



Fading of a Monoazo Reactive Dye and of its Copper Complex on Cellulose in the Presence of Oxygen and Substrate under Wet Conditions

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ABSTRACT

The fading of a monoazo dye (dye 1) and its copper complex (dye 2) on cellulose was examined in aqueous solutions in the presence of oxygen and substrate. The rates of fading for dyes 1 and 2 on cellulose were very similar in aerated water and in anaerobic DL-mandelate solution. On exposure of dyes 1 and 2 on cellulose in an aerobic DL-mandelate solution, oxidative and reductive fading was observed; the oxidative process occurred initially at a low rate and was suppressed in later stages of the fading. On exposure in an oxygen-saturated DL-mandelate solution, only oxidative fading was observed. When copper was extracted from dye 2 (dye 3) on cellulose by EDTA, the rate of fading for dye 3 was four times greater than for dyes 1 and 2 in aerated water but similar in anaerobic DL-mandelate (0.05 M) solution. The oxidation products formed on cellulose were readily split off in the subsequent photoreduction.

1 INTRODUCTION

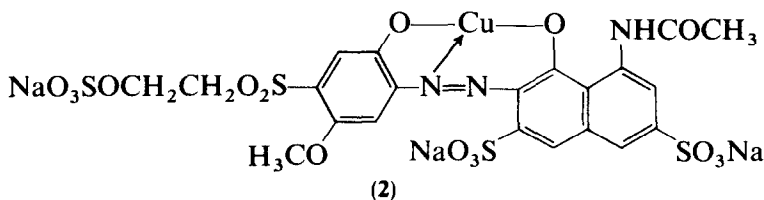
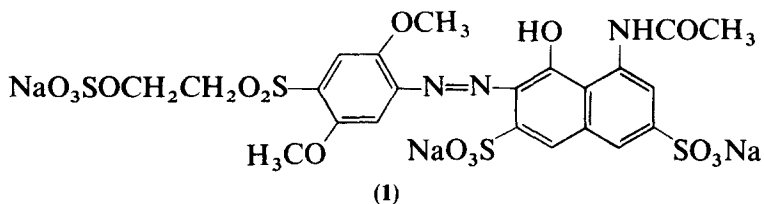
Monoazo dyes derived from H-acid and related compounds as coupling components, and their copper complexes, have been widely used as red and violet reactive dyes. Sirbiladze *et al.*¹ studied the fading of several monoazo dyes having a similar structure, but not containing copper, and proposed a fading mechanism via a polymer radical. Graves *et al.*² investigated the effect of metallization on singlet oxygen formation by azo dyes. The present authors have reported the simultaneous oxidative and reductive fading of some vinylsulfonyl (VS) reactive dyes on cellulose in the presence of oxygen and substrates under wet conditions.³

In a previous paper⁴ we reported the fading of C.I. Reactive Red 22 and Black 5 in the presence of oxygen and substrate, and these results confirmed that both oxidative and reductive fading occurred depending upon the conditions of exposure.

In the present paper the kinetics of the simultaneous oxidation/reduction on the exposure of a monoazo dye (dye 1) and its copper complex (dye 2) on cellulose in an aqueous solution containing both oxygen and substrate is investigated by the method of spectral analysis.⁴ The effect of copper extraction from dye 2 by ethylenediamine tetra-acetic acid (EDTA) on the rate of fading is also examined.

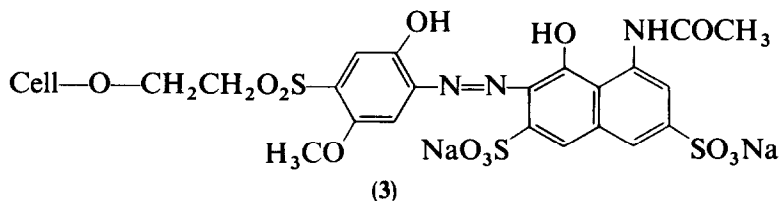
2 EXPERIMENTAL

The violet monoazo dye 1 and the blue copper complex dye 2 were supplied by Mitsubishi Chemical Corp. (Chiyoda-ku, Tokyo 100, Japan). They were used without further purification and have the following structures:

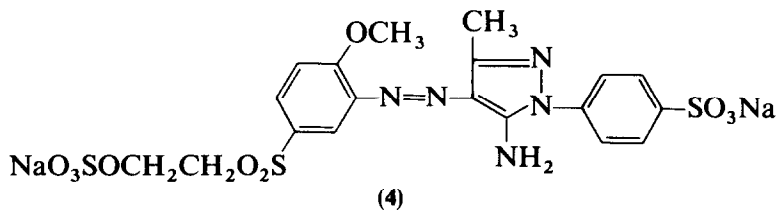


Cellophane films were dyed by established methods.³ The dyed film was immersed in an aqueous solution and exposed to a carbon arc lamp.^{3,4} The absorption spectra of the dyes on cellophane were measured by a double monochro spectrophotometer (Ubest-50 type, Japan Spectroscopic Co. Ltd, Hachioji, Tokyo 192) equipped with a spectral analyzer. The aerated aqueous substrate solutions were prepared according to the method reported previously.⁴ The other chemicals used were of reagent grade.

