines and pyrimidines.

## 3 EXPERIMENTAL

### 3.1 Materials

First- or technical-grade reagents were used for the syntheses. Special-grade reagents or their equivalents, and water purified by ion exchange, were used for analysis, dyeing and fastness test. The scoured and bleached unmercerized cotton knitted fabrics for dyeing were obtained from Nitto Boseki Co. Ltd.

### 3.2 Measurement

Visible absorption maxima were recorded on a Hitachi UV-visible spectrophotometer model 228A, using water as solvent.

### 3.3 Synthesis

All dyes were synthesized as sodium salts following the previously reported method[10–12] and purified by repeated recrystallization until chromatographically pure.

### 3.4 Pseudo first-order rate constant

A $2.0 \times 10^{-5}$ M solution of each of dyes **1–5**, **11–15**, **17**, **19–28**, **30–33** and **36** was prepared, using an aqueous pH 7.0 buffer solution (M/15 $KH_2PO_4$–M/15 $Na_2HPO_4$ of 4:6 v/v ratio). A known amount of freshly estimated NaOCl solution (100 mol per mole of dye) was added to the solution, while ensuring homogeneity by vigorous stirring. The reaction mixture was then quickly transferred to a 1 cm quartz cell in the spectrophotometer, and the resultant absorbance at $\lambda_{max}$ of each dye solution was monitored over 50 to 100% reaction at 24°C.

The above method was repeated with 30 mol of NaOCl per mole of dye, pH 6.0 (M/15 $KH_2PO_4$–M/15 $Na_2HPO_4$ of 9:1 v/v ratio) and 20°C instead of 100 mol of NaOCl per mole of dye, pH 7.0 and 24°C, respectively, for dyes **4** and **6–10**.

The pseudo first-order rate constant $k$ was obtained from the initial slope of $\ln A_0/A_t$ versus $t$ plot, where $A_0$ and $A_t$ are the absorbance at times 0 and $t$ (in seconds), respectively. The half-life was calculated from the equation of $t_{1/2} = (1/k) \times \ln 2$.

### 3.5 Dyeing

Each of dyes **37–51** (0.1 g) was dissolved in water (200 ml). Sodium sulphate (10 g) and cotton (10 g) were added to the dye solution, which was then heated to 60°C. After 20 min with stirring, sodium carbonate (4.0 g) was added, and dyeing was continued at the same temperature for 1 h. The dyed cotton was rinsed with cold water, then thoroughly washed with boiling water to remove unfixed dyes, and finally dried at 80°C. Of the respective controls for comparison, those giving dyeings of relatively high or low colour depth were redyed so as to give dyeings having a similar colour depth to each other.

### 3.6 Chlorine fastness

The test was carried out on the dyeings obtained according to ISO 105–E03 (effective chlorine: 20 mg/dm$^3$, 25°C, 4 h). The results were assessed in ratings: 1, poor; 2, fair; 3, good; 4, very good; 5, excellent.

## 4 CONCLUSIONS

The most important finding of this study is that not all azo dyes based on 2-(2'-sulphonatophenylazo)-1-naphthol-3-sulphonates being chlorine-fast are resistant to chlorine; susceptible azo dyes, usually those containing an active amino or substituted amino group on the naphthalene ring, can undergo quite profound decoloration, depending on the reactivity and environment of the group. The problem is best resolved by reducing the electron density of the amino-nitrogen, which is possible without difficulty since *N*-acylation readily occurs. Some protection can be obtained by incorporation of a(n) (un)substituted phenylazo group into the neighbouring position of the amino group, provided that J-acid, *N*-methyl J-acid and H-acid are used as coupling components of susceptible *o*-hydroxyazo dyes. These results, including those obtained in the *o*-aminoazo dyes, are applicable to the design of chlorine-fast reactive dyes ranging in shade from orange through red to navy blue.

## ACKNOWLEDGEMENT

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