Dyes and Pigments 46 (2000) 181–192

The reaction of triphenodioxazine dyes with bleaching agents, hypochlorite and hydrogen peroxide, in aqueous solution

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Received 2 May 2000; accepted 1 June 2000

Abstract

The reaction of four triphenodioxazine (TPDO) reactive dyes on cellulosic films with bleaching agents, hypochlorite and hydrogen peroxide (HP), was examined in the aqueous solutions and redox potentials for two dyes were measured by cyclic voltammetry. The reaction of TPDO dyes on cellulosic films with HP at different pHs implied a nucleophilic reaction with HP anions, while the reaction with hypochlorite implied an electrophilic one with undissociated species of hypochlorite and a nucleophilic one with hypochlorite anion, although the relative reactivity among TPDO dyes was attributed mainly to the electrophilic one. The rates of hypochlorite bleaching for 4,11-bis(vinylsulfonyl)TPDO dyes on cellulosic film were smaller than those for 3,10-bis(disubstituted triazinyliminoethylimino)TPDO dyes, while the rates of HP bleaching showed the reverse relation. Oxidative bleaching of TPDO dyes on cellulosic films by hypochlorite and HP decomposed TPDO chromophore to leave only reactive groups bound with cellulose, although each reaction mechanism is different. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Triphenodioxazine reactive dyes; Redox potential; Nucleophilic reaction with hydrogen peroxide anion; Nucleophilic reaction with hypochlorite anion; Electrophilic reaction with hypochlorite

1. Introduction

In the previous paper [1], the aggregation of triphenodioxazine (TPDO) dyes in aqueous solution in the absence and presence of neutral electrolyte as well as on cellulosic substrate was examined. TPDO vinylsulfonyl dyes have a higher aggregation tendency in aqueous solution, especially in the presence of electrolyte as well as on cellulosic substrate, than the triazinyl dyes. The aggregation tendency in aqueous solution is similar to that of typical ionic dyes with high aggregation tendency [2–5]. It was spectrophotometrically proved that TPDO vinylsulfonyl dyes existed partially as dimer on cellulose and the swelling of dyed cellulosic films by water promoted the aggregation [1]. A copper phthalocyanine (CuPc) vinylsulfonyl dye did not undergo the latter behavior, although it also existed partially as a dimer on cellulose [1,6].

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PII: S0143-7208(00)00047-4

In a series of recent reports on the reaction of azo dyes with some bleaching agents, Unilever chemists revealed that the maximum oxidation rates exist at the pH of midpoint between the pK_a's for bleaching agents and hydroxyl groups in azo dyes [7–14]. They attributed the maximum to the electrophilic reactions of the dissociated species of azo dyes with the undissociated species of bleaching agents and/or the nucleophilic reactions of the undissociated species of azo dyes with the dissociated species of bleaching agents [11–14]. They proposed the reaction schemes for the azo-hydrazone tautomerism of C.I. Acid Orange 20 (Orange I) [11], for the oxidation reactions of C.I. Acid Orange 7 (Orange II) and Orange 20 with hypochlorite [12], and for the reaction of C.I. Acid Orange 7 with peracids [13] and with hydrogen peroxide (HP) [14]. Since, in principle, both the electrophilic and nucleophilic reactions occur simultaneously, the observed rates of reaction should be the sum of the rates of both reactions depending on the pH of the reaction solution examined and the reactant properties such as pK_a. However, product analysis was found to be extremely complex due to the degradation of initial reaction products into small highly water-soluble fragments [12].

In general, TPDO dyes have low color fastness to chlorinated water and poor wash-off property due to the high substantivity [15,16], although they have a brilliant royal blue color and high stability to photo-reduction as advantages. Preliminary experiments in the present study confirmed that TPDO dyes did not ionize over a wide range of pH except for sulfonic acid or carboxyl groups. TPDO dyes may experience nucleophilic reaction with anions of bleaching agents [11–14].

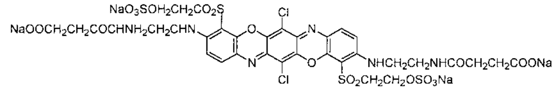
In this study, by examining pH-dependence of oxidative bleaching of TPDO dyes on cellulosic films by hypochlorite and HP, the nucleophilic and electrophilic reactions of undissociated species of TPDO dyes with oxidizing agents are kinetically examined. By measuring the absorption spectra of dyed cellulosic films after the bleaching, it is also examined what end products bound with cellulose are generated by the decomposition of four TPDO dyes in aqueous hypochlorite and HP solution.

2. Experimental

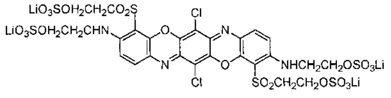
2.1. Dyes

The TPDO dyes used were the same as those used in the previous study [1]. Color fastness of these dyes on cotton fabrics is listed in Table 1. Chemical structure of the dyes are shown below:

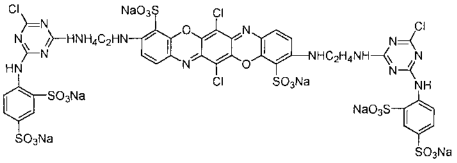
(1) A triphenodioxazine dye with two vinylsulfone anchors (VS-TPDO).



(2) A triphenodioxazine dye with two vinylsulfone anchors (PVS-TPDO)



(3) A triphenodioxazine dye with two monochlorotriazine anchors (MCT-TPDO)



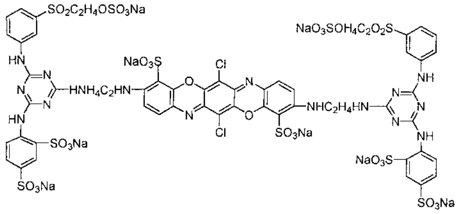
(4) A triphenodioxazine dye with two vinylsulfone anchors through a triazine ring (BF-TPDO).