The disodium salt of EDTA was dissolved and the solution was neutralized to pH 6. The copper extraction was made by immersing cellophane dyed with dye **2** in aqueous EDTA (0.05 mol dm^{-3}) solution at 50°C for more than 2 days, renewing the solution. The film was then thoroughly scoured in boiling water to remove EDTA. By extracting copper the structure of dye **2** bound with cellulose (Cell—OH) was changed to the *o*-hydroxy compound:³



In order to estimate the apparent photosensitivity of dyes **1–3** an aminopyrazoliny azo dye (dye **4**) was used, as in a previous study:⁵



3 RESULTS AND DISCUSSION

3.1 Reductive fading of dyes **1** and **2**

The absorption spectra for dye **1** after exposure in anaerobic aqueous DL-mandelate, and those for the photodecomposed products of dyes **1** and **2** after the exposure, are shown in Fig. 1. Exposure of the dyed film in anaerobic aqueous DL-mandelate usually gives reductive fading.^{3,4} The presence of an amino group in the reduction products on cellulose was established in a previous paper.³ The absorption spectrum of the reduction

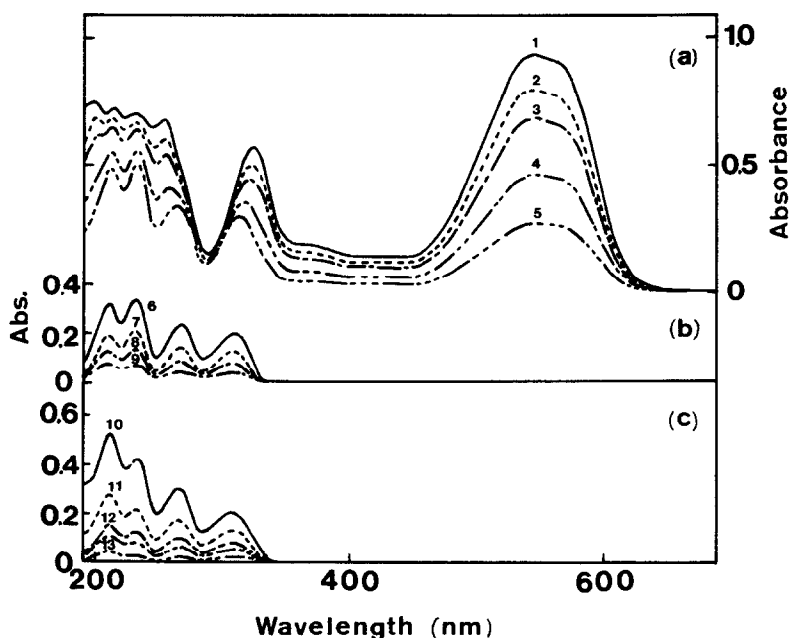


Fig. 1. (a) Absorption spectra for dye **1** (1) on cellophane and those after exposure in anaerobic aqueous DL-mandelate (0.05 mol dm^{-3}) for 1 h (2), 2 h (3), 3 h (4) and 4 h (5) (original concentration of dye **1** = $1.44 \times 10^{-2} \text{ mol kg}^{-1}$). (b) Absorption spectra for the photoreduction products of dye **1** on exposure in anaerobic DL-mandelate solution for 4 h (6), 3 h (7), 2 h (8), and 1 h (9) after subtracting the spectrum of dye **1** of corresponding concentration. (c) Absorption spectra for the photoreduction products of dye **2** on exposure in anaerobic mandelate solution for 4 h (10), 3 h (11), 2 h (12), 1 h (13), and 0.5 h (14) after subtracting the spectrum of dye **2** of corresponding concentration (original concentration of dye **2** = $1.35 \times 10^{-2} \text{ mol kg}^{-1}$).

products for dye **1** was shown to be similar to that of a model compound, 4-(β -hydroxyethylsulfonyl)-2,5-dimethoxyaniline.³ The absorption spectrum of the reduction product for dye **2** was slightly different from that of the model compound, because the reduction product of dye **2** is the 2-hydroxy homolog.

