Dyes and Pigments **16** (1991) 205–221

Simultaneous Oxidative and Reductive Photofading of C.I. Reactive Red 22 and Black 5 on Cellulose in the Presence of Oxygen and Substrate under Wet Conditions

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(Received 23 August 1990; accepted 10 October 1990)

ABSTRACT

The reductive and oxidative photofading of Red 22 and Black 5 on cellulose on exposure in substrate solutions was kinetically examined by spectral analysis. In the presence of DL-mandelate and oxygen, the oxidative and reductive fading of both the dyes occurred simultaneously from the beginning, and later the oxidative fading was suppressed depending upon the concentration of oxygen. On exposure of Red 22 in the presence of lactate of high concentration and oxygen, oxidation initially occurred and was followed by reduction with complete inhibition of oxidation. An increase in the concentration of oxygen promoted the initial oxidation and an increase in the concentration of substrate promoted subsequent reduction. On exposure of Black 5 in the presence of lactate of high concentration and oxygen, similar fading behavior to that in DL-mandelate solutions was observed, but the oxidation products formed were immediately further photo-reduced.

1 INTRODUCTION

It is known that the primary step in the fading of azo dyes on cellulose is oxidative.[1-10] The reductive fading of azo dyes on cellulose has also been observed in the presence of substrates such as amines, lactic acid or mandelic acid, although the mechanism has not been clearly elucidated.[10-15] In principle, both oxidative and reductive fading would be feasible.[16,17]

In previous papers, we have shown that no fading of vinylsulfonyl (VS) reactive dyes on cellulose occurred in the absence of oxygen under wet conditions,[18] and that the fading of VS dyes on cellulose was oxidative in the absence of substrate.[19,20] In the presence of both oxygen and substrates,[21] the fading of VS dyes has been confirmed to occur simultaneously by photo-oxidation via singlet oxygen mechanism and by photo-reduction through hydrogen abstraction from the substrate. Anaerobic conditions accelerated the latter and inhibited the former, while aerobic conditions retarded the latter. Reductive fading of VS dyes on cellulose on exposing the dyed film in an aqueous solution of substrate was similar to that on cotton fabrics immersed in the same solution before the exposure, although some differences between them are apparent.[21,22]

In this present paper, the kinetics of the simultaneous oxidation/reduction reaction on exposure of C.I. Reactive Red 22 and Black 5 on cellulose in an aqueous solution containing both oxygen and substrate is analyzed by spectral analysis to elucidate the mechanism of the fading. On the basis of the results, comparisons between the fading behavior of Red 22 and Black 5 and between the effects of substrates on the fading are made.

2 EXPERIMENTAL

C.I. Reactive Red 22 and Black 5 and the methods of dyeing and exposure were the same as previously described.[18] The other VS dyes used were supplied by Sumitomo Chemical Co. Ltd, Osaka, Japan. The absorption spectra of dyes on cellophane were measured by a double monochro spectrophotometer (Ubest-50 type, Japan Spectroscopic Co. Ltd, Tokyo, Japan) and were evaluated by a spectral analyzer linked to it. Aqueous oxygen-saturated or aerated substrate solutions were freshly prepared for each experiment. DL-mandelic acid or lactic acid of a known amount as appropriate was added to the oxygen-saturated or aerated water and the liquor was neutralized to pH 6·0. After adjusting the concentration, the aqueous solution was added to a glass vessel filled with oxygen or air, and kept for *c.* 1 h. The glass vessel in which a glass cell for the sample was set, was again filled with oxygen or air and was then exposed in a fadeometer.

3 RESULTS AND DISCUSSION

3.1 Fading of C.I. Reactive Red 22

The exposure of dyed film in the presence of DL-mandelate or lactate in a nitrogen atmosphere yielded absorption spectra characteristic only of reductive fading,[21] while that in an aerated solution in absence of substrate was characteristically only of oxidative fading.[18-20] The spectra of the oxidation and reduction products were obtained by exposing the dyed film in an aerated Rose Bengal (RB) solution and in an anaerobic lactate solution (Fig. 1, Spectra 2 and 1). The molar extinction coefficients for both the products on cellulose were determined from these spectra. The similarity in the absorption spectra of the reduction product and the corresponding model compound, 3-(β-hydroxyethylsulfonyl)-2-anisidine has been previously confirmed.[21] Exposure of the dyed film in an anaerobic DL-mandelate

