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Photofading of Monochlorotriazinyl Reactive Dyes on Cellulose under Wet Conditions

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ABSTRACT

The fading of seven monochlorotriazinyl (MCT) reactive azo dyes (three monoazo and four disazo) on cellulose was investigated under wet conditions. It was shown by spectral analysis that these dyes on cellulose were faded via photoreduction on exposure in de-aerated water in spite of the absence of substrate. Oxygen suppressed the reductive fading for some of the dyes or inhibited it, resulting in oxidative fading. Thus four dyes were photoreduced on exposure in aerated water at a rate lower than that in de-aerated water, whilst the other dyes were photo-oxidized at a higher rate. The chemical structure of the dyes and the environmental conditions during exposure determine whether oxidative or reductive fading of MCT dyes on cellulose occurs under wet conditions.

1 INTRODUCTION

The photofading of vinylsulfonyl (VS) reactive dyes on cellulose under wet conditions in the presence of oxygen and in the absence of substrate has been shown to occur via photo-oxidation by singlet oxygen.[1–3] Although

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photosensitivity and the ease with which VS dyes are oxidized vary widely with the dye structure, the lightfastness of the dyes depends mainly on the latter property. In the presence of substrate and in the absence of oxygen,[4,5] fading occurs only by photoreduction. In the presence of oxygen and substrate,[4,5] photo-oxidation and/or photoreduction occur, depending on the conditions. Some VS dyes, such as C.I. Reactive Red 22 and Black 5 on cellulose, however, undergo reductive fading on exposure in de-aerated water irrespective of the absence of substrate, and also on exposure on dry cellulose.[6] Thus the fading behavior of dyes on cellulose depends on the chemical structure of the dye and on the conditions of exposure.

The fading of monochlorotriazinyl (MCT) dyes under wet conditions has been explained by a radical mechanism by Datyner *et al.*[7] Calin *et al.*[8] concluded that MCT dyes were faded after the dye–fiber bond was broken. Hladík & Švec[9] studied the photochemical degradation of five mono- and di-chlorotriazinyl dyes, and discussed the rate of photodegradation in connection with the chemical structure, dye–fiber bond and substituents on the triazine ring. The poor lightfastness was explained in terms of a facile fission of the azo group between the two naphthalene rings on exposure. Baumgarte & Wegerle[10] have reviewed the photofading of reactive dyes on cellulose, noting their own new data.

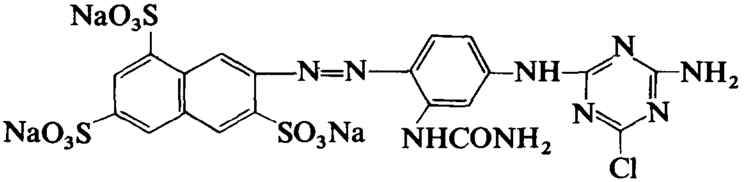
In the present paper the fading behavior of seven MCT azo dyes on cellulose is examined by spectral analysis under various wet conditions. Photo-oxidation of the dyes on exposure in Rose Bengal solution and photoreduction on exposure in aqueous DL-mandelate and in de-aerated water were shown to occur. Reference to the absorption spectra of the photodecomposition products is used to elucidate whether oxidative or reductive fading on exposure in aerated water occurs.

2 EXPERIMENTAL

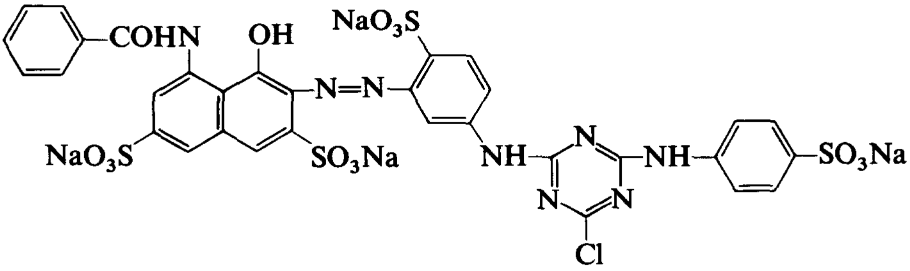
2.1 Dyes used

Seven MCT dyes and Rose Bengal were used. The chemical structure of the MCT dyes, their C.I. numbers and their abbreviations are as follows.

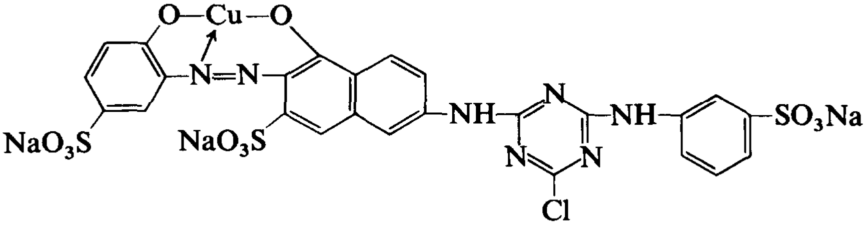
(1) A monoazo dye (Yellow R)



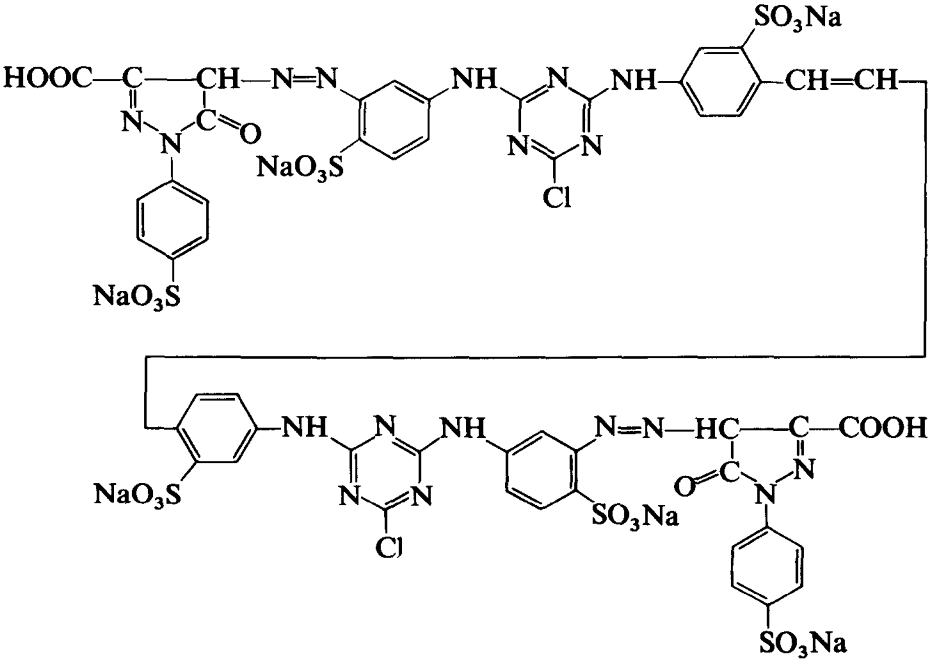
(2) C.I. Reactive Red 4; C.I. 18105 (Red 4)