As shown in Fig. 2(a), the rates of fading for dyes **1** and **2**, estimated from the decrease in the optical density at the wavelength of the maximum absorption of the exposed film, were in agreement with those of the formation of the reduction product estimated from increase in the optical density of the UV region (cf. Fig. 1), implying a one-to-one conversion into the photoreduction products from the corresponding dyes. In order to estimate the concentration of the reduction products for dyes **1**–**3** by optical density at the same wavelength, the optical density at the absorption maximum of the first absorption band from the longer-wavelength side was

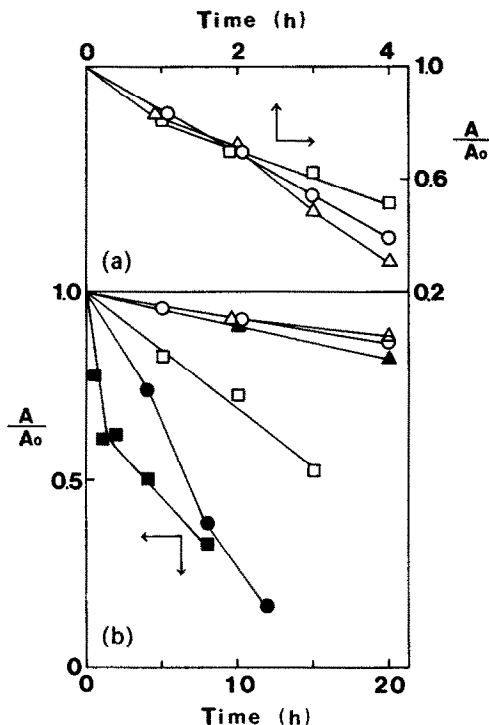


Fig. 2. (a) Rates of fading for dyes 1 (Δ), 2 (\circ) and 3 (\square) on exposure in anaerobic aqueous DL-mandelate (0.05 mol dm⁻³) in a nitrogen atmosphere (original concentration of dyes 1 and 2: cf. Fig. 1; original concentration of dye 3 = 1.78×10^{-2} mol kg⁻¹). (b) Rates of fading for dyes 1 (Δ), 2 (\circ) and 3 (\square) on exposure in aerated water (original concentration: dye 1, 1.40×10^{-2} mol kg⁻¹; dye 2, 1.04×10^{-2} mol kg⁻¹; dye 3, 1.67×10^{-2} mol kg⁻¹), and rates of fading for dyes 1 (\blacktriangle), 2 (\bullet) and 3 (\blacksquare) in aerobic Rose Bengal (3.3×10^{-4} mol dm⁻³) solution containing Na₂SO₄ (0.05 mol dm⁻³). (Original concentration: dye 1, 1.38×10^{-2} mol kg⁻¹; dye 2, 1.47×10^{-2} mol kg⁻¹; dye 3, 1.79×10^{-2} mol kg⁻¹.)

used, because the extinction coefficient of the absorption maximum of the first absorption band was not altered by the change from *o*-methoxy to *o*-hydroxy substitution.

The rate of reductive fading for dye 1 was similar to that for dye 2 in the initial period of exposure, and became greater than that with increasing time of exposure [Fig. 2(a)].

3.2 Oxidative fading of dyes 1 and 2 on cellulose

3.2.1 Exposure of aerated water

The absorption spectra for dye 1 on cellulose after exposure in aerated water are shown in Fig. 3(a). Dye 2 showed absorption spectra similar to those for dye 1 on exposure in aerated water.⁶ Absorption intensities for the two dyes

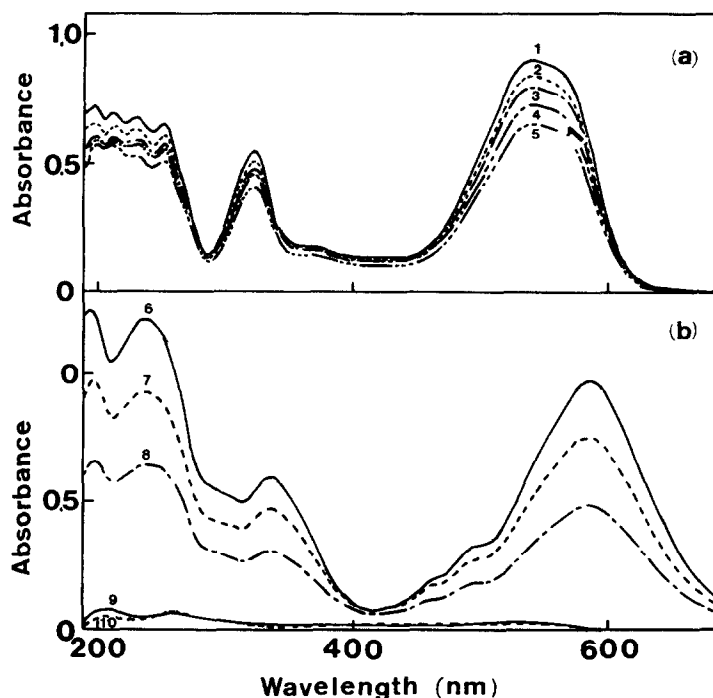


Fig. 3. (a) Absorption spectra for dye 1 after exposure in aerated water for 0 h (1), 10 h (2), 20 h (3), 40 h (4), and 80 h (5). (b) Absorption spectra for dye 2 after exposure in aerated water for 0 h (6), 40 h (7), and 80 h (8), and those of the photodecomposed products for dye 2 on exposure for 40 h (9) and 80 h (10) after subtracting the spectrum of the original dye of corresponding concentration. (No spectrum of the decomposed products remained after exposure for less than 40 h. Original dye concentration: cf. Fig. 2.)