Table 1
Light fastness and color fastness to chlorinated water for TPDO reactive dyes (N/3) on cotton fabrics

Dye	Light[a]	Chlorinated water[b]
PVS-TPDO	5–6	2–3
VS-TPDO	5–6	2
MCT-TPDO	5	1
BF-TPDO	4–5	1

[a] JIS L 0842 (carbon arc).

[b] ISO 105/E03, available chlorine 20 mg dm^{-3}, pH 7.5, 27°C, 1 h, and liquor ratio 1:100.



All the chemicals used were of reagent grade except for bleaching agents and were used without further purification.

2.2. Methods

The method of dyeing cellophane films is the same as before [1]. In order to examine the essential properties of TPDO dyes on cellulose, oxidation reaction with hypochlorite and HP was estimated in aqueous solution.

2.2.1. Determination of redox potential

In order to examine the redox potential of TPDO dyes, the cyclic voltammograms for PVS- and MCT-TPDO were measured in aqueous solution using a polarographic analyzer (Yanaco; Model P-1100). The experimental conditions used are given in Fig. 1.

2.2.2. Estimation of rates of reaction with sodium hypochlorite and HP

In order to perform the oxidation of TPDO dyes, aqueous sodium hypochlorite (available chlorine: usually 0.0051 g dm^{-3}) and HP (active H_2O_2: usually 16.0 g dm^{-3}) solutions were prepared. The pH of the hypochlorite solution (that of diluted hypochlorite solution with water was ca. 9.2.) was adjusted by adding a small quantity of sodium dihydrogen phosphate or trisodium phosphate solution, while that of the HP solution was adjusted by preparing an equal mixture of HP (32.0 g dm^{-3}) and sodium hydroxide (0.01, 0.05, 0.2, 0.3 and 0.5 M) of prescribed concentration. The pH deviation during bleaching was checked to be within experimental errors. (For example, the initial pH of 11.27 of the HP solution became 11.40 after 2 h at 40°C. The bleaching experiments were carried out within 1 h.) Available chlorine and HP were determined by iodometry with sodium thiosulfate. In the solutions of sodium hypochlorite (22.5°C) and HP (40°C), cellulosic films dyed with each reactive dye were immersed for a prescribed time and the relative fading (A/A_o) at the λ_{max} or at the isosbestic point [1] was measured.

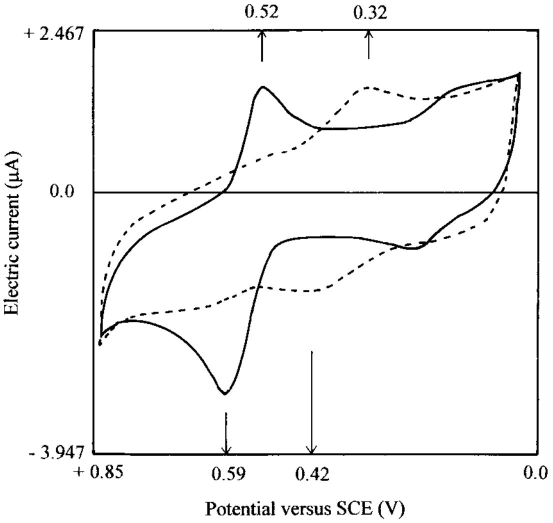


Fig. 1. Cyclic voltammograms for the first reduction and oxidation step of PVS-TPDO (1.06×10^{-4} mol dm^{-3}) (solid line) and MCT-TPDO (7.52×10^{-3} mol dm^{-3}) (broken line) in aqueous KCl (1.0 M) solution at 16°C. Plus interval, 0.10 s. Potential in volts is expressed as a difference between working and reference electrodes. Working electrode, glassy carbon electrode. Reference electrode, saturated calomel electrode (SCE).

3. Results and discussion

3.1. Redox potential of TPDO dyes by cyclic voltammetry

Redox potentials determined by some electrochemical methods such as cyclic voltammetry for aromatic compounds are known to correlate with their reactivity to oxidative and reductive agents [17–19]. The cyclic voltammograms for PVS- and MCT-TPDO are shown in Fig. 1 and the values of redox potentials are listed in Table 2. The redox potentials of water-soluble dyes may be determined by cyclic voltammetry, if they are reversible [19]. Since this is not the case, no

Table 2
Redox potential versus SCE for TPDO dyes by cyclic voltammetry (cf. Fig. 1)

Dyes	Oxidation potential (V)	Reduction potential (V)
PVS-TPDO	+0.59	+0.52
MCT-TPDO	+0.42	+0.32

absolute relative values can be determined. Then, the values were determined from the first cycle of the voltammograms. Comparing the oxidation potentials of PVS-TPDO with those of MCT-TPDO in aqueous electrolyte of high concentration, PVS-TPDO is more stable against oxidation and reduction circumstances than MCT-TPDO.

TPDO dyes on cellulosic films were reduced in aqueous sodium dithionite solution (for example, 0.01 M $Na_2S_2O_4$, at 40°C) to extinguish the color, but the color revived gradually in air and/or in aerated water. The rate of reduction for MCT-TPDO was very much faster than that for PVS-TPDO. The reduction of TPDO dyes by sodium dithionite may be reversible and the oxidation by bleaching agents may be irreversible. The oxidation of TPDO dyes on cellulose in aqueous solution of some bleaching agents is examined below (cf. 3.2). PVS-TPDO has a higher stability to oxidative and reductive attacks in aqueous solution and the results of cyclic voltammetry may display the relative stability of both the dyes.