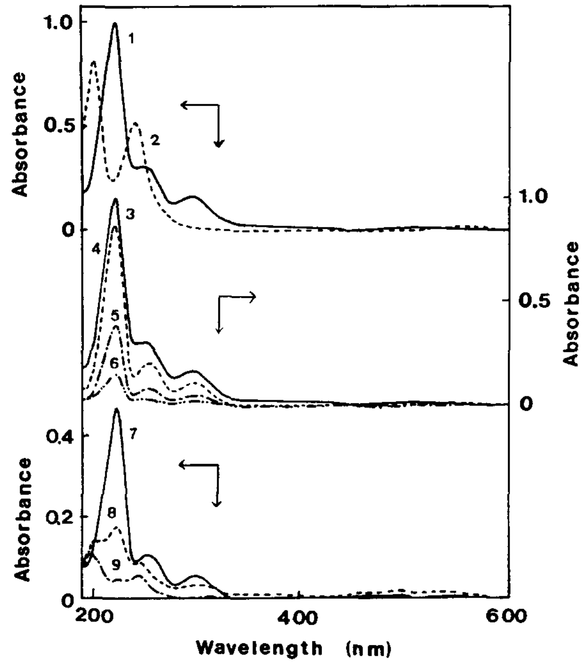


Fig. 1. Absorption spectra of the photo-decomposed products for Red 22 (original dye concentration for spectra 1, 3–9 = $2{\cdot}47 \times 10^{-2}$ mol/kg) on cellophane after exposure in aqueous solutions (cf. Fig. 2). 1, In an anaerobic sodium lactate (0·50 mol/dm^3) solution in a nitrogen atmosphere for 7 h; 2, in Rose Bengal ($3{\cdot}3 \times 10^{-5}$ mol/dm^3 + 0·05 mol/dm^3 Na_2SO_4) solution for 26 h (original dye concentration = $2{\cdot}47 \times 10^{-2}$ mol/kg, 91·5% relative fading; the spectrum of the original dye was subtracted); 3–6, in an anaerobic sodium lactate (0·50 mol/dm^3) solution in a nitrogen atmosphere for 7 h, 5 h, 2 h and 1 h, respectively; 7–9, in an aerobic sodium lactate (0·50 mol/dm^3) solution for 10 h, 5 h and 2 h, respectively.

solution gave the same absorption spectrum as that in the lactate solution, a similar reduction product.[21]

Absorption spectra for Red 22 on cellophane after exposure were measured, and from which the corresponding spectrum of the original dye was subtracted so as to give no absorption at the wavelength of maximum absorption, as shown in Fig. 1 (Spectra 3–6). Although absorption spectra of dyed cellophane during exposure in an aqueous aerobic solution of substrate could not be measured, those at wavelengths longer than 210 nm after the exposure were confirmed to coincide with the sum of the spectra of the original dye, the oxidation product and the reduction product. An intermediate to the corresponding amines, probably a hydrazine derivative (no existence of which could be spectroscopically observed) may be easily reduced further or oxidized by singlet oxygen to revert to the original form.

3.1.1 Exposure in aqueous lactate solution

From a spectral analysis of the absorption spectra, the photo-decomposition behavior of Red 22 and the formation of the reduction product on exposure in lactate solutions are shown in Fig. 2. Since an increase in the concentration of the reduction product was equal to the decrease in that of the original dye at the same time of exposure within the experimental error, the scission of the dye–fiber bond during exposure in water at pH 6·0 and 50°C was confirmed to be negligible. The similarity in absorption spectra of the reduction products at various times of exposure could indicate the formation of only one type of reduction product, with no by-product. This behavior was also observed for the oxidation products on exposure in aerated water and in an aerated Rose Bengal solution.[19–21] Comparing the relative fading of Red 22 at λ_{max} with the increase in the absorption of the oxidation product, the concentration of oxidized product on cellulose was also determined.

The exposure of dyed film in an aerated lactate solution, i.e. in presence of both substrate and oxygen, yielded the degradation product whose absorption spectra are also shown in Fig. 1 (Spectra 7–9), where the spectra of unfaded original dye were subtracted. Assuming the additivity of the spectra (Spectra 2 and 1) of both oxidation and reduction products, the concentrations of both the products were estimated. Thus, the concentrations of reduction and oxidation products were obtained by solving simultaneous equations which gave the absorbance at two wavelengths (222 and 245 nm). The concentrations were further modified by comparing the additive spectra for each component of corresponding concentration with the experimental spectra for the photo-decomposed products.

On exposure of Red 22 in an aerated or an oxygen-saturated lactate solution, the reductive fading was initially inhibited and only the oxidative

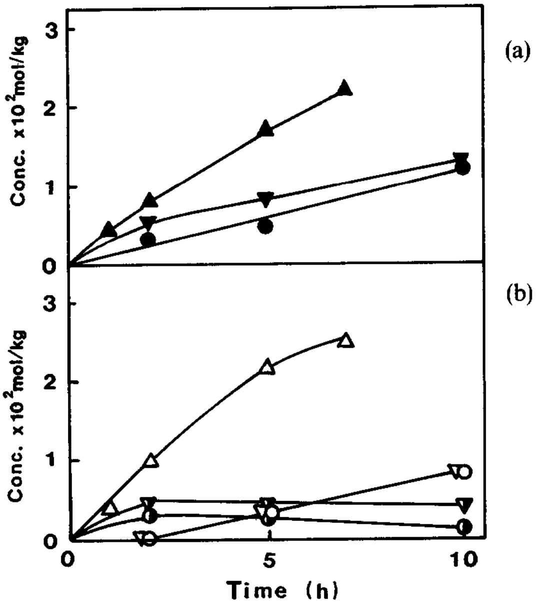


Fig. 2. (a) Decomposition and (b) formation of reduction and oxidation products for Red 22 (original dye concentration = 2·47 × 10^{-2} mol/kg) in anaerobic and aerobic sodium lactate (0·50 mol/dm^3) solutions (cf. Fig. 1).