decreased over the whole wavelength range with time of exposure. Subtracting the spectrum from the original dye of corresponding concentration from that after the exposure indicated that small amounts of oxidation product remained on the cellulose only after a prolonged period of exposure [Fig. 3(b)]. The oxidation products may be further photodecomposed on subsequent exposure. Absence of absorptions for the photodecomposed products desorbed into aerated water in which the dyed film was exposed was confirmed within the range of wavelengths longer than 280 nm, implying that the azo groups of the dye were photo-oxidized.

The decomposition of the photo-oxidation products may be reductive, since it is considerably inhibited on exposure in aerated Rose Bengal (RB) solution (cf. Section 3.2.2), and the oxidation products for VS dyes examined in a previous paper⁴ were presumed to be photoreduced. We have also observed that some azo reactive dyes were photoreduced, even in the absence of substrate under wet conditions,⁷ when they had proton-donating

groups in their molecule. The reductive falling-off of the photo-oxidation product on cellulose was also confirmed by immersing the exposed film in aqueous sodium dithionite (0.1 mol dm^{-3} , 70°C), when the absorption spectra of the photo-oxidation products disappeared immediately (cf. Section 3.2.2).

The fading behavior for dyes 1 and 2 in aerated water is shown in Fig. 2(b). The rate of fading for dye 1 was the same as that for dye 2; this similarity in the fading rates for dyes 1 and 2 in aerated water is coincidental, because the ease with which each dye is oxidized is different. The high sensitivity for dye 1 and the low sensitivity for dye 2 were confirmed by the fading behavior of dye 4 (Yellow) on cellulose dyed in admixture with dye 1 or 2, using the same method as previously described,⁵ as is shown in Fig. 4. The f and k values for dyes 1 and 2 were estimated from Fig. 4 and are shown in Table 1. The f value for dye 1 is considerably larger than that for dye 2, whilst the k value for dye 1 is smaller than that for dye 2.⁵

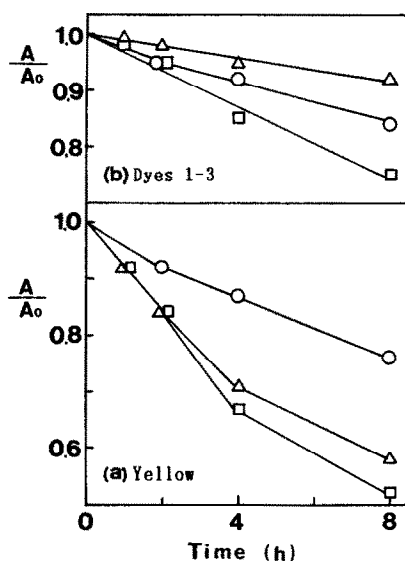


Fig. 4. (a) Relative rate of fading for dye 4 (Yellow) on water-swollen cellophane dyed in admixture with dyes 1-3; (b) that for the partner dye on the same cellophane.

Concentration (mol kg^{-1})	
Yellow (dye 4)	Partner dye
\triangle 5.61×10^{-3}	Dye 1 (1.24×10^{-2})
\circ 6.25×10^{-3}	Dye 2 (1.07×10^{-2})
\square 6.00×10^{-3}	Dye 3 (1.19×10^{-2})

TABLE 1

Relative Fading, A/A_0 , for Dyes 1, 2 and 3 on Cellophane on Exposure in Aqueous DL-Mandelate, in Aerated Water, and in an Aerated Rose Bengal Solution, and Values of the Apparent Photosensitivity, f , and the Rate Constant, k_0 , of the Second-Order Reaction with $^1\text{O}_2$ of these Dyes (cf. Fig. 4)

Dye	Concentration (mol. kg ⁻¹)	A/A_0			k_0 (dm ³ mol ⁻¹ s ⁻¹)			f
		Water in air (8 h)	RB solution ^a in air (3.3×10^{-4} mol dm ⁻³) (time of exposure)	Sodium DL-mandelate ^b (0.05 mol dm ⁻³ , 2 h)				
				In N ₂	In air	In O ₂		
1	1.41×10^{-2}	0.933	0.907 (10 h)	0.722	0.767	0.760	0.038	0.3 ₁
2	1.43×10^{-2}	0.934	0.740 (4 h)	0.700	0.804	0.790	0.25	0.01 ₅
3	1.70×10^{-2}	0.742	0.786 ^c (30 min)	0.710	0.541	0.232	1.7	0.3 ₀

^a Na₂SO₄ (0.05 mol dm⁻³) was added.