Cyclic voltammetry measurements require the use of an electrolyte of high concentration. In such an aqueous electrolyte solution, PVS-TPDO may exist mainly as larger aggregates than monomer, while MCT-TPDO at best as a mixture of monomer and dimer [1]. However, the aggregation seems to have smaller effects on the stability of PVS-TPDO than that of MCT-TPDO. The redox potentials determined under such conditions may result in nearly inherent ones, even for PVS-TPDO.

3.2. Nucleophilic or electrophilic reaction of PVS- and MCT-TPDO with hypochlorite

According to Oakes et al. [7–12], Bredereck and Schumacher [20], and Gregory and Stead [21], azo dyes suffer oxidative fading due to electrophilic and/or nucleophilic reactions with bleaching agents in aqueous solution. Since hypochlorite undergoes two kinds of dissociation equilibrium ($K_a = 4.5\times10^{-4}$ and 3.2×10^{-8}), there are three kinds of reactant, HOCl, ClO^{-1}, and Cl_2, whose mol fractions are dependent upon the pH of solution. In the present study, we examine only the reactions above pH 6 and discuss how TPDO dyes on cellulose undergo such reactions with HOCl and ClO^-.

In the beginning, the dissociation of PVS-TPDO was examined in going from acid to alkaline aqueous solution. No change in the absorption spectra of PVS- and MCT-TPDO was confirmed over a pH range from 5 to 12 implying no dissociation of the dye except for sulfonic acid and carboxyl groups. It may undergo, therefore, only nucleophilic reaction with anionic species of bleaching agents. Oakes et al., however, reported that undissociated species of HOCl acts as an electrophile [8]. Bredereck and Schumacher [20] examined both the reactions (1) between HOCl and azo dyes whose hydroxyl groups dissociated and (2) between HOCl and azo dyes whose hydroxyl groups did not dissociate. Whether or not undissociated TPDO dyes undergo electrophilic reaction with hypochlorite is experimentally confirmed by pH-dependence of the rates of fading, as well as nucleophilic one with a hypochlorite anion.

3.2.1. Electrophilic oxidation by aqueous sodium hypochlorite

The oxidation of TPDO dyes was too fast to determine the rate of reaction in aqueous sodium hypochlorite solution of the concentrations $\geqq 0.002$ g dm^{-3} available chlorine at pH 6.8, although Oakes et al. [7–10] used a very low concentration of bleaching agents to reduce the rates. Lowering the concentration of oxidant resulted in the consumption of hypochlorite accompanied by incomplete decolorization to give imperfect reaction of pseudo-first-order. In order to examine the reactivity of TPDO dyes, the relative rates of fading of dyed cellulosic films by immersing in aqueous hypochlorite solution were estimated. Cellulosic substrate suppresses considerably the rate of fading and enables the estimation of the relative fading for PVS-TPDO by hypochlorite.

Since the value of pK_a is 7.53 for hypochlorous acid, the rates of apparent fading of PVS-TPDO decreased with an increase in pH above pH 6, as shown in Fig. 2(a). Thus, hypochlorite (HOCl) acts at least as an electrophile in the oxidizing reaction with PVS-TPDO under neutral and weakly alkaline conditions. As will be mentioned in next section, however, it was confirmed that the experimental rates of fading by hypochlorite deviated from the pH-dependence of the electrophilic reaction with HOCl with an increase in pH.

3.2.2. Apparent rate constants of the reaction with hypochlorite

The variations in the rate of fading of the dyed cellulosic films in Fig. 2(a) should correspond to the variation in the concentration of active species of oxidizing agents. In order to examine whether the variation can be quantitatively treated or not, the kinetics of fading are discussed below.

When hydrogen ion concentration changed, the total concentrations of bleaching agents ($[OX_1] = [HOCl] + [ClO^-]$ for hypochlorite, where square brackets describe the concentration [mol dm^{-3}]) can be practically kept constant at the analytical concentration, if the liquor ratio is large (> 500) and the consumption of oxidant is negligible. Although the reactions proceed in a heterogeneous system, the apparent rate of reaction with HOCl and ClO^-, whose second-order rate constants are k_2^E ($dm^3\ mol^{-1}\ s^{-1}$) and k_2^N ($dm^3\ mol^{-1}\ s^{-1}$), respectively, is given by:

$$-\frac{d[D]}{dt} = k_2^E[D][HOCl] + k_2^N[D][ClO^-], \qquad (1)$$

where D denotes TPDO dyes, t the reaction time. Here, the electrophilic and nucleophilic reactions, which are described by superscripts, E and N, respectively, of symbol k_2, are assumed to occur independently. The subscript of the symbols indicates second-order. Since one of the reactants, the dye, does not dissociate, only the concentrations of active species, HOCl and ClO^-, change, depending upon the pH of reaction solution and the values of K_a for hypochlorite. Integrating Eq. (1) gives the following equation:

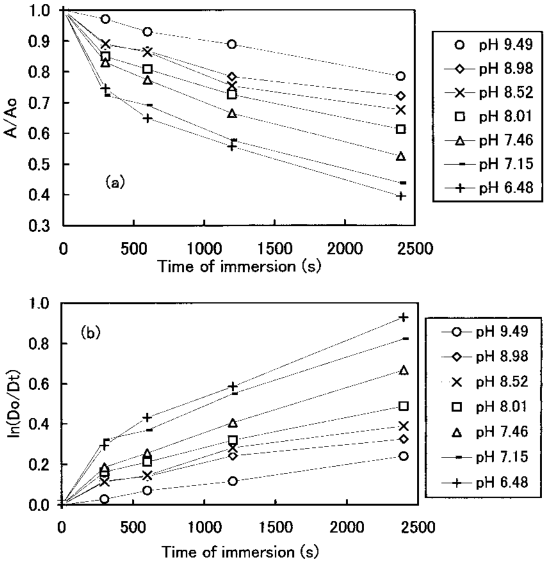


Fig. 2. (a) Relationship between relative fading, A/A_0, measured at λ_{max} and time of treatment, t (s), for PVS-TPDO on cellophane on immersing in aqueous hypochlorite (available chlorine, 0.0051 g dm^{-3}) at pH 6.48, 7.15, 7.46, 8.01, 8.52, 8.98 and 9.49 at 22.5°C, and (b) the relationships between $\ln [D_0]/[D_t]$ and t.