Exposure in	(a) *Decomposition*	(b)	
		Reduction product	*Oxidation product*
Anaerobic solution in a nitrogen atmosphere	▲	△	—
Aerobic solution	●	○	◑
Oxygen-saturated solution	▼	▽	⧩

process occurred (Fig. 2). An increase in the concentration of oxygen gave only a rise in the initial rate of photo-oxidation. Later, the oxidative fading was inhibited in the aerated and oxygen-saturated solutions and reductive fading then proceeded. The rate of reduction in the latter half of the exposure, however, was smaller than that under anaerobic conditions, showing a suppression effect by oxygen. The initial rate of fading in an aerated solution was smaller than that under anaerobic conditions at the same substrate concentration owing to the mutual suppression effect. The oxidation was completely inhibited in the middle of the exposure, after which time only photo-reduction was observed and the concentrations of oxidation product gradually decreased. After the reduction occurred, the sum of the concentrations of reduction and oxidation products did not coincide with the concentration of Red 22 decomposed, but the sum of the concentration of the reduction product and the maximum concentration of the oxidation product was equal to twice the amount of Red 22 decomposed. This implies the possibility that the phenyl ring of the oxidation product on cellulose was later reduced. There is evidence for this reaction in the absorption spectrum of the degradation products (see Section 3.2). Moreover, this fact implies that no break of dye–fiber bond occurs when either reductive or oxidative fading takes place exclusively.

3.1.2 Exposure in aqueous DL-mandelate solution

On exposure in anaerobic and aerobic DL-mandelate solutions, the behavior of the photo-decomposition for Red 22 and of the formation of both products are shown in Fig. 3. In spite of being a tenth of the concentration, DL-mandelate gave a similar rate of fading for Red 22 to that in lactate solution. The rate of fading for Red 22 by DL-mandelate in an anaerobic solution was estimated to be thirteen times larger than that by lactate, taking the difference in concentration into consideration.

On exposure in an aerobic DL-mandelate solution, both oxidative and reductive fading occurred simultaneously from the beginning of exposure.

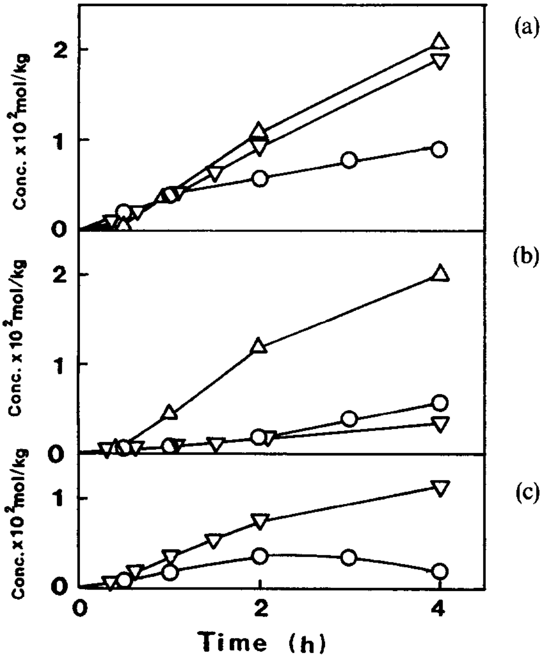


Fig. 3. (a) Decomposition and (b) formation of reduction product and (c) formation of the oxidation product for Red 22 (original dye concentration = 2·47 × 10^{-2} mol/kg) in anaerobic (△), aerobic (○) and oxygen-saturated (▽) sodium DL-mandelate (0·05 mol/dm^3) solutions.