^b Na₂SO₄ (0.05 mol dm⁻³) was added and the pH of the solution was adjusted to 6.0.

^c The value of A/A_0 for 1 h was 0.612.

Since dye 1 is much less readily oxidized than dye 2 and also has a higher photosensitivity in generating singlet oxygen, the similarity between dyes 1 and 2 in their rate of fading on exposure in aerated water is due to the counterbalance of these two factors.

3.2.2 Exposure in aerated Rose Bengal solution

Since RB is a powerful photosensitizer for singlet oxygen, photo-oxidation of dyes 1 and 2 may occur. Since RB was partially faded on prolonged exposure in the case of dye 1, the aqueous RB solutions were renewed every 20 h of exposure. On subtracting the spectra of the corresponding original dye from the spectra after exposure, the absorption spectra of the photodecomposed products for dyes 1 and 2 on cellulose were observed (Fig. 5), i.e. the formation of photo-oxidation products whose photoreduction might be inhibited by the high sensitivity of RB during the initial period of exposure.

The photofading behavior of dyes 1 and 2 on exposure in aerated RB solution is shown in Fig. 2(b) and Table 1. Although the rates of fading for both the dyes were similar on exposure in aerated water, dye 2 showed a higher rate of oxidative fading than dye 1 on exposure in the RB solution.

By continuing the exposure of the RB solution the amount of oxidation products on cellulose gradually decreased due to their progressive photoreduction; this is probably relatable to an increase in the concentration of substrate originating from the photodecomposed fragments desorbed into the aqueous solution, as in the case of dyes 1 and 2 in aerated

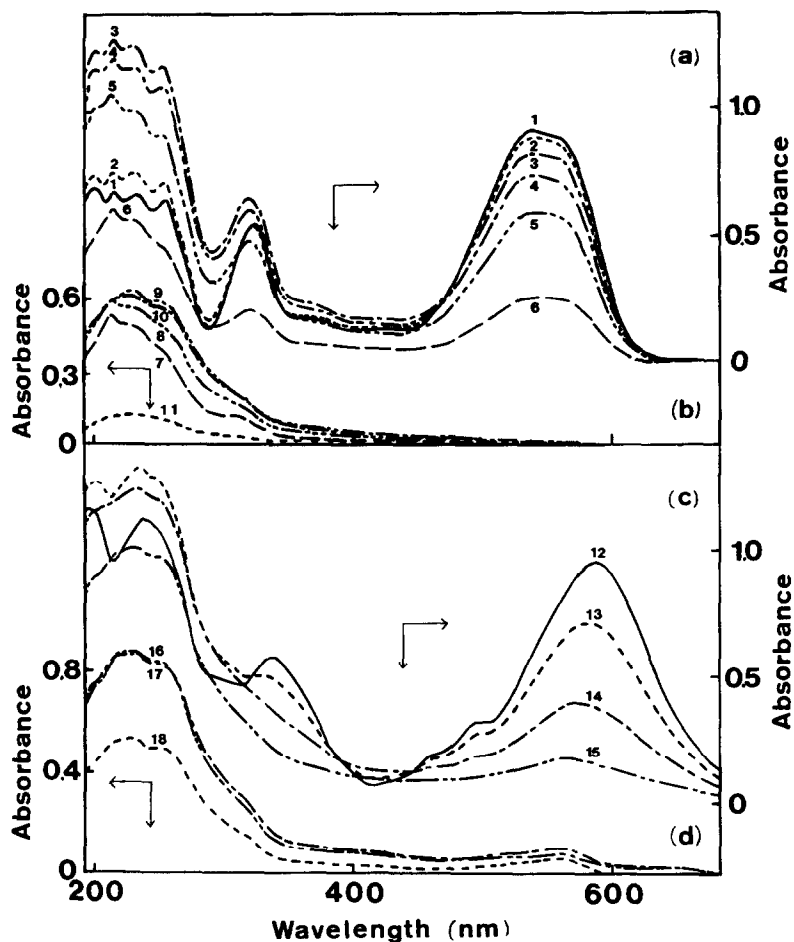


Fig. 5. (a) Absorption spectra for dye 1 after exposure in aerated aqueous Rose Bengal ($3.3 \times 10^{-4} \text{ mol dm}^{-3}$) containing Na_2SO_4 (0.05 mol dm^{-3}) for 0 h (1), 1 h (2), 10 h (3), 20 h (4), 40 h (5), and 80 h (6). (The aqueous RB solutions were renewed every 20 h of exposure.) (b) Absorption spectra for the photodecomposed products of dye 1, which were obtained by subtracting the spectrum of the original dye of corresponding concentration from the spectra [(a) spectra 2–6] after exposure in the RB solution for 80 h (7), 40 h (8), 20 h (9), 10 h (10), and 1 h (11). (c) Absorption spectra for dye 2 after exposure in the aerated RB solution for 0 h (12), 4 h (13), 8 h (14), and 12 h (15), and those for the photodecomposed products for dye 2 on exposure in aerated RB solution for 12 h (16), 8 h (17) and 4 h (18) after subtracting the spectrum of the original dye of corresponding concentration. (Original dye concentration: cf. Fig. 2.).