$$\ln\frac{[D_0]}{[D_t]} = \left(k_2^E[HOCl] + k_2^N[ClO^-]\right)t \qquad (2)$$

where $[D_0]$ and $[D_t]$ denote the dye concentration on cellulose (mol kg^{-1}) at $t = 0$ and t, respectively. Since the ratio of $[D_0]/[D_t]$ is a dimensionless parameter, the square brackets that describe the concentration are hereafter omitted except for in the mathematical equations. The concentrations of HOCl and ClO^- are given as the relationship between the total concentration and their mole fraction, x_{HOCl} and x_{ClO^-}. The mol fraction x_{HOCl} is described by:

$$x_{HOCl} = \frac{1}{1 + 10^{pH - pK_a^1}} \qquad (3)$$

where K_a^1 is the acid dissociation constant of hypochlorite. Applying the data of kinetics in Fig. 2(a) to these equations, linear plots of $\ln [D_0]/[D_t]$ against t were obtained as shown in Fig. 2(b), although in some cases, the initial rates of reaction deviated from the linearity. The dye concentrations were assumed to be proportional to the absorbance on cellulosic films at λ_{max}. From the slope of the linear part of plots for different pHs, the relationships between the values of slopes and mol fraction x_{HOCl} were obtained as shown in Fig. 3. The functional relationship, which is derived from Eq. (2), is given by:

$$\frac{\ln([D_0]/[D_t])}{[OX_1]t} = k_2^N + (k_2^E - k_2^N)x_{HOCl}, \qquad (4)$$

from which the values of k_2^N and k_2^E for the reaction between PVS-TPDO and hypochlorite can be obtained as listed in Table 3. This relation proves experimentally that HOCl acts as an electrophile and at the same time ClO^- as a nucleophile in the reaction between PVS-TPDO and hypochlorite depending upon the concentration of oxidant species over a pH range examined, which is kinetically described by Eqs. (1) or (4).

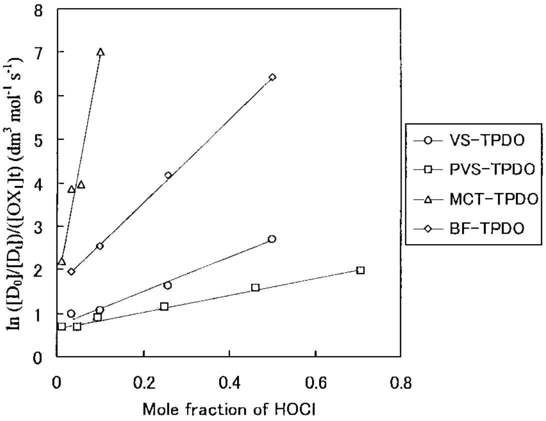


Fig. 3. Relationship between $\ln([D_0]/[D_t])/([OX_1]t)$ and mol fraction x_{HOCl} for four TPDO dyes: VS-TPDO, PVS-TPDO, MCT-TPDO, and BF-TPDO, on cellophane on immersing in aqueous hypochlorite (available chlorine, 0.0051 g dm^{-3}) at different pHs and 22.5°C.

3.2.3. Electrophilic and nucleophilic reactions of four TPDO dyes with hypochlorite

The fading of the other three TPDO dyes on cellulosic films immersed in aqueous hypochlorite solution was treated similarly and illustrated as the relationships of Eq. (4) as shown in Fig. 3. MCT-TPDO showed too large rates of fading to determine the rates by the same concentration of hypochlorite. Hypochlorite whose concentrations caused a similar amount of fading was used. When the same concentration range of hypochlorite was applied, MCT-TPDO showed larger fading but smaller rates of fading due to a decrease of dye concentration as a result of too large initial fading. Rates of bleaching for four TPDO dyes on cellulose were in the following order:

$$\text{MCT-TPDO} >> \text{BF-TPDO} >> \text{VS-TPDO} > \text{PVS-TPDO} \qquad (5)$$

This order coincides well with the color fastness to chlorinated water shown in Table 1. The apparent rate constants, k_2^E and k_2^N, for the reaction of TPDO dyes with HOCl and ClO^-, respectively, are listed in Table 3. The differences in the values of k_2^E among dyes are large, while those of k_2^N are small. Thus, their fading by hypochlorite is predominantly due to the electrophilic reaction with undissociated species of hypochlorite, although the nucleophilic reaction with ClO^- contributes also to the fading.

3.2.4. Fading of TPDO dyes on cellulosic films immersed in aqueous hypochlorite solution

The ratios, A/A_0, of absorbance of TPDO dyes on cellulosic films at λ_{max} on immersing in hypochlorite solution of lower concentration were plotted against time of immersion as shown in Fig. 4. In order to examine the gradual

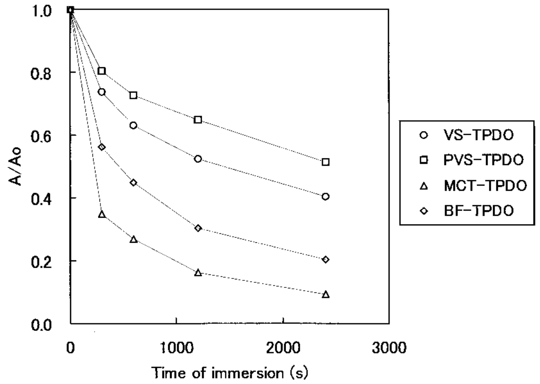


Fig. 4. Relationship between relative fading, A/A_0, measured at λ_{max} and time of treatment for four TPDO dyes: VS-TPDO, PVS-TPDO, MCT-TPDO, and BF-TPDO, on cellophane on immersing in aqueous hypochlorite (available chlorine, 0.0026 g dm^{-3}) at pH 7.14 and 22.5°C.