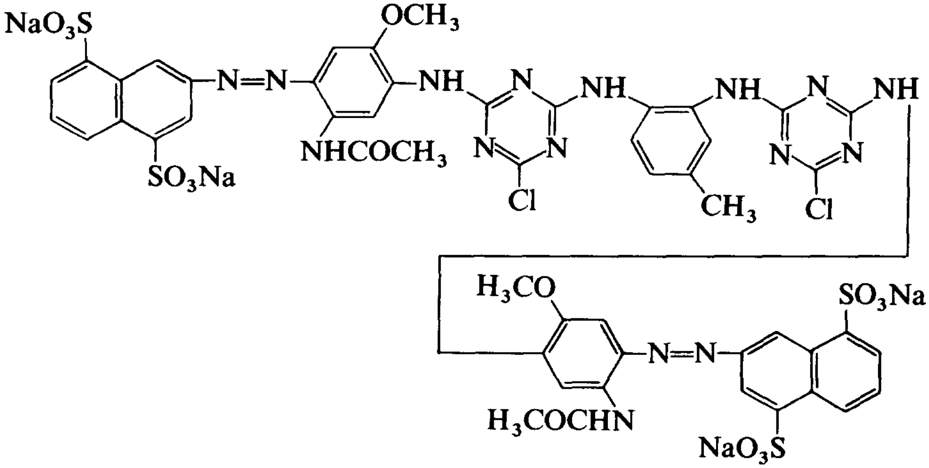
(3) C.I. Reactive Red 7; C.I. 17912 (Red 7)



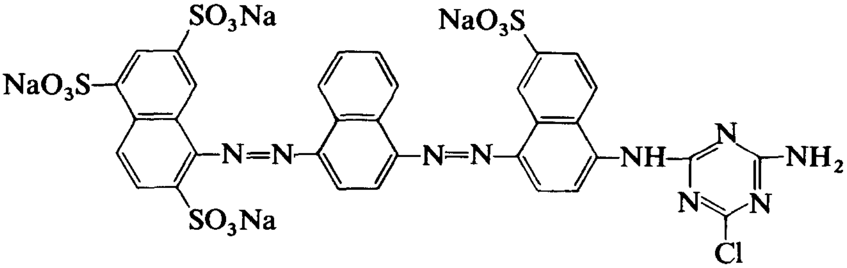
(4) A stilbene pyrazolinyl disazo dye (Yellow)



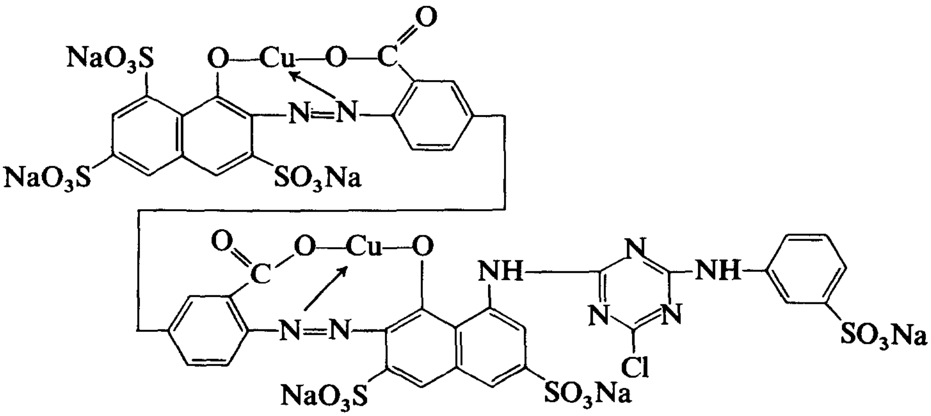
(5) An *o*-phenylenediamine disazo dye (Orange)



(6) A disazo dye (Brown)



(7) A 1:2 copper-complex disazo dye (Blue-2Cu)



The MCT dyes were supplied by Nippon Kayaku Co. Ltd, Tokyo, Japan. Red 7 was a commercial product (Cibacron Rubine E-A) manufactured by the Ciba–Geigy Corp. They were used without further purification.

2.2 Dyeing and exposure

In the dyeing of cellophane films, sodium sulfate ($75\,g\,dm^{-3}$) was added stepwise to the dyebath (liquor ratio 300:1) containing a given concentration of dye ($0{\cdot}05$–$0{\cdot}10\,g\,dm^{-3}$) to obtain an exhaustion of more than 80% at 80°C. In the case of Blue-2Cu, the exhaustion was lower than 80%. Sodium carbonate ($20\,g\,dm^{-3}$) was then added to the dyebath to obtain fixation and dyeing was continued for 90 min. After dyeing, the dyed films were scoured with 10% aqueous dimethylformamide (DMF) solution at 60°C until no coloration of the solution was observed; the films were then scoured three times with boiling water containing a non-ionic surfactant ($2\,g\,dm^{-3}$) to remove DMF. The absorption spectra for Yellow R, Orange and Blue-2Cu on cellophane were changed by the DMF scouring. The immersion of the dyed film into aqueous DMF solution was repeated until no coloration of the scouring solution was observed and the final absorption spectra of the dyes on cellulose were then obtained.