water (cf. Section 3.2.1) and also as in the case of Red 22 and Black 5 on exposure in aerated substrate solution.⁴

On prolonged exposure of dye **1** in aerated RB solution, a small amount of photoreduction products was apparent in the absorption spectrum of dyed film exposed for 40 and 80 h [Fig. 5(a) and (b)]. Very slow photoreduction of dye **1** occurred, because of the decrease in the reduction of the photo-oxidation products occurring concurrently with the oxidative fading (cf. Sections 3.1 and 3.2.1). By immersing the exposed films of dye **1** in a dithionite (0.1 mol dm^{-3}) solution at 50°C only the absorption spectra of reductive products similar to those for dyes **2** and **3** were observed, implying a change of the *o*-methoxy groups of dye **1** into *o*-hydroxy groups during the exposure. The photo-oxidation products were split off by the thermo-chemical reduction with dithionite and unfaded dye **1** was also reduced. The relative intensities of the absorption maxima of the second to the fourth absorption bands for the photoreduction products of dye **1** gradually varied on exposure in aerobic solutions.

3.3 Fading of dye **3** on cellulose

The copper of dye **2** on cellophane was extracted by immersing the dyed film in aqueous EDTA (0.05 mol dm^{-3}), giving dye **3**. Completion of the copper extraction required a prolonged time and repeated immersion of the dyed film in the solution was necessary. The extraction of copper from some other copper-complex dyes on cellophane by EDTA and histidine will be reported elsewhere (Okada, Y., Kato, T. & Morita, Z., unpublished).

The same falling-off behavior of the photo-oxidation products for dye **3** on cellulose as those for dyes **1** and **2** was observed on exposure in aerated water and in aerated RB solution (Fig. 5). Thus the photo-oxidation products of dyes **1–3** are more easily photoreduced than the original dye by substrates, which are their photodecomposed fragments desorbed into the aqueous solution. Since the concentration of such substrates increases with time of exposure, the photoreduction of the photo-oxidation products occurs more readily with increase in time. Even during the photo-oxidation process photodecomposed products which are desorbed into the aqueous solution may act as substrates for the photoreduction, if the original dye has a proton-donating group, as in the case of dyes **1–3**. Amino compounds produced in the photoreduction process may also play a role as substrate.

Comparison of the fading behavior of dyes **1** and **3** shows the effect of the *o*-substituent on the lightfastness, and comparison of dyes **2** and **3** shows the effect of copper chelation. The rate of reductive fading for dye **3** on exposure in anaerobic DL-mandelate solution was similar to those for dyes **1** and **2**, subsequently became smaller, showing an order dye **1** > dye **2** > dye **3** [Fig.

2(a)], while the rate of oxidative fading for dye 3 on exposure in aerated water became four times larger [Fig. 2(b)]. In the case of photoreduction copper chelation gave no retardation effect on the reductive fading of dye 3, in contrast to oxidative fading.

The apparent sensitivity and the ease with which dye 3 is oxidized are shown in Fig. 4 and Table 1, where the estimations were again made as previously described.⁵ The reactivity of dye 3 with singlet oxygen is seven times higher than that of dye 2 and *c.* 40 times higher than that of dye 1. In spite of the similarity in the absorption spectra of these dyes, the apparent sensitivity for dyes 1 and 3 is higher than that for dye 2 by a factor of one.

Comparing the photosensitivity for dye 2 with that for dyes 1 and 3, an increase in the lightfastness by copper chelation may be attributed to a large decrease in the photosensitivity. This conclusion is consistent with the results of the mechanistic study by Graves *et al.*,² who presumed that the generation of singlet molecular oxygen by the interaction between ground-state oxygen and the triplet excited state of the dye was strongly inhibited in some metal-complex dyes by triplet energy transfer from the excited dye moiety to the metal ion. The *o*-hydroxy homolog formed by extracting copper from dye 2 is easily photo-oxidized and has high sensitivity. Replacement of the *o*-methoxy group by the *o*-hydroxy group has a large influence on the reactivity with singlet oxygen but not on the sensitivity.

In the case of incomplete extraction the absorption maximum for dye 3 was shifted to longer wavelength on exposure in aerated water, implying a preferential fading of dye 3 to that of dye 2 (Okada, Y., Kato, T. & Morita, Z., unpublished).