Table 3
Reaction of TPDO dyes on cellulose with hypochlorite in aqueous solution at 22.5°C (cf. Fig. 3)

Dye	$[OX_2]$ (mol dm^{-3})	pH	x_{HOCL}	$\ln([D_0]/[D_t])/t$ (s^{-1})	$\ln([D_0]/[D_t])/([OX_1]t)$ (dm^3 mol^{-1} s^{-1})	Apparent rate constant of reaction
PVS-TPDO	1.44×10^{-4}	7.15	0.706	2.87×10^{-4}	1.99	$k_2^E = 2.54$ dm^3 mol^{-1} s^{-1}
		7.46	0.460	2.29×10^{-4}	1.59	$k_2^N = 0.68$ dm^3 mol^{-1} s^{-1}
		8.01	0.249	1.65×10^{-4}	1.15	
		8.52	0.093	1.31×10^{-4}	0.910	
		8.98	0.046	9.80×10^{-5}	0.694	
		9.49	0.011	1.01×10^{-4}	0.701	
VS-TPDO	1.44×10^{-4}	7.53	0.500	3.89×10^{-4}	2.70	$k_2^E = 4.73$ dm^3 mol^{-1} s^{-1}
		7.99	0.257	2.36×10^{-4}	1.64	$k_2^N = 0.67$ dm^3 mol^{-1} s^{-1}
		8.49	0.099	1.53×10^{-4}	1.06	
		8.99	0.034	1.41×10^{-4}	0.98	
MCT-TPDO	7.19×10^{-5}	7.98	0.262	8.08×10^{-4}	11.23	
	1.44×10^{-4}	8.49	0.099	1.01×10^{-3}	7.01	$k_2^E = 54.9$ dm^3 mol^{-1} s^{-1}
		8.77	0.054	5.70×10^{-3}	3.96	$k_2^N = 1.75$ dm^3 mol^{-1} s^{-1}
		8.99	0.034	5.53×10^{-4}	3.84	
		9.50	0.011	3.16×10^{-4}	2.19	
BF-TPDO	1.44×10^{-4}	7.53	0.500	9.26×10^{-4}	6.43	$k_2^E = 11.2$ dm^3 mol^{-1} s^{-1}
		7.99	0.257	6.00×10^{-4}	4.17	$k_2^N = 1.65$ dm^3 mol^{-1} s^{-1}
		8.49	0.099	3.66×10^{-4}	2.54	
		8.99	0.034	2.81×10^{-4}	1.95	

variation in the concentration of TPDO dyes on cellulose in the course of fading by hypochlorite, we repeated immersing the dyed cellulosic films in the solution of lower concentration for 30 min and measured the absorption spectra of dyed films after every immersion. The immersion in the solution of higher concentration resulted in too much fading to give gradual variation of the spectra.

The absorption spectra after the every repeated immersion are shown in Fig. 5. They show a decrease in the absorption of the dye over the whole range of spectra with the progress of fading except for the UV region of the shortest wavelengths. Lowering the concentration of oxidant may result in consumption of hypochlorite to suspend the oxidation.

In spite of a tenth concentration of hypochlorite, the complete decoloration was obtained by repeating the immersion for 30 min. All the visible parts of the spectra for TPDO dyes examined were decreased proportionally with the repeated times of immersion. In the final case of

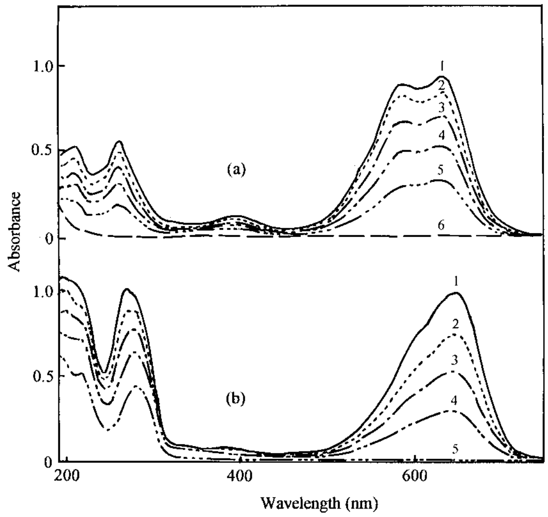


Fig. 5. Absorption spectra of (a) PVS-TPDO: no treatment (1), once (2), 4 times (3), 5 times (4), 6 times (5), and 10 times (6); and (b) MCT-TPDO: no treatment (1), once (2), twice (3), 3 times (4), and 6 times (5), on water-swollen cellophane immersed repeatedly in sodium hypochlorite solution (0.0010 g available chlorine dm^{-3}, pH 9.71) at 22.5°C for 30 min.

PVS-TPDO, a small fragment of absorption near 200 nm remained, while in the case of MCT-TPDO, aromatic residues, which may correspond to phenyl and triazinyl nuclei, remained. VS- and BF-TPDO showed a similar change in the spectra by the same treatment. It means that the TPDO nucleus was easily decomposed by hypochlorite without showing the existence of the intermediates to give the residue of reactive groups without chromophore.