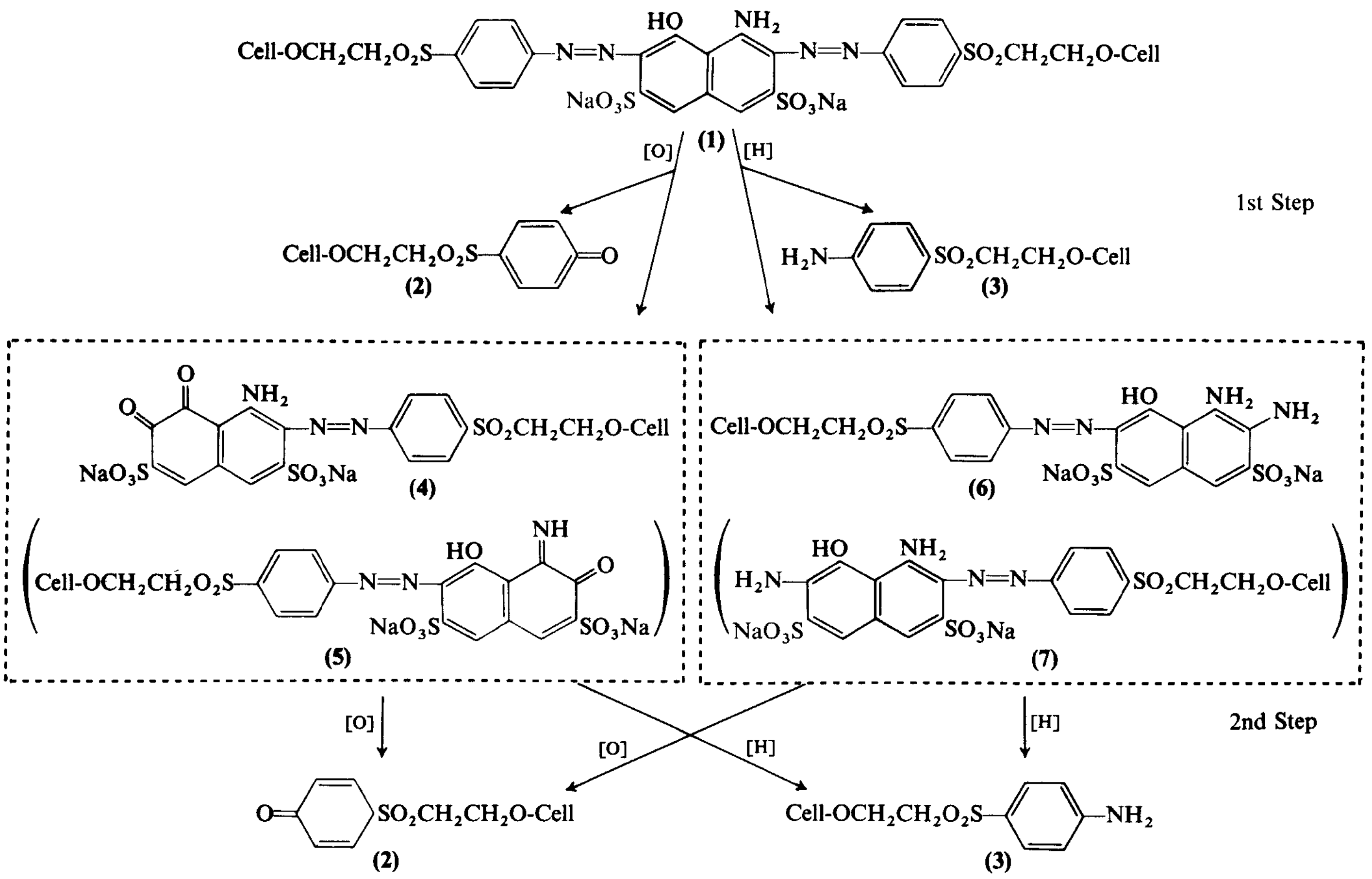
Under aerobic conditions, the rate of photo-oxidation for Red 22 was initially larger than that of photo-reduction, and later the rate of reduction became larger. On exposure in an oxygen-saturated solution, the subsequent rate of photo-oxidation became smaller than the initial rate, although the photo-oxidation was not inhibited. After the middle of the exposure, the sum of the amount of oxidation and reduction products became smaller than the amount of fading. The oxidation product may be photo-reduced by DL-mandelate. In the presence of oxygen, the photo-reduction of Red 22 by substrate may be suppressed by singlet oxygen owing to the high sensitivity of Red 22.

3.2 Fading of Black 5

Since Black 5 has an asymmetric structure, the ease with which either azo group is reduced or oxidized may be different. According to Yamamoto *et al.*,[23] azo groups adjacent to the amino group of Black 5 exist mainly in the azo form and those adjacent to the hydroxyl group in the hydrazone form. The latter azo groups may be more easily oxidized than the former, and the former more easily reduced than the latter. A photo-reaction scheme for Black 5 whose two reactive groups are bonded with cellulose, is outlined in Scheme 1. Because there is also Black 5 bonded to cellulose by either of the two reactive groups, and the fragment of the degradation products is split off by the photo-reaction, the actual reaction scheme for Black 5 is more complicated than that shown. Moreover, since azo groups adjacent to the amino group may be also oxidized and those adjacent to the hydroxyl group reduced, though their reactions may occur only in minor amounts, as shown in parentheses, four kinds of monoazo intermediates may be produced. These intermediates may be further oxidized and/or reduced in the second step.

3.2.1 Reductive fading

As in the case of Red 22, exposure of Black 5 on cellulose immersed in an anaerobic DL-mandelate or lactate solution in a nitrogen atmosphere was shown to cause reductive fading. The absorption spectrum of the reduction product was confirmed to have a close resemblance to that of the corresponding model compound, 4-(β-hydroxyethylsulfonyl)aniline described in a previous paper.[21] The coincidence of the absorption spectrum of the reductive product for Black 5 with that for Orange 16 (Fig. 4, Spectrum 1) was also confirmed. The molar extinction coefficient of the reduction product for Black 5 on cellulose was obtained from the reduction of Orange 16 (Fig. 4, Spectrum 1).



Scheme 1. Photo-oxidation and reduction of Black 5 bonded with cellulose on exposure. (Photo-decomposed products split off from cellulose were neglected.)