3.4 Simultaneous oxidative and reductive fading

3.4.1 Exposure in aerated substrate solution

Simultaneous oxidative and/or reductive fading occurs on exposure in an aerated or oxygen-saturated substrate solution.^{3,4} The rates of oxidative and reductive fading are mutually suppressed whenever they occur simultaneously or exclusively.

The absorption spectra for dye 2 before and after the exposure in an aerated DL-mandelate solution are shown in Fig. 6(a) and (b), and clearly indicate that only the photoreduction products remained on cellulose after the exposure. From the spectra for dyes 1 and 3, and from Fig. 6, the rates of photoreduction for dyes 1–3 were estimated. The fading behavior is shown in Fig. 7 and is summarized in Table 1. Since the oxidation products for these dyes are easily decomposed by photoreduction, as noted above (*cf.* Sections 3.2 and 3.3), little photo-oxidation product was observed in the absorption spectrum of dyed film exposed in substrate solutions. The differences in the

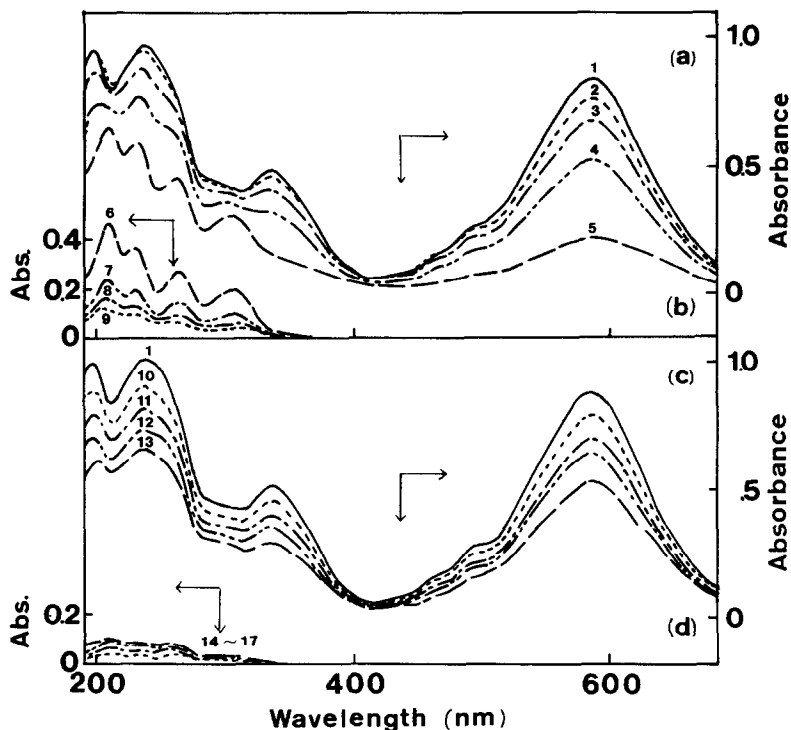


Fig. 6. (a) Absorption spectra for dye **2** after exposure in aerated aqueous sodium DL-mandate (0.05 mol dm^{-3}) containing NaCl (0.05 mol dm^{-3}) for 0 h (1), 1 h (2), 2 h (3), 3 h (4), and 4 h (5). (Original concentration of dye **2**, $1.28 \times 10^{-2} \text{ mol kg}^{-1}$.) (b) Absorption spectra for the photodecomposed products of dye **2**, which were obtained by subtracting the spectrum of the original dye of corresponding concentration from the spectra [(a) spectra 2–5] after exposure for 4 h (6), 3 h (7), 2 h (8), and 1 h (9). (c) Absorption spectra for dye **2** after exposure in the oxygen-saturated solution for 0 h (1), 1 h (10), 2 h (11), 3 h (12), and 4 h (13). (Original concentration of dye **2**, $1.37 \times 10^{-2} \text{ mol kg}^{-1}$.) (d) Absorption spectra for the photodecomposed products of dye **2**, which were obtained by subtracting the spectrum of the original dye of corresponding concentration from the spectra [(a) spectra 10–13] after exposure for 4 h (14), 3 h (15), 2 h (16), and 1 h (17).

amount of the photodecomposed dye and the photoreduction products may, however, correspond to the amounts of photo-oxidation products [Fig. 7(c)].

The initial rates of fading for these dyes exposed in an aerated substrate solution were in the following order: dye **3** \gg dye **2** = dye **1**. This corresponds to the order of the initial rates of photo-oxidation. Thus, on exposure in an aerated aqueous DL-mandate solution, rapid photo-oxidation of dyes **1**, **2** and **3** occurred initially, while the photoreduction was completely inhibited. However, the rates of oxidative fading for these dyes were lower than those on exposure in aerated water, showing a suppression effect of the substrate.