In order to examine the effect of aggregation on the fading by hypochlorite, the absorption spectra in Fig. 5 were measured on water-swollen cellulosic films, since water promotes aggregation [1]. PVS-TPDO shows a clear existence of dimer on the original sample, while MCT-TPDO little existence of dimer. No preferential decomposition of monomer for PVS-TPDO was observed from the absorption spectra after every treatment by hypochlorite unlike the photofading of CuPc dye [6]. The spectra of VS-TPDO exhibited the same behavior. It is concluded that the oxidation of TPDO dyes on cellulose by immersing in aqueous bleaching agent solution results in no preferential decomposition of the monomer.

3.3. Nucleophilic oxidation by HP

Bredereck and Schumacher [22] concluded that the dissociated hydroxyazo dyes were predominantly relevant to the degradation reaction by HP anion. Oakes et al. [7–10] reported that anionic species of peroxides and peracids undergo a nucleophilic reaction with azo dyes to perform the oxidation. By using the same procedure as that of hypochlorite, the decomposition of PVS-TPDO on cellulosic films immersed in aqueous HP solution at different pHs and 40°C is also illustrated as the plots of values of A/A_0 at λ_{max} vs. the time of treatment in Fig. 6(a). Since the value of pK_a is 11.75 for HP, the concentration of nucleophiles (HO_2^-) may increase with an increase in pH below pH corresponded to pK_a of HP. If hydrogen peroxide anion acts as a nucleophile to oxidize PVS-TPDO, the rates of fading of the dyes should increase with increasing pH of the solution. The results illustrated in Fig. 6 show that such a reaction occurred.

3.3.1. Apparent rate constants of the reaction

The variations in the degree of fading of the dyed cellulosic films by HP, illustrated in Fig. 6(a), should correspond to the variation in the concentration of an active species of oxidizing agents. In order to examine whether the variation can be quantitatively treated or not, the kinetics of fading are discussed below.

When hydrogen ion concentration changed, the total concentration of bleaching agents ($[OX_2] = [H_2O_2] + [HO_2^-]$ for HP) can be kept constant as the analytical concentration. Although the reactions proceed in a heterogeneous system, the apparent rate of reaction of TPDO dyes with H_2O^-, whose second-order rate constant is k_2^N ($dm^3\ mol^{-1}\ s^{-1}$), is given by:

$$-\frac{d[D]}{dt} = k_2^N[D][HO_2^-] \qquad (6)$$

Although TPDO dyes do not dissociate, only the concentrations of active species of bleaching agents change depending upon the pH of reaction

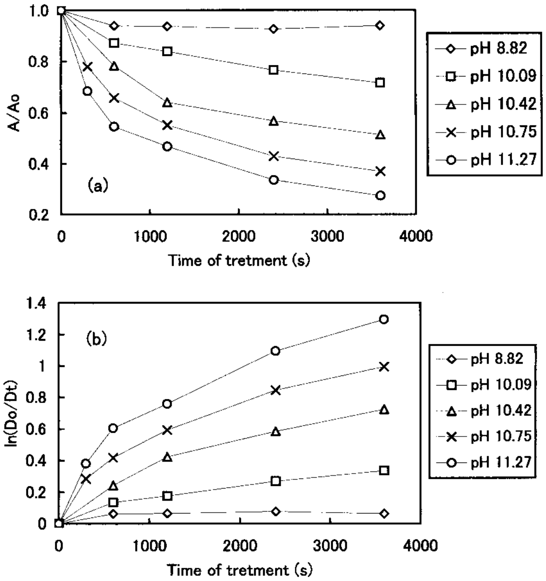


Fig. 6. (a) Relationship between relative fading, A/A_0, measured at λ_{max} and time of treatment, t (s), for PVS-TPDO on cellophane on immersing in aqueous HP solution (available HP, 16.0 g dm^{-3}) at pH 8.82, 10.09, 10.42, 10.75 and 11.27 at 40°C, and (b) the relationships between ln $[D_0]/[D_t]$ and t.

solution and the values of K_a^2 for bleaching agent. The concentration of HP anion is described by:

$$[HO_2^-] = [OX_2]x_{HO_2^-} \qquad (7)$$

And mole fraction $x_{HO_2^-}$ is given by:

$$x_{HO_2^-} = \frac{10^{pH-pK_a^2}}{1+10^{pH-pK_a^2}} \qquad (8)$$

where K_a^2 is the acid dissociation constant of HP. Integrating Eq. (6) leads to following equation:

$$\ln\frac{[D_0]}{[D_t]} = k_2^N[OX_2]x_{HO_2^-}t \qquad (9)$$

By applying the data of kinetics for PVS-TPDO to these equations, we can illustrate the relationship of Eq. (9) as a function of mole fraction as shown in Fig. 7. The linear relationship through the origin shows that Eq. (6) holds well for the oxidation reaction of PVS-TPDO with HP. The values of k_2^N, listed in Table 4, are nearly constant over a pH range examined. It is concluded that HO_2^- acts as only a nucleophile to react with PVS-TPDO.

3.3.2. Rates of fading of TPDO dyes by HP

The relative rates of fading for the other three TPDO dyes on cellulosic films were also examined by immersing in aqueous HP solution at 40°C, and analyzed by the same method as shown in Fig. 7. The values, k_2^N, for the apparent rates of bleaching by HP were in the following order:

$$\text{PVS-TPDO} > \text{VS-TPDO} >> \text{MCT-TPDO} > \text{BF-TPDO} \qquad (10)$$

This order (10) is completely reverse to the order (5). The reaction of TPDO dyes with HO_2^- that results in order (10) is due to a nucleophilic one, while that with hypochlorite that results in order (5) is due to a electrophilic one. The contribution of electrophilic reaction to the fading by HP was negligible even at small mol fraction of HO_2^- or at large mol fraction of H_2O_2 for all TPDO dyes.