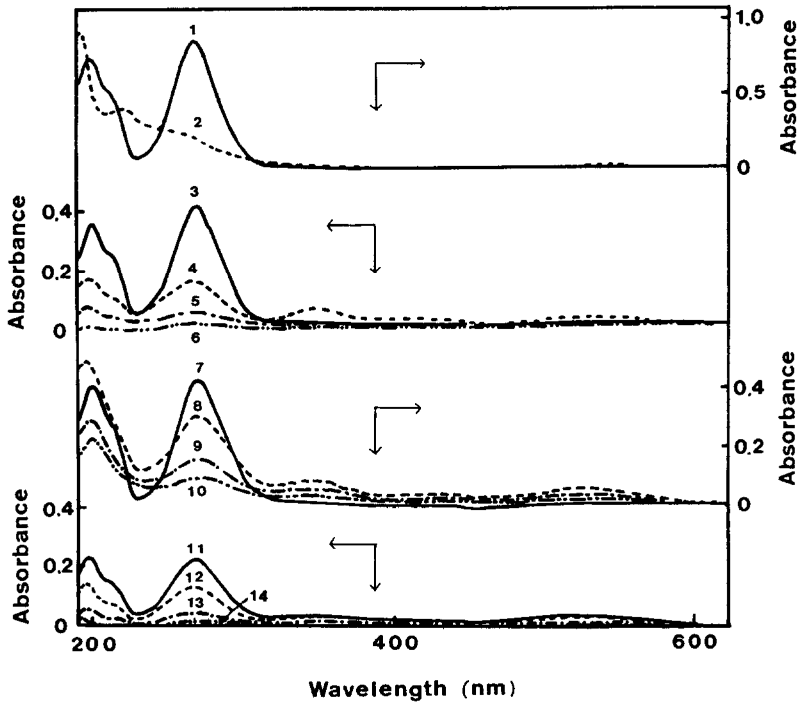


Fig. 4. Absorption spectra of the photo-decomposed products for Black 5 on cellulose by exposure in aqueous solutions in a nitrogen atmosphere, and those for the reduction and oxidation products for Orange 16. (Original dye concentration for Black 5 in spectra 3–14 = $5{\cdot}84 \times 10^{-3}$ mol/kg.) 1, Reduction product ($1{\cdot}65 \times 10^{-2}$ mol/kg) for Orange 16 after exposure in an anaerobic DL-mandelate (0·05 mol/dm^3) solution for 10 h; 2, oxidation product ($1{\cdot}06 \times 10^{-2}$ mol/kg) for Orange 16 on cellulose after exposure for 20 h in an aqueous Rose Bengal ($3{\cdot}3 \times 10^{-5}$ mol/dm^3 + 0·30 mol/dm^3 Na_2SO_4) solution (the spectrum of the original form was subtracted); 3–6, Black 5 after exposure in an anaerobic sodium lactate (0·50 mol/dm^3) solution for 10 h, 5 h, 2 h and 1 h; 7–10, Black 5 after exposure in an anaerobic sodium DL-mandelate (0·05 mol/dm^3) solution for 6 h, 4 h, 2 h and 1 h; 11–14, Black 5 after exposure in an oxygen-saturated sodium lactate (0·50 mol/dm^3) solution for 20 h, 10 h, 5 h and 2 h.

Subtracting the corresponding spectrum of the original dye from the spectrum of the dyed film exposed in an anaerobic lactate or DL-mandelate solution, the absorption spectra of the photo-decomposed products for Black 5 were obtained as shown in Fig. 4 (Spectra 3–10). The visible spectra of the monoazo intermediates may be regarded as having maximum absorption with low extinction coefficient at 530 nm. Judging from the absorption at 530 nm, the formation of the intermediates was saturated in the middle of the exposure at low DL-mandelate concentration, and at earlier times of exposure at a higher concentration. Thus, on exposure in the anaerobic solution of high DL-mandelate or lactate concentration, no or negligible amounts of such a monoazo intermediate **6** (see Scheme 1) were recognized in the reductive fading except in the initial period of exposure. At low DL-mandelate concentration, the reduction intermediates were not further reduced.

The formation behavior for **3**, the intermediate **6** and probably **7** in minor amounts and the decomposition behavior for Black 5 under anaerobic conditions are shown in Fig. 5. At the initial period of exposure, the reduction product **3** was formed at the same rate as that of the decomposition of Black 5, when Black 5 might be reduced to yield **3** and **6** due to reduction of the azo group adjacent to the amino group, and **3** was later formed at a larger rate, when both the azo groups might be reduced.

If both the azo groups of Black 5, whose two reactive groups were both bonded to cellulose, were reduced, two molecules of **3** must be formed from one molecule of Black 5. The molar ratio of the reduction product to Black 5,

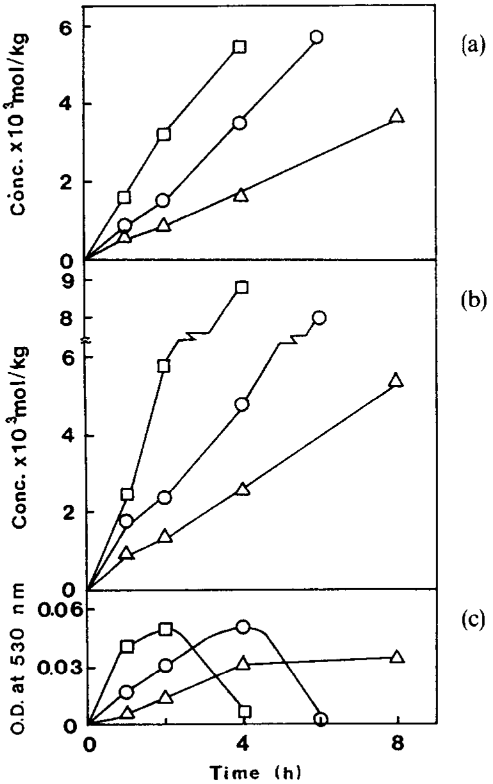


Fig. 5. (a) Decomposition and (b) formation of reduction products, and (c) formation of the reduction intermediates for Black 5 (original dye concentration = 5·84 × 10^{-3} mol/kg) after exposure in an anaerobic sodium DL-mandelate solution of concentrations 0·02 (△), 0·05 (○) and 0·10 (□) mol/dm^3 in a nitrogen atmosphere.

however, was estimated to be 1·4–1·7. This may be due to the reaction either of the vinylsulfonyl groups with water during the dyeing process or to the reduction of the phenyl ring during exposure, although the relative contribution of these could not be estimated.