The method of exposure and the apparatus were the same as those previously used.[1,2,6] Aqueous sodium DL-mandelate solutions were freshly prepared before every exposure experiment by neutralizing the acid solution with aqueous sodium hydroxide, and the concentrations were adjusted by dilution. A sheet of dyed film was set in a glass cell filled with the aqueous solution and was exposed in a fadeometer. Other chemicals used were of reagent grade.

The absorption spectra of the dyes on cellophane were measured using a double monochro spectrophotometer (U-best 50; JASCO Corp., Tokyo, Japan) and were treated by a spectral analyzer integrated with the photometer.

3 RESULTS AND DISCUSSION

3.1 Fading of MCT dyes on cellulose under anaerobic conditions

3.1.1 Exposure in aqueous DL-mandelate

Most VS azo dyes are photoreduced on exposure in an anaerobic substrate solution to yield the corresponding amino compounds bound with cellulose.[1,2] In the initial experiments the fading of seven MCT azo dyes on cellulose was examined by exposure in anaerobic aqueous sodium DL-mandelate ($0{\cdot}05\,mol\,dm^{-3}$). Their fading behavior on exposure is shown in Fig. 1(a).

The rate of fading in aqueous DL-mandelate appeared to increase with time of exposure, contrary to the fading in aerated water. Concentration

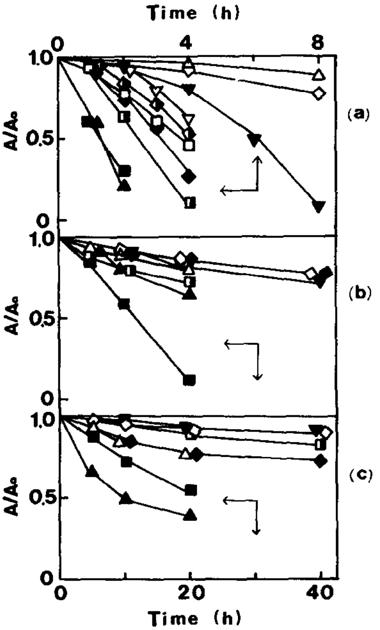


Fig. 1. Fading behavior for monochlorotriazinyl reactive dyes on cellulose on exposure: (a) in anaerobic aqueous sodium DL-mandelate (0·05 mol dm^{-3} + 0·5 mol NaCl dm^{-3}); (b) in de-aerated water; and (c) in aerated water. Dye, symbol [initial concn on cellulose × 10^{-2} mol kg^{-1}]: Yellow R, ▽ [(a) 1·35], ▼ [(a) 1·92, (b) 1·90, (c) 1·88]; Red 4, ⬗ [(a) 1·44], ◆ [(a) 0·852, (b) 1·02, (c) 0·963]; Red 7, ▲ [(a) 0·743, (b) 0·720, (c) 0·739]; Yellow, △ [(a) 0·556, (b) 0·556, (c) 0·506]; Orange, ◇ [(a) 1·48, (b) 1·32, (c) 1·39]; Brown, □ [(a) 0·537], ◨ [(a) 0·415, (b) 0·412, (c) 0·414] and Blue-2Cu, ■ [(a) 0·769, (b) 0·748, (c) 0·686].

dependence on the rate of fading of Yellow R, Red 4 and Brown in aqueous DL-mandelate was also examined at different concentration levels, as shown in Fig. 1(a). They showed a decrease in the rate of fading with increase in the concentration on cellulose. Each sample was dyed within the range of concentration where the dyes showed a smaller concentration dependence on the rates of fading. A comparison of the rates of fading was then made with dyed samples whose absorbance at λ_{max} was in the range 0·8–0·9 (Table 1). The order of the rate of fading was as follows:

$$\text{Red 7} \simeq \text{Blue-2Cu} > \text{Brown} > \text{Red 4} > \text{Yellow R} > \text{Orange} > \text{Yellow} \quad (1)$$

The absorption spectra of seven dyes on cellophane and those of the photodecomposition products after the exposure are shown in Figs 2–8. On exposure of Yellow and Orange, a higher concentration of DL-mandelate was used to obtain the photoreduction products (Figs 5 and 6). These MCT dyes were reduced by aqueous sodium dithionite (0·1 mol dm^{-3}, 70°C, 30 min), giving products having the same absorption spectra as those of the

TABLE 1

Relative Rate, A/A_0, of Fading (Time of Exposure) and Fading Behavior of Monochlorotriazinyl Dyes on Cellulose under Various Conditions

Dye	*Exposure in*			
	MA soln,[a] *4 h*	*De-aerated water, 20 h*	*Aerated water, 20 h*	*Aerated RB soln,*[b] *4 h*
Yellow R	0·799 (Red.)	0·847 (Red.)	0·942 (Red.)	0·900 (Oxid.)
Red 4	0·540 (Red.)	0·873 (Red.)	0·771 (Oxid.)	0·436 (Oxid.)
Red 7	0·586[c] (1 h, Red.)	0·645 (Red.)	0·386 (Oxid.)	0·702 (20 min, Oxid.)
Yellow	0·961 (Red.)	0·829 (Red.)	0·761 (Oxid.)	0·708 (Oxid.)
Orange	0·910 (Red.)	0·874 (Red.)	0·930 (Red.)	0·939 (Oxid.)
Brown	0·450 (Red.)	0·718 (Red.)	0·886 (Red.)	0·785 (Oxid.)
Blue-2Cu	0·589[d] (1 h, Red.)	0·132 (Red.)	0·552 (Red.)	0·507[e] (Oxid. + Red.)

Abbreviations: MA, sodium DL-mandelate; Oxid., oxidation; Red., reduction.

[a] Anaerobic aqueous MA (0·05 mol dm^{-3} + 0·5 mol NaCl dm^{-3}) solution.

[b] Aerated aqueous Rose Bengal (1·0 × 10^{-5} mol dm^{-3} + 0·5 mol Na_2SO_4 dm^{-3}) solution.

[c] A/A_0 for other times of exposure: 0·211 (2 h) and 0·023 (3 h).

[d] A/A_0 for other times of exposure: 0·302 (2 h) and 0·023 (3 h).

[e] A/A_0 for other times of exposure: 0·942 (20 min).