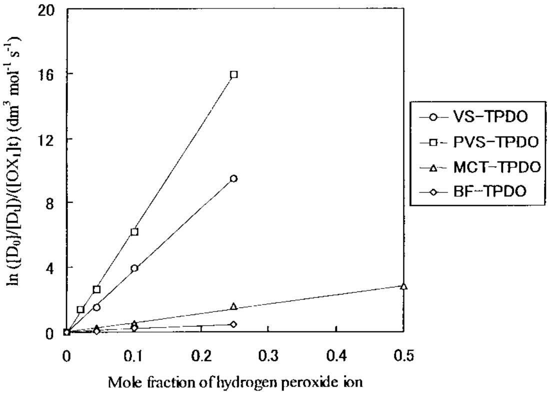


Fig. 7. Relationship between $\ln([D_0])/[D_t]/([OX_1]t)$ and mole fraction of HP ion HO_2^- for four TPDO dyes: VS-TPDO, PVS-TPDO, MCT-TPDO, and BF-TPDO, on cellophane on immersing in aqueous HP solution (available HP, 16.0 g dm^{-3}) at different pHs and 40.0°C.

3.3.3. Absorption spectra of decomposition products by HP

In order to obtain the absorption spectra of large fading by HP, the immersion of MCT- and BF-TPDO on cellulosic films into HP solution at pH 11.75 for 6 h and the immersion of VS- and PVS-TPDO on cellulosic films into the solution at pH 11.27 for less than 1 h were carried out. As expected from Fig. 6, Fig. 8 shows that TPDO dyes on cellulosic films experience initially large and subsequently slow fading. An increase in fading by HP decreased the light absorption of MCT- and PVS-TPDO on cellulosic films immersed in HP solution over the wavelengths from 200 to 750 nm (Fig. 8). Subtracting the absorption spectrum corresponded to the original one from the spectrum of the immersed sample, by spectral analysis, leaves the spectrum of the decomposition products, which are bound with cellulose. The spectra of four TPDO dyes on cellulose after immersing in HP solution were similar in shape to the spectra on cellulosic films immersed in hypochlorite solution (cf. Fig. 5).

The relation between the amounts of decomposition products for MCT- and BF-TPDO, illustrated by the height of double peak below 300 nm, and those of fading described by A/A_0 at λ_{max} was the same for the cases of HP and hypochlorite. The amounts of decomposition products for both the dyes were proportional to those of fading. Compared with the ratio of the amount of

Table 4
Reaction of TPDO dyes with hydrogen peroxide at 40°C (cf. Fig. 7)

Dye	$[OX_2]$ (mol dm^{-3})	pH	$x_{HO_2^-}$	$\ln([D_o]/[D_t])/t$ (s^{-1})	$\ln(D_0/D_t)/([OX_2]t)$ ($dm^3\ mol^{-1}\ s^{-1}$)	Mean apparent rate constant of reaction
PVS-TPDO	0.471	10.09	0.0214	6.61×10^{-5}	1.40×10^{-4}	$k_2^N = 6.25\times10^{-3}$ $dm^3\ mol^{-1}\ s^{-1}$
		10.42	0.0447	1.25×10^{-4}	2.65×10^{-4}	
		10.75	0.101	2.91×10^{-4}	6.18×10^{-4}	
		11.27	0.249	$7.51\times10{-}4$	1.59×10^{-3}	
VS-TPDO	0.471	10.42	0.0447	8.92×10^{-5}	1.89×10^{-4}	$k_2^N = 3.98\times10^{-3}$ $dm^3\ mol^{-1}\ s^{-1}$
		10.75	0.101	1.98×10^{-4}	3.93×10^{-4}	
		11.27	0.249	4.47×10^{-4}	9.48×10^{-4}	
MCT-TPDO	0.471	10.42	0.0447	1.29×10^{-5}	2.74×10^{-5}	$k_2^N = 5.93\times10^{-4}$ $dm^3\ mol^{-1}$ s−1
		10.75	0.101	2.69×10^{-5}	5.72×10^{-5}	
		11.06	0.170	6.06×10^{-5}	1.29×10^{-4}	
		11.27	0.249	7.43×10^{-5}	1.58×10^{-4}	
		11.75	0.500	1.33×10^{-4}	2.81×10^{-4}	
BF-TPDO	0.471	10.42	0.0447	4.33×10^{-6}	9.19×10^{-6}	$k_2^N = 1.86\times10^{-4}$ $dm^3\ mol^{-1}\ s^{-1}$
		10.75	0.101	7.50×10^{-6}	1.59×10^{-5}	
		11.27	0.249	2.30×10^{-5}	4.88×10^{-5}	

fading and formation of products, it was observed that HP treatment at pH 11.75 gave a smaller ratio than hypochlorite. HP treatment at high pH may result in dye–fiber bond scission partially, although the bond breakage was small with shorter and not too high pH treatment.

3.3.4. Effect of aggregation on the fading by HP

From the viewpoint of aggregation effect on the rate of oxidation by HP, the absorption spectra of treated samples may be analyzed on the basis of monomer–dimer equilibrium by use of absorption at corresponding wavelengths. As mentioned in the previous paper [1], the aggregation of VS- and PVS-TPDO on cellulosic films is promoted by the swelling of water, while MCT-TPDO shows only a small spectral shift.

During the treatment of TPDO dyes with HP, little variation of the equilibrium was observed in the shape of the main absorption band (cf. Fig. 8), although in the case of VS- and PVS-TPDO there was found a tendency that monomer species were decomposed a little faster than dimer species. It is concluded that the aggregation of TPDO dyes on substrates has a very small effect on the rates of bleaching.