Van Beek *et al.*[24–27] studied the photo-reduction of azo dyes in the presence of DL-mandelate and proposed a reaction scheme containing the formation of a ketyl radical. However, the photo-reaction processes shown in Figs 2, 3 and 5 appear to be too complex to allow full discussion of the mechanism.

3.2.2 Simultaneous oxidative and reductive fading in DL-mandelate solution

Subtracting the original spectrum for Black 5 from the spectra of the dyed film exposed in aerated DL-mandelate solutions, so as to give no absorption at λ_{max}, the absorption spectra of the photo-decomposed products are shown in Fig. 6, and give evidence for the existence of the oxidation product **2** in the spectrum near 200 nm. However, no clear difference was noticed between the visible spectra of the intermediates formed under anaerobic and aerobic conditions. The fact that the oxidation product **3** for Black 5 was the same as that for Orange 16 was confirmed previously[21] by the coincidence of

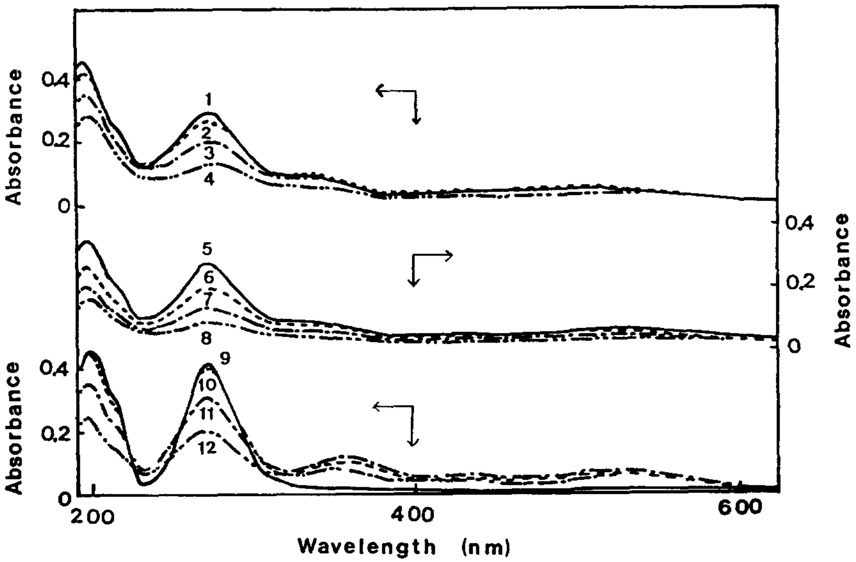


Fig. 6. Absorption spectra of the photo-decomposed products for Black 5 (original dye concentration = 5·84 × 10^{-3} mol/kg) and Orange 16 after exposure in aqueous solutions. 1–4, Black 5 in an oxygen-saturated sodium DL-mandelate (0·10 mol/dm^3) solution for 8 h, 4 h, 2 h and 1 h; 5–8, Black 5 in an aerobic sodium DL-mandelate (0·05 mol/dm^3) solution for 8 h, 4 h, 2 h and 1 h; 9–12, Black 5 in an aerobic sodium DL-mandelate (0·20 mol/dm^3) solution for 8 h, 4 h, 2 h and 1 h.

their absorption spectra on the exposed film. It supports indirectly Scheme 1 for the oxidative fading and at the same time proves the formation of the intermediate **4**.

The concentration on an arbitrary scale for the intermediates (mainly **4** and **6**) was assumed as a first approximation to be described by the absorbance at 530 nm, and those of **2** and **3** were calculated by use of simultaneous equations from the absorbance at 230 and 270 nm, respectively. Extrapolating the absorbance at each wavelength at respective times of exposure to the initial time, the absorbance for the intermediates at each wavelength at the initial time were obtained. The values at the respective times were obtained by subtracting the contribution of the intermediates, assuming the proportionality of the absorbance at each wavelength to that at 530 nm. The concentrations of **2** and **3** on cellophane were calculated by using the absorption spectra of the oxidation and reduction products of Orange 16. The results are shown in Fig. 7 as the decomposition behavior for Black 5, the formation of **2** and **3**, and the variation of absorbance at 530 nm.

As in the case of Red 22 in DL-mandelate solution, the reduction and oxidation occurred simultaneously. Azo groups adjacent to the hydroxyl group of Black 5 might be oxidized to give **2** and **4**, while those adjacent to the amino group might be reduced to give **3** and **6**. At low DL-mandelate (0·02M) concentration, **2** and **3** are initially formed at nearly similar concentrations. With an increase in the concentration of DL-mandelate, the amount of **3** was increased.