The absorbance at λ_{max} for dyed film was in the range 0·8–0·9.

photodecomposition products on exposure, except for Yellow, Red 7 and Blue-2Cu. The differences in the absorption spectra for the latter three dyes are examined in the next section (cf. Section 3.1.2). During the reduction of the disazo dyes on cellophane, the corresponding monoazo intermediates were recognized as being formed, from the color change or the change in the absorption spectrum.

The presence of amino groups in the photoreduction products was confirmed by diazotization and coupling with β-naphthol, except for those from Yellow R.

The photoreduction of either of the azo groups for the four disazo dyes gives monoazo intermediates, which are very readily photoreduced to yield the corresponding photodecomposition products (Figs 5–8), because the concentration of the monoazo intermediates was always negligible during exposure.

In the case of the asymmetric disazo dyes, such as Brown and Blue-2Cu, the azo group nearest to the triazine ring may be preferentially photoreduced. The formation of monoazo intermediates for Brown, showing low absorption in the visible region, was confirmed to be negligible, as in the case of symmetrical disazo dyes, while a small amount of such intermediates for Blue-2Cu was recognized (Figs 7 and 8).

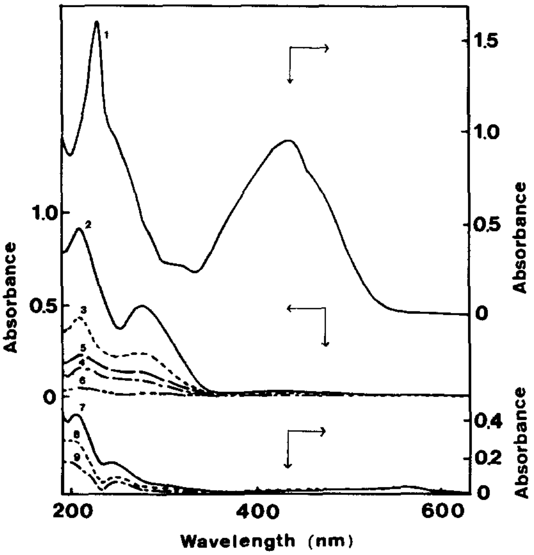


Fig. 2. Absorption spectra for Yellow R (1·92 × 10^{-2} mol kg^{-1}) on cellophane (1); those for the photoreduction products of Yellow R exposed in anaerobic aqueous sodium DL-mandelate (0·05 mol dm^{-3}) for 8 h (2), 6 h (3) and 4 h (4); those for the photoreduction products of Yellow R exposed in de-aerated water for 40 h (5) and in aerated water for 80 h (6) after subtracting the spectrum of Yellow R of corresponding concentration; and those for the photo-oxidation products for Yellow R (2·32 × 10^{-2} mol kg^{-1}) on cellulose exposed in an aerobic Rose Bengal (1·0 × 10^{-5} mol dm^{-3}) solution for 40 h (7), 20 h (8) and 10 h (9) after subtracting the spectrum of Yellow R of corresponding concentration. The absorption spectrum for the thermal product on cellulose with sodium dithionite coincided with spectrum 2.

3.1.2 Multi-step photoreduction

No change in the absorption spectra of the thermal products for Yellow, Red 7 and Blue-2Cu was observed on repeating the treatment with a sodium dithionite solution. The absorption spectrum of the product for Yellow showed an absorption band at λ_{max} 356 nm, that for Red 7 at λ_{max} 278 nm with a shoulder at 315 nm, and that for Blue-2Cu showed a broad band (λ_{max} 341 nm) in the near-UV region (Figs 4, 5 and 8). These products may correspond to photoreduction intermediates which can absorb radiation longer than 290 nm, and undergo further photoreduction, since carbon-arc light of a fadeometer contains radiation longer than 290 nm.[1,4]

In order to confirm this conclusion, the thermally reduced products for Yellow, Red 7 and Blue-2Cu on cellophane were exposed in anaerobic aqueous sodium DL-mandelate (0·50 mol dm^{-3}). The absorption spectra of the end-products seems to be the same as those of the corresponding photoreduction products on cellulose exposed in DL-mandelate (0·05 mol dm^{-3}) solution for a long period (Figs 4, 5 and 8). The absorption spectra of

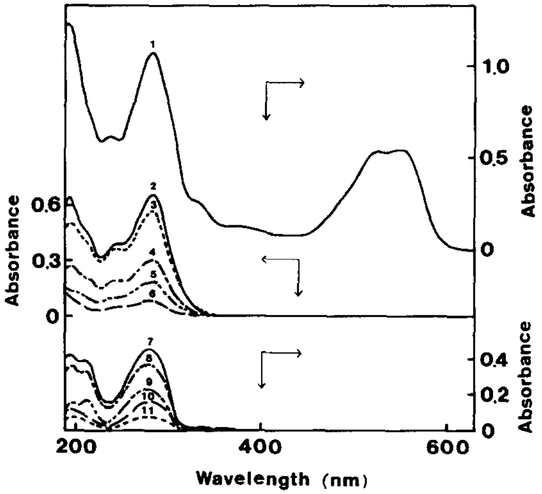


Fig. 3. Absorption spectra (1) for Red 4 ($8{\cdot}52 \times 10^{-3}$ mol kg^{-1}) on cellophane; that of the thermal product with aqueous sodium dithionite (2); those of the photoreduction products for Red 4 exposed in anaerobic aqueous sodium DL-mandelate (0·05 mol dm^{-3}) for 4 h (3) and 3 h (4); those of the photoreduction products on exposure in de-aerated water for 40 h (5) and 10 h (6) after subtracting the spectrum of Red 4 of corresponding concentration; and those of the photo-oxidation products for Red 4 ($7{\cdot}97 \times 10^{-3}$ mol kg^{-1}) on cellophane exposed in an aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 40 h (7), 20 h (8) and 10 h (9), and exposed in aerated water for 40 h (10) and 10 h (11) after subtracting the spectrum of Red 4 of corresponding concentration.