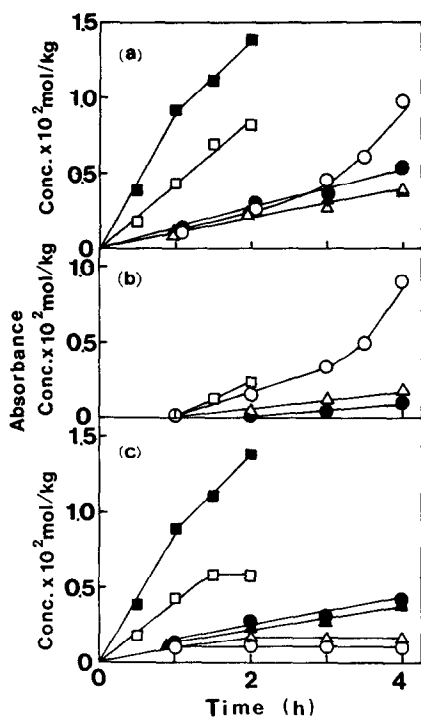


Fig. 7. (a) Photodecomposition behavior, (b) formation behavior of the photoreduction products, and (c) that for photo-oxidation products for dyes 1 (Δ), 2 (\circ), and 3 (\square) on exposure in aerated and oxygen-saturated DL-mandelate solutions (cf. Fig. 6 for dye 2). Closed symbols are used in case of oxygen-saturated solution. (Original concentrations: dye 1, $1.39 \times 10^{-2} \text{ mol kg}^{-1}$; dye 3, $1.77 \times 10^{-2} \text{ mol kg}^{-1}$).

After initial exposure, a small reductive fading proceeded concurrently with the oxidative fading, whilst the latter was almost completely suppressed. The subsequent rates of reductive fading on continuing the exposure were in the order dye 3 > dye 2 > dye 1. The subsequent rate of reductive fading for dye 2 increased with time of exposure, because the reductive fading was accelerated, probably by the photodecomposed fragments. The rates of the reductive fading for these dyes were smaller than those of reductive fading on exposure in the corresponding anaerobic substrate solution, indicating a suppression effect of oxygen. The initially formed oxidation products of these dyes were completely decomposed on further exposure.

3.4.2 Exposure in oxygen-saturated substrate solution

The absorption spectra for dye 2 before and after exposure in an oxygen-saturated DL-mandelate solution are shown in Fig. 6(c) and (d), suggesting that trace amounts of photoreduction products and a small amount of photo-oxidation products remained on the cellulose after the exposure.

On exposure of these dyes in an oxygen-saturated DL-mandelate solution, only oxidative fading occurred, while the reductive fading was completely suppressed except for dye 2. In spite of the presence of a high concentration

of oxygen, the photo-oxidation products on cellulose were photoreduced by DL-mandelate, as in the case of exposure in aerated water. The initial rates of fading, i.e. photo-oxidation, were in the following order: dye 3 \gg dye 2 > dye 1. The rate of oxidative fading for dye 2 was slightly larger than that for dye 1 because of the greater ease with which dye 2 is oxidized. On continuing the exposure, photoreduction was observed only for dye 2 concurrently with photo-oxidation, since it might inhibit more strongly the generation of singlet oxygen than dyes 1 and 3.²

Dye 1 shows the property of being photoreduced and hardly photo-oxidized. Since azo dyes are photoreduced from the azo form, dye 1 may exist preferentially in the azo form. Dye 3, on the other hand, is very easily oxidized and is photoreduced similarly to dye 1. Dye 3 exists preferentially in the hydrazone form, since according to Yamamoto *et al.*⁸ the azo dye from H-acid coupled with orthonilic acid *ortho* to the hydroxyl group of H-acid exists preferentially in the hydrazone form. It is, however, not clear that dye 1 exists preferentially in the azo form. Differences between the photofading behavior of these dyes exposed in aerated and oxygen-saturated solutions may well be attributed to their photosensitivity and the ease with which they are oxidized.

4 SUMMARY

Azo dyes derived from *N*-acetamido-H-acid coupled with 4-vinylsulfonyl-2,5-dimethoxyaniline or 2-amino-4-methoxy-5-vinylsulfonylphenol show a wide variation in their oxidative fading, but in reductive fading *o*-substituents and copper chelation had more specific influence. Extraction of the copper from dyes on cellulose by chelating agents had a significant influence on the lightfastness.

The dyes showed oxidative and/or reductive fading similar to that of C.I. Reactive Red 22 and Black 5⁴ on exposure in aerobic aqueous substrate solutions. The photo-oxidation products formed initially from the dyes were easily split off by the subsequent photoreduction. In the coexistence of oxygen and substrate the rates of oxidative and reductive fading were mutually suppressed, if they occurred simultaneously or exclusively.

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