In an oxygen-saturated DL-mandelate solution, on the other hand, the oxidation proceeded rapidly in the beginning, irrespective of a high DL-mandelate concentration (0·1M). The reduction was initially considerably suppressed and later it proceeded at the same rate as that in 0·05M DL-mandelate solution. Thus, in the initial period of exposure in an oxygen-saturated DL-mandelate (0·10M) solution, oxidation occurred mainly, and Black 5 was faded at the same rate as that in an aerated 0·1M DL-mandelate solution. Later, the oxidation was completely inhibited, the reduction proceeded at the same rate as that in an aerated 0·05M DL-mandelate solution, and the rate of fading for Black 5 in the oxygen-saturated solution fell in between the rates in 0·1M and 0·05M DL-mandelate solutions.

The suppression effect of oxygen on the photo-reduction of Black 5 was smaller than the effect on that of Red 22. The oxidation product **2** which was formed in a small amount, seemed to be decomposed by the subsequent exposure in an aerobic solution of high DL-mandelate ($\geq$0·1M) concentration. In contrast, the rate of formation of the oxidation product was decreased with an increase in the substrate concentration, i.e., a suppression effect by the substrate on the photo-oxidation. The photo-oxidation was

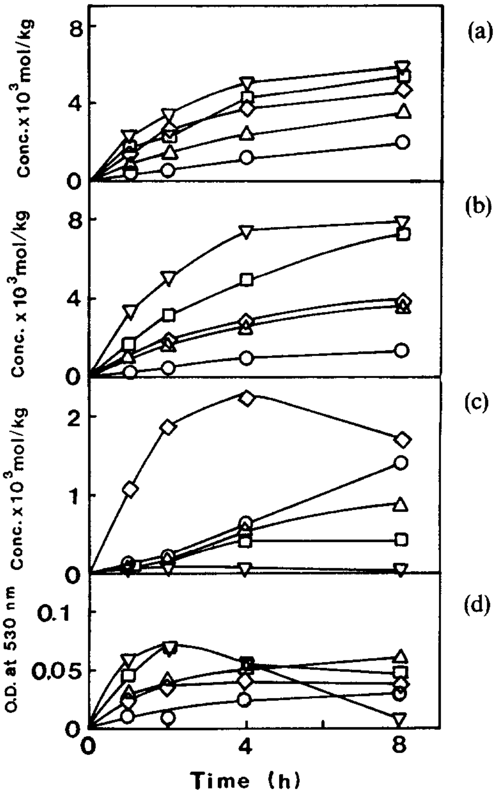


Fig. 7. (a) Decomposition and (b) formation of the reduction products, (c) formation of oxidation product, and (d) formation of intermediates for Black 5 (original dye concentration = $5{\cdot}84 \times 10^{-3}$ mol/kg) in aerobic aqueous sodium DL-mandelate solutions of concentrations 0·02 (○), 0·05 (△), 0·10 (□) and 0·20 (▽) mol/dm^3 and in an oxygen-saturated sodium DL-mandelate (0·10 mol/dm^3) solution (◇).

suppressed from the middle of the exposure in higher substrate concentrations (≥0·1 M) but not in low concentrations, as shown by the small increase in the concentrations of **2** and the intermediates after that period.

The reduction or decomposition of the intermediates formed initially was observed only in exposures in an aerobic DL-mandelate solution of high concentration (≥0·1 M), but not in the oxygen-saturated solution, irrespective of the high DL-mandelate concentration. The decrease in the concentration of the intermediates could be confirmed by a comparison of the decrease in the absorbance at 530 nm with the increase in that of **3**, due to the further reduction of the intermediates, thus supporting the photoreduction in the second step in Scheme 1.

In DL-mandelate (0·1 M) solution, oxygen gave profound effects on the rate of formation of photo-products, a suppression effect on the rate of formation of 3 and a large promotion effect on that of 2. Thus, an increase in the concentration of oxygen changed the formation ratio of 2 and 3, but had little effect on the rate of fading of Black 5.

3.2.3 Simultaneous oxidative and reductive fading in lactate solution

The same fading experiments for Black 5 to those in DL-mandelate solutions were carried out in aqueous sodium lactate (0·50M) solution. The absorption spectra of the dyed film after exposure, from which the spectrum of corresponding original dye was subtracted, are shown in Fig. 4. They are nearly similar to those after exposure in anaerobic substrate solutions, although the rates of fading are different. The fading behavior and the formation of reduction product and intermediates are shown in Fig. 8. This fading behavior is similar to that of Red 22, as shown in Fig. 2. In this case, the rate of fading was the largest under anaerobic conditions and the smallest under aerobic conditions. However, the rates of formation of the reduction product and intermediates decreased with an increase in the concentration of oxygen, a suppression effect of photo-reduction by oxygen. The absence