Red 7 and Blue-2Cu on cellulose, exposed in DL-mandelate solution for 3 and 4 h, respectively, show that the photodecomposition products contain the thermal products and their photoreduction end-products (spectra 2 and 7–9 in Fig. 4, and spectra 1, 8 and 9 in Fig. 8).[11,12] Both the azo groups of Yellow may be photoreduced on exposure in a DL-mandelate solution to yield a stilbene derivative, which is the thermal product, and which is further photoreduced on subsequent exposure as examined above (spectra 2, 3 and 6–8 in Fig. 5). Although no chemical structure for the intermediates and end-products for Red 7 and Blue-2Cu could be determined, their fading behavior may be explained by the same multi-step mechanism as that of Yellow, since the absorption spectra for such intermediates and end-products for Red 7 and Blue-2Cu were observed in the photoreduction processes. The carbonyl groups of these dyes may take part in the photoreaction, since carbonyl chromophores are known to have the possibility to undergo various photochemical reactions.[13]

3.1.3 Exposure in de-aerated water

On exposure of these dyes on cellulose in de-aerated water, they underwent reductive fading, which was confirmed by the absorption spectra of the

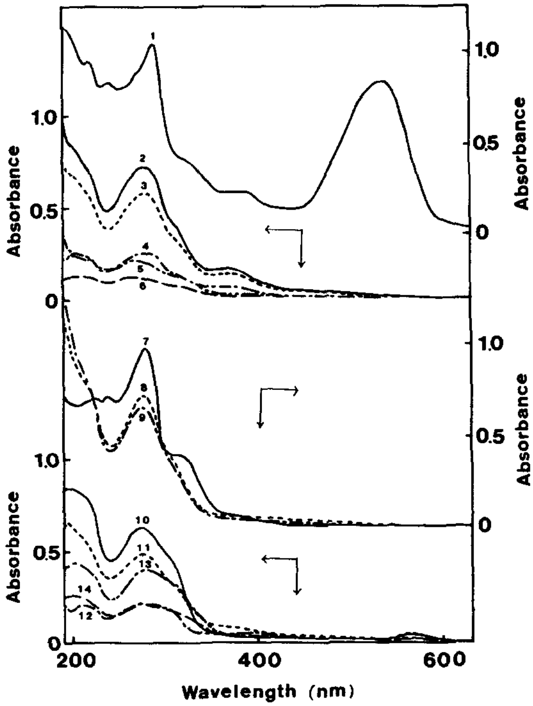


Fig. 4. Absorption spectra for Red 7 ($7{\cdot}43 \times 10^{-3}$ mol kg^{-1}) on cellophane (1); those of the photoreduction products for Red 7 exposed in anaerobic aqueous sodium DL-mandelate ($0{\cdot}05$ mol dm^{-3}) solution for 4 h (2), 2 h (3) and 1 h (4); those of the photoreduction products on exposure in de-aerated water for 20 h (5) and 10 h (6) after subtracting the spectrum of Red 7 of corresponding concentration; the spectra of the thermally reduced product (7) for Red 7 with aqueous sodium dithionite ($0{\cdot}1$ mol dm^{-3}, 70°C, 30 min) after exposure in anaerobic aqueous sodium DL-mandelate ($0{\cdot}5$ mol dm^{-3}) for 20 h (8) and 10 h (9); those of the photooxidation products for Red 7 ($7{\cdot}13 \times 10^{-3}$ mol kg^{-1}) exposed in an aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 12 h (10), 40 min (11) and 20 min (12); and those of the photoreduction products on exposure in aerated water for 20 h (13) and 5 h (14) after subtracting the spectrum of Red 7 of corresponding concentration.

photodecomposition products (Figs 2–8). The fading behavior for MCT dyes in de-aerated water is shown in Fig. 1(b). The order of rates of fading was as follows:

$$\text{Blue-2Cu} > \text{Red 7} > \text{Brown} > \text{Yellow} > \text{Yellow R} > \text{Red 4} \simeq \text{Orange} \quad (2)$$

The order of this fading, and that in Section 3.1.1, are partially different. In general, the order in the rate of photoreduction for various dyes is unchanged with substrates.[4,5] Comparing the rate of fading in these two cases, however, the photoreduction for Red 4 and Red 7, on exposure in de-aerated water, was more accelerated by DL-mandelate than the other MCT dyes, whilst the fading of Yellow and Orange in DL-mandelate solution was

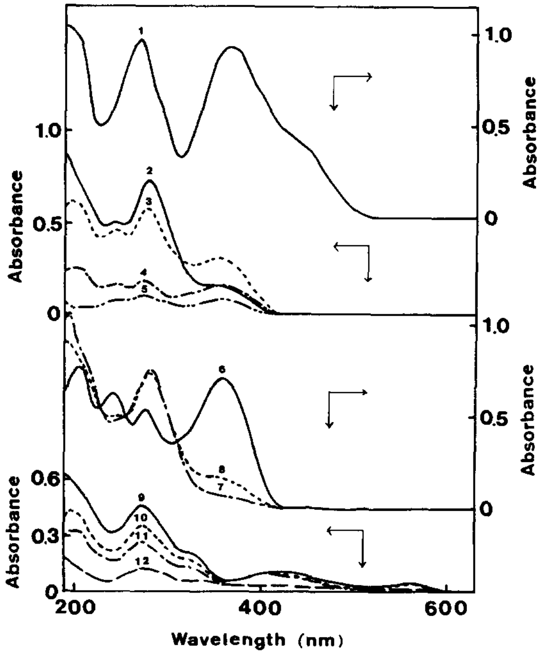


Fig. 5. Absorption spectra for Yellow ($5{\cdot}56 \times 10^{-3}$ mol kg^{-1}) on cellophane (1); those of the photoreduction products for Yellow exposed in anaerobic aqueous sodium DL-mandelate ($0{\cdot}50$ mol dm^{-3}) solution for 20 h (2), 10 h (3) and 5 h (4), and in de-aerated water for 20 h (5) after subtracting the spectrum of Yellow of corresponding concentration; the spectrum of the thermally reduced product (6) for Red 7 with aqueous sodium dithionite ($0{\cdot}1$ mol dm^{-3}, 70°C, 30 min); those of the thermal product on cellulose after exposure in anaerobic aqueous sodium DL-mandelate ($0{\cdot}50$ mol dm^{-3}) for 20 h (7) and 10 h (8); and those of the photo-oxidation products for Yellow ($5{\cdot}89 \times 10^{-3}$ mol kg^{-1}) exposed in an aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 20 h (9), 10 h (10) and 4 h (11), and in aerated water for 10 h (12) after subtracting the spectrum of Yellow of the corresponding concentration.

less accelerated than the others (cf. Table 1). The acceleration effects for Yellow R, Brown and Blue-2Cu were in between both cases. Thus the reductive fading for monoazo dyes on cellulose on exposure in de-aerated water was more accelerated by the substrate than that for similar fading of some symmetric disazo dyes.