3.4. Response or reactivity of TPDO dyes to various stimuli

As mentioned above, TPDO dyes possess solubilizing groups and reactive group anchors at the common positions, besides the common large TPDO nucleus. TPDO dyes have little substitution effects on the difference between HOMO and LUMO energy levels to give nearly the same absorption spectra in the visible region and the common royal blue color.

We developed the studies on the oxidation reaction of azo dyes with hypochlorite and HP by the pioneers, Gregory and Stead [20], Bredereck and Schumacher [19,21] and Oakes and Gratton [7–10] by the use of different dyes. Each successor made some revisions of the reaction mechanism by each pioneer, as mentioned above (cf. 1, 3.2 and 3.3). Since TPDO dyes used in the present study have no dissociable groups such as hydroxy and amino ones, the kinetics and reaction mechanisms of bleaching agents were quantitatively analyzed by changing the pH of the bleaching agent solution. In neutral and alkaline region, it was unambiguously proved that hypochlorite acts mainly as an electrophile and simultaneously as a nucleophile,

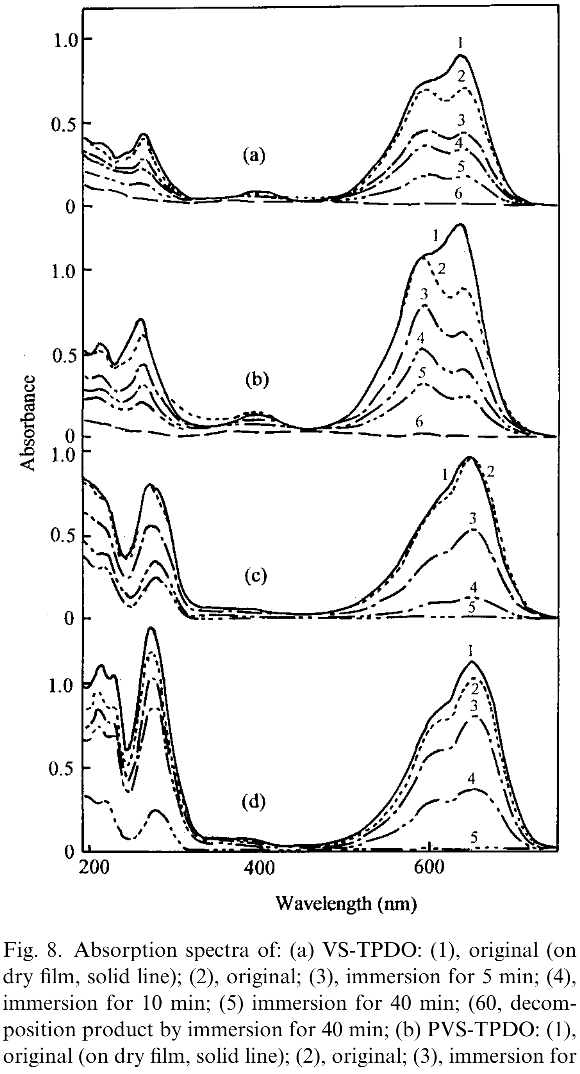


Fig. 8. Absorption spectra of: (a) VS-TPDO: (1), original (on dry film, solid line); (2), original; (3), immersion for 5 min; (4), immersion for 10 min; (5) immersion for 40 min; (60, decomposition product by immersion for 40 min; (b) PVS-TPDO: (1), original (on dry film, solid line); (2), original; (3), immersion for 5 min; (4), immersion for 20 min; (5), immersion for 60 min; (6), decomposition product by immersion for 60 min, (c) MCT-TPDO and (d) BF-TPDO: (1), original (on dry film, solid line); (2), original; (3), immersion for 1 h; (4), immersion for 6 h; 5, decomposition product by immersion for 6 h, on water-swollen cellophane immersed in aqueous HP solution (available HP, 16.0 g dm^{-3}) at pH 11.27 (for VS- and PVS-TPDO) or pH 11.75 (for MCT- and BF-TPDO) and 40°C.

while HP only as a nucleophile. We could estimate the reactivity of TPDO dyes by the values of second-order rate constant for the reaction with the bleaching agents and at the same time the reactivity of hypochlorite and HP with the same TPDO dyes.

In spite of the small effects of the substituents on the electronic spectra of TPDO dyes [16], however, the diversity in the thermal reaction with bleaching agents (cf. 3.2 and 3.3) and in the color fastness to various attacks (cf. Table 1) and the large differences in the aggregation tendency [1] were observed. Such diversity should have its origin in the substituents at the common positions as well as TPDO ring, because TPDO dyes differ only in the substituents of solubilizing groups and reactive group anchors. The reason why such varieties appear in the responses to various stimuli remains to be solved.

4. Summary

TPDO dyes on cellulose film experience nucleophilic oxidative reaction in hydrogen peroxide solution in the alkaline region, while the dyes experience electrophilic reaction as well as nucleophilic one of minor contribution in hypochlorite solution from neutral to alkaline region. The former nucleophile is HO_2^-, while the latter electrophile is HClO and the latter nucleophile is ClO^-.

The rates of fading for TPDO dyes with higher aggregation tendency by hypochlorite were smaller than those for the dyes with lower one. But, the order of the rates of fading for four TPDO dyes by HP was reverse to that by hypochlorite. It is concluded that the contribution of aggregation to the oxidative fading is small.

In spite of different reaction mechanisms, the oxidative attacks of bleaching agents decomposed TPDO nuclei to leave the same aromatic bridge system with reactive groups bound with cellulose.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research by the Minister of Education, Science and Culture, Japan, to whom thanks are due.

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