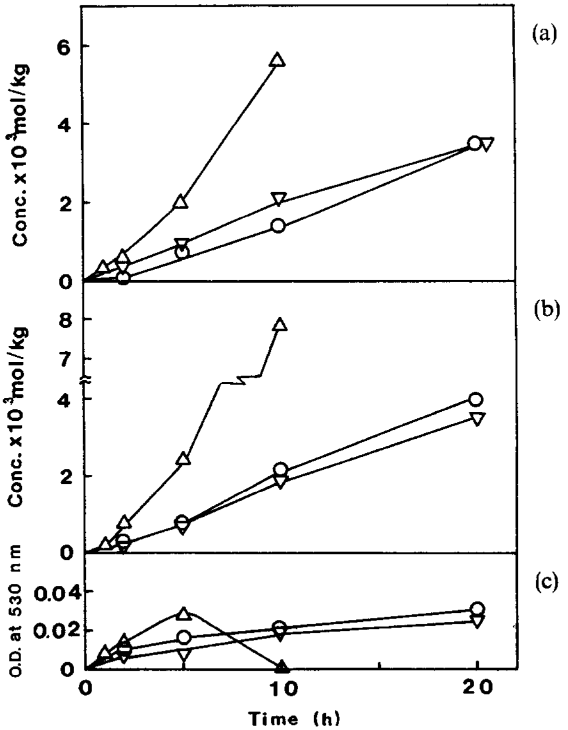


Fig. 8. (a) Decomposition and (b) formation of reduction products, and (c) formation of intermediates for Black 5 (original dye concentration = 5·84 × 10^{-2} mol/kg) in anaerobic (△), aerobic (○) and oxygen-saturated (▽) sodium lactate (0·50 mol/dm^3) solutions.

of any formation of oxidation products was confirmed by the spectra after exposure in aerobic and oxygen-saturated lactate solutions. Although the concentration of the intermediates formed could not be estimated, the molar ratios of the reduction product to the decomposed dye decreased with the concentration of oxygen. From these observations, it may be inferred that Black 5 is partially oxidized, but the oxidation products are immediately photo-reduced by lactate of high concentration. The amount of oxidized products produced may be increased with an increase in the concentration of oxygen.

Although the rate of fading for Black 5 on exposure under anaerobic conditions increased with time, that in a DL-mandelate solution was fourteen times larger than that in lactate solution, taking the difference in concentration into consideration. The rate of fading for Red 22 was initially 3·8 times and later 2·2 times larger than that for Black 5 in an anaerobic lactate (0·50M) solution, and was initially nearly similar to, and later 1·4 times larger, than that for Black 5 in an anaerobic DL-mandelate (0·05M) solution.

Since Black 5 has two kinds of reaction sites, either oxidation or reduction of the individual dye occurs, but as a whole processes occur simultaneously. Thus, this dye is faded via two kinds of decomposition route, both rates of which are influenced by the concentration of oxygen and substrates, a mutual suppression effect. The overall rate of fading for Black 5, however, is promoted by increasing the concentration of substrates but not that of oxygen. On exposure in aerobic lactate solutions of high concentration, photo-reduction of Black 5 occurs mainly and the photo-oxidized products are further photo-reduced. Although the fading of Black 5 is thus complicated and is influenced by many factors, the fading of this dye on fabrics may be markedly influenced by the concentration of substrates on the fabrics. When high concentration of lactate exists on the fabrics, the reduction of Black 5 may mainly occur on exposure.

4 SUMMARY

Fading of C.I. Reactive Red 22 and Black 5 on cellulose on exposure in aqueous solutions containing oxygen and substrate such as lactate or DL-mandelate was examined by spectral analysis. Red 22 and Black 5 were photo-decomposed at the position of the azo group to give reduction and oxidation products bound to cellulose, without by-product in the initial period of exposure, the oxidation products later being photo-reduced when exposed in concentrated substrate solution.

The rate of reductive fading for Black 5 increased with time of exposure, especially in an anaerobic lactate solution, and that for Red 22 was also

increased in DL-mandelate solution. The rates of photo-reduction for Red 22 and Black 5 by DL-mandelate were about ten times larger than those by lactate under anaerobic conditions. The rate for Red 22 was initially four times greater, and later twice as large as that for Black 5 in lactate solution, and was initially nearly similar and later 1·4 times larger than that for Black 5 in DL-mandelate solution.

On exposure of Red 22 on cellulose in aerated aqueous lactate solutions, only the oxidative fading was initially observed and later only the reductive fading, the rates of both fadings being mutually suppressed. On exposure in aerated aqueous DL-mandelate solution, the oxidative and reductive fading occurred simultaneously from the beginning, and later, depending upon the concentration of oxygen, the oxidative fading was suppressed and the reductive fading was promoted.

On exposure of Black 5 on cellulose in anaerobic aqueous substrate solutions, Black 5 was initially photo-reduced to yield an aniline derivative and monoazo intermediates, and later only the aniline derivative was formed, this being followed by further reduction of the intermediates depending upon the concentration of the substrates.

On exposure in aerobic aqueous DL-mandelate solutions, the oxidation and reduction end products, as well as some monoazo intermediates, were initially formed depending upon the concentration of substrate and oxygen. The formation of oxidation products was suppressed from the middle of the exposure at high substrate concentration and the intermediates were also further reduced. On exposure in aerobic aqueous lactate solution of high concentration, similar fading behavior to that in DL-mandelate solutions was observed, but the photo-oxidized products were immediately reduced further.

The present experimental method is useful for an accelerated testing method for the colorfastness of dyes to light as well as to the simultaneous effect of light and substrates.

ACKNOWLEDGEMENTS

The authors thank the Sumitomo Chemical Co. Ltd and Mitsubishi Chemical Corp. for their assistance in the preparation of this paper.

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