Although Blue-2Cu has a high ability to abstract hydrogen from some substrates on exposure, whether or not this dye has a phototendering property with cellulose has not yet been examined.

3.2 Fading of MCT dyes on cellulose under aerobic conditions

3.2.1 Exposure in Rose Bengal solution

In the case of VS dyes examined in previous papers,[1-5] the absorption

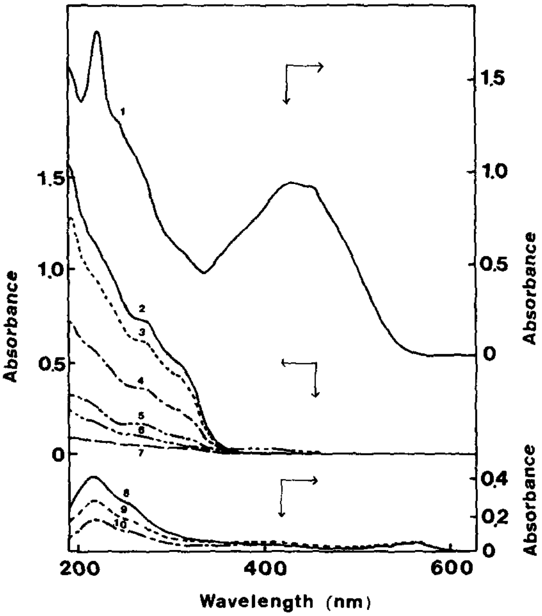


Fig. 6. Absorption spectra for Orange ($1{\cdot}48 \times 10^{-2}$ mol kg^{-1}) on cellophane (1); those of the photoreduction products for Orange exposed in anaerobic aqueous DL-mandelate ($0{\cdot}50$ mol dm^{-3}) solution for 30 h (2), 20 h (3), 10 h (4) and 5 h (5), in aerated water for 10 h (6), and in de-aerated water for 20 h (7) after subtracting the spectrum of Orange of the corresponding concentration; and those of the photo-oxidation products for Orange ($1{\cdot}41 \times 10^{-2}$ mol kg^{-1}) on cellophane exposed in an aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 40 h (8), 20 h (9) and 10 h (10) after subtracting the spectrum of Orange of the corresponding concentration. The absorption spectrum for the thermal product on cellulose with sodium dithionite coincided with spectrum 2.

spectra of VS dyes on cellophane after exposure in aerated water were similar to those after exposure in aerated Rose Bengal (RB) solution, with some exceptions.[6] In order to keep the amount of RB adsorption constant irrespective of variation in the number of sulfonic acid groups, a large amount of sodium sulfate was added to the RB solution. No effect of the addition of sodium sulfate to the dye solution on the redox potential of MCT dyes was confirmed by cyclic voltammetry.

The absorption spectra of the photodecomposition products for MCT dyes on exposure in an aerated RB solution are shown in Figs 2–8. As in the case of VS dyes examined in previous papers,[4–6] the absorption spectra of the photodecomposition products for these MCT dyes exposed in aerated RB solution were observed to be different from those of the corresponding photoreduction products. There were large differences in the absorption spectra of the photoreduction and photo-oxidation products for Yellow, Yellow R, Orange, Red 4, Brown and Blue-2Cu, and small differences for

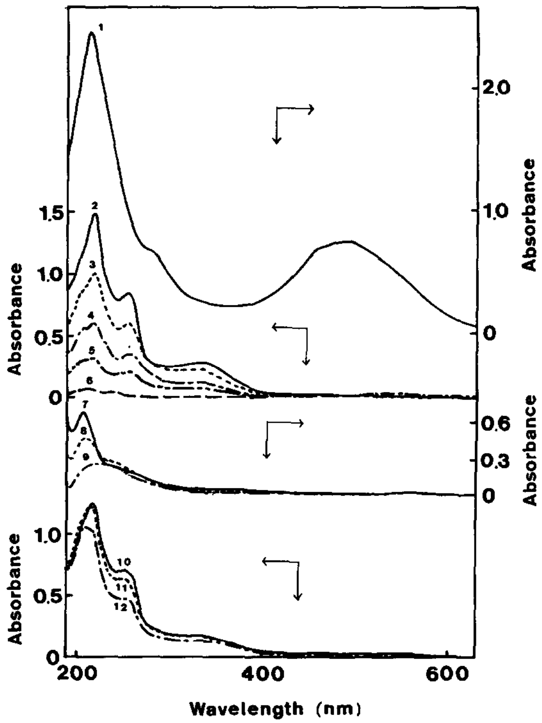


Fig. 7. Absorption spectra for Brown ($5{\cdot}37 \times 10^{-3}$ mol kg^{-1}) on cellophane (1); those of the photoreduction products for Brown exposed in anaerobic aqueous DL-mandelate ($0{\cdot}05$ mol dm^{-3}) solution for 10 h (2), 8 h (3) and 4 h (4), and exposure in de-aerated water for 20 h (5) and in aerated water for 40 h (6) after subtracting the spectrum of Brown of corresponding concentration; those of the photo-oxidation products for Brown ($5{\cdot}36 \times 10^{-3}$ mol kg^{-1}) exposed in aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 60 h (7), 40 h (8) and 20 h (9) after subtracting the spectrum of Brown of the corresponding concentration; and those for the thermally reduced products of the samples (spectra 7–9) after exposure in Rose Bengal solution for 60 h (10), 40 h (11) and 20 h (12). The absorption spectrum for the thermal product on cellulose with sodium dithionite coincided with spectrum 2.

Red 7. Thus it was confirmed that photo-oxidation products for these MCT dyes were always formed by exposure in aerated RB solution.

The ease with which MCT dyes are oxidized, and the rate constants of reaction with singlet oxygen, have been examined elsewhere.[14] The order of the rate of fading in RB solution was as follows (Table 1):

Red 7 > Red 4 > Blue-2Cu > Yellow > Brown > Yellow R > Orange (3)

Comparing this sequence (3) with the sequence (1) (Section 3.1.1), variations in the order are recognized for Blue-2Cu, Yellow and Yellow R. The fading of Yellow in RB solution became relatively faster and that of

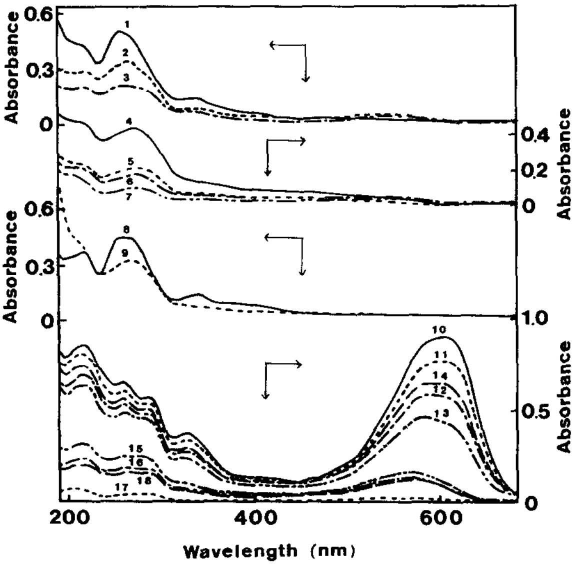


Fig. 8. Absorption spectra of the photoreduction products for Blue-2Cu ($7{\cdot}69 \times 10^{-3}$ mol kg^{-1}) on cellophane after exposure in anaerobic aqueous DL-mandelate ($0{\cdot}05$ mol dm^{-3}) solution for 3 h (1), 2 h (2) and 1 h (3), and exposure in de-aerated water for 20 h (4) and 10 h (5) and in aerated water for 20 h (6) and 10 h (7) after subtracting the spectrum of Blue-2Cu of the corresponding concentration; the spectrum of the thermally reduced product (8) for Blue-2Cu with aqueous sodium dithionite ($0{\cdot}1$ mol dm^{-3}, 70°C, 30 min); that of the thermal product on cellulose after exposure in anaerobic aqueous sodium DL-mandelate ($0{\cdot}5$ mol dm^{-3}) for 10 h (9); that for Blue-2Cu ($7{\cdot}13 \times 10^{-3}$ mol kg^{-1}) on cellophane (10); those of the photo-oxidation products after exposure in aerobic Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 40 min (11), 2 h (12) and 4 h (13), and in oxygen-saturated Rose Bengal solution for 40 min (14); those for the photo-oxidation products of Blue-2Cu exposed in the Rose Bengal solution for 4 h (15), 2 h (16) and 40 min (17) after subtracting the spectrum of Blue-2Cu of the corresponding concentration; and that for Blue-2Cu on cellulose after exposure in oxygen-saturated Rose Bengal ($1{\cdot}0 \times 10^{-5}$ mol dm^{-3}) solution for 40 min (18). The spectra for Blue-2Cu and the photo-oxidation products after exposure in aerobic Rose Bengal solution for 40 min were similar to those after exposure in oxygen-saturated solution for 20 min.

Blue-2Cu and Yellow R slower. This is because Yellow R, Orange, Brown and Blue-2Cu have a tendency to undergo reductive fading on exposure in aerated water, as is shown below (cf. Section 3.2.4). Yellow has a moderate tendency to show oxidative fading, although it has a very small rate of reductive fading in DL-mandelate solution.

Considering the azo–hydrazone tautomerism of a dye, the hydrazone form reacts with singlet oxygen generated by energy transfer mainly from the triplet state of both the forms[15–17] and the triplet state of the azo form abstracts hydrogen from the substrate to yield semi-reduced dye.[18] When the azo–hydrazone tautomerism is not inclined towards either side, the rates of reductive and oxidative fading may have a similar order. This may be the case with Red 4 and Red 7. Yellow R, Orange and Brown exist predominantly in the azo form, whilst Yellow contains the hydrazone form to some extent. This is why Yellow R, Orange and Brown have small rates of oxidative fading, whenever it occurs, but Yellow has a relatively large rate of oxidative fading. Thus reductive and oxidative fading behavior for these MCT dyes may be explained in terms of azo–hydrazone tautomerism.

3.2.2 Exposure of Brown in aerobic Rose Bengal solution

The azo group nearest to the triazine ring in Brown was readily reduced on exposure under anaerobic conditions, and this dye showed a low rate of oxidative fading under aerobic conditions. Brown on cellulose, when exposed in aerated RB solution, gave a photo-oxidation product with a low absorption band in the UV region (spectra 7–9 in Fig. 7). The increase in the amount, as shown by the absorbance in the UV region, of the photodecomposition products did not always coincide with the amount of fading. When the exposed film was immersed in aqueous sodium dithionite (0·1 mol dm^{-3}, 70°C, 30 min), the thermal reduction product showed nearly the same absorption spectrum as that of the photoreduction product formed on exposure in DL-mandelate solution. The samples of various relative fading after exposure in aerobic RB solution showed a decrease in the amount of the thermal product with an increase in the relative fading (spectra 10–12 in Fig. 7). This implies that, on exposure in aerated RB solution, the azo group further away from the triazine ring was mainly oxidized, to give a monoazo intermediate; on prolonged exposure, some of the azo group near to the triazine ring may also be photo-oxidized.

3.2.3 Exposure of Blue-2Cu in aerobic Rose Bengal solution

Blue-2Cu has two azo groups showing different fading behavior. In reductive fading on exposure in DL-mandelate solution, the azo group nearer the triazine ring was preferentially photoreduced (cf. Section 3.1.1). In oxidative fading on exposure in aerated RB solution, considerable amounts of violet monoazo intermediates were observed (spectra 15 and 16 in Fig. 8). The exposure of Blue-2Cu on cellulose in oxygen-saturated RB solution gave an increase in the rate of fading and also in the formation of the monoazo intermediate, compared with the case of exposure in aerated RB solution (cf. spectrum 18 in Fig. 8). It was confirmed that the azo group further away from the triazine ring has a higher tendency to be photo-oxidized. Thus both the azo groups may be reduced and oxidized by exposure, but the azo group nearer the triazine ring has a higher tendency to be reduced than the other azo group, and the other azo group also has a higher tendency to be oxidized.

In order to confirm these properties for Blue-2Cu, the photodecomposition products on cellophane produced by exposure in aerated and oxygen-saturated RB solution were further exposed in aqueous sodium DL-mandelate (0·50 mol dm^{-3}). Compared with the absorption spectra of the original sample exposed under the same conditions, the photoreduction of the previously exposed sample seemed to proceed further than the original one (cf. spectra 8 and 9 in Fig. 8). The intermediates produced previously by photo-oxidation appeared to have almost no effect on the structure of the end-product. This implies that the azo group nearer the triazine ring in Blue-2Cu is readily photoreduced, and is hardly photo-oxidized. The larger fading of the exposed sample may be attributed to the high concentration dependence of reductive fading, and to the high ease with which the photo-oxidation products are photoreduced, as in the case of VS dyes.[19]

3.2.4 Exposure in aerated water

Seven MCT dyes on cellulose were exposed in aerated water. By use of the absorption spectra of the reduction and oxidation products for the corresponding dye, whether photoreduction or photo-oxidation of MCT dyes on cellulose occurs on exposure in aerated water can be determined. The results are summarized in Table 1. It was confirmed that, on exposure in aerated water, Yellow, Red 4 and Red 7 underwent oxidative fading, whilst Yellow R, Orange, Brown and Blue-2Cu underwent reductive fading (Figs 2–8).

The order of rate of fading in aerated water, shown in Fig. 1(c), was as follows:

$$\begin{aligned}&\text{Red 7} > (\text{Blue-2Cu}) > \text{Yellow} > \text{Red 4}\\&\quad > (\text{Brown}) > (\text{Orange}) > (\text{Yellow R})\end{aligned}\tag{4}$$

Dyes in parentheses undergo reductive fading in aerated water. Since the light stability for Yellow, Red 4 and Red 7 is dependent upon the ease with which they are oxidized, they have nearly the same order to that of the sequence (3) (Section 3.2.1). The reversal of the order between Yellow and Red 4, probably due to the largest molar extinction coefficient for Yellow and the small one for Red 4, is not notable, because the differences in A/A_0 were small. Since all MCT dyes have a photosensitivity to generate singlet oxygen,[14] reductive fading under aerobic conditions is suppressed by oxygen. Ideally, all the singlet oxygen is better consumed in oxidizing the semi-reduced species, the suppression effect on reductive fading by oxygen giving no fading. That is why the rates of reductive fading for Yellow R, Orange, Brown and Blue-2Cu in aerated water became smaller than those in de-aerated water (Table 1).

3.3 Fading behavior of MCT dyes

MCT dyes used in the present study undergo photoreduction on exposure in de-aerated water as in the case of C.I. Reactive Red 22 and Black 5.[6] This may be attributed to abstraction of hydrogen by the triplet state of the dye from the substrate; Rusznák *et al.*[20,21] assigned this as cellulose, although similar origins from dyed or undyed fiber have been noted.[19,22,23] What is real substrate remains to be studied.

Since the absorption spectra of the thermally reduced cellophane samples for some MCT dyes before and after exposure under various conditions were the same, no fission of dye–fiber bonds on exposure was confirmed. Triazine–fiber bonds seem to have high stability to exposure.

According to a previous paper,[6] the fading behavior on dry cellulose is intermediate between that on exposure in de-aerated and aerated water. The seven MCT dyes on dry cellulose, therefore, may undergo reductive fading or simultaneous oxidative and reductive fading on exposure in air, in addition to oxidative fading.

Dyes which show no fading on exposure in de-aerated water have a high lightfastness if the ease with which they are oxidized is low. Some anthraquinone dyes belong to this type. On the other hand, azo dyes which show reductive fading on exposure in de-aerated water have a high fastness if they have a low ability to abstract hydrogen from the substrate, or if the relative concentration of the azo form, which has a lower ability to abstract hydrogen from substrate, is very high. These dyes may have a tendency to show reductive fading, but not to show oxidative fading, on dry cellulose. Thus, if oxygen in cellulose suppresses the rate of reductive fading, the dye has a high lightfastness. Some disazo MCT dyes belong to this class. Monoazo dyes showing a fading behavior of the latter type, e.g. Yellow R, have a relatively low stability to the simultaneous effect of light and substrate, if there is some substrate on the cellulose. Disazo dyes in which one of the azo groups is photoreduced and another azo group is photo-oxidized (cf. Blue-2Cu) have a low stability to the simultaneous effect, although the lightfastness depends on both the ease of oxidation and reduction, as described above.

On exposure of some dyes when dyed in admixture on cellulose in anaerobic aqueous DL-mandelate, it has been reported that only the excited state of the dye takes part in the photoreduction.[4] No acceleration effect by the partner dye, but a small suppression effect, probably due to a filter effect, was recognized.

Although these properties of the dyes are dependent upon the chemical structure, the basic relationships between the chemical structure and these properties remains to be elucidated. The diversity of mechanisms reported so far[7–10] may be summarized in this present series of studies,[6] the fading mechanism depending on both the chemical structure of the dye and the conditions of exposure.

4 SUMMARY

Seven MCT azo dyes on cellulose showed reductive fading on exposure in de-aerated water. Four dyes on cellulose underwent reductive fading on exposure in aerated water, whilst the others showed oxidative fading. The lightfastness of some MCT dyes is in general determined by the ease with which they are oxidized, whilst the fastness of other dyes is determined by the ease with which they are reduced. Whether MCT dyes on cellulose are photoreduced or photo-oxidized is dependent upon the chemical structure of dyes, as well as the concentration of oxygen. Reductive fading of monoazo dyes on cellulose on exposure in de-aerated water was more accelerated by the addition of substrate than that for some symmetric disazo dyes. In addition to the formation of monoazo intermediates from disazo dyes in reductive fading, some mono- and dis-azo dyes underwent multi-step photoreduction on exposure. As a first approximation, the reductive and oxidative fading behavior for MCT azo dyes on cellulose can be explained in terms of azo–hydrazone tautomerism.

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