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The light stability of azo dyes and azo dyeings IV. Kinetic studies on the role of dissolved oxygen in the photofading of two heterobifunctional azo reactive dyes in aqueous solution

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Abstract

Heterobifunctional reactive derivatives of two previously studied azo chromophores were exposed to light in aqueous solution. In the presence of artificial perspiration, the initial and final rate of photofading depended on the oxygen level of the dye solution. An initial low rate of light-induced dye decomposition was followed by a much higher rate in the final stages of exposure. The lower the initial oxygen concentration the shorter the initial period low dye degradation and the higher the rate of photodegradation in the final stages. Light-induced dye decomposition follows first order kinetics. A reductive mechanism for perspiration assisted, light-induced degradation was supported by results from the photofading of the dyes in the presence of reductive compounds. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Azo reactive dyes; Kinetics of photofading; Perspiration-light stability; Role of oxygen

1. Introduction

An initial induction period has been characteristic in the kinetic curve describing the rate of photofading of heterobifunctional azo reactive dyes in aqueous solution in the presence of artificial perspiration. No such phenomenon could be observed in the absence of perspiration [1].

It has been demonstrated in earlier studies [2–6] that the presence of certain redox systems in the aqueous solution of azo reactive dyes decelerated their photofading in the initial period of exposure. Tartaric acid, succinic acid and mandelic acid as well as their salts, were the most frequently employed reducing compounds in those redox systems, whereas dissolved oxygen was the oxidizing agent. The reducing agents accelerated photofading of the dissolved dyes in the absence of oxygen. Reductive light-induced degradation of the dye molecules

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was influenced by the proton donating ability of the R_1-CHOH-R_2 residues in the reducing agents.

In the presence of dissolved oxygen, however, different reactions could take place, such as the oxidation of the photoactivated reducing agents, the oxidation of the products of reductive photodegradation, and series of radical reactions.

The joint presence of dissolved oxygen and a reducing agent in the aqueous dye solution results in a very slow initial photofading step followed by a much faster second step [6]. When dissolved oxygen was missing from the same system, the speed of both steps became equally high [6]. Okada [7,11] studied the photofading of azo reactive dyes on cellulose in the presence of oxygen and sodium-DL-mandelate, respectively, in order to obtain a correlation between the rate of photofading and the environmental conditions.

Many cellulosic vinylsulfonyl (VS) reactive azo dyeings are subjects of oxidative photofading if exposed to light in aerated water [7–9]. Some monochlorotriazinyl (MCT) dyeings undergo — under identical conditions — reductive or oxidative fading [10,11], while some other MCT dyeings undergo reductive photofading in deareated water, also in the absence of any reducing additive [10]. Most azo reactive dyeings undergo reductive fading when exposed to light in the presence of a reductive additive containing water [10]. In addition to dye structure, the type of dye-fibre bond determines whether an oxidative or reductive pathway will be dominant in the photofading of a dyed substrate under wet conditions [13–15]. In the presence of dissolved oxygen, the oxidative pathway is promoted and the reductive process is suppressed. If, however, the reducing species is in excess in an aqueous system, the reductive pathway is dominant.

The following radical mechanisms have been suggested [2] for both types of processes:

(a) In the presence of XH in the light exposed, oxygen-free aqueous dye (D) solution:

$$D + h\nu \rightarrow D^* \tag{1}$$

$$D^* + XH \rightarrow DH^\bullet + X^\bullet \tag{2}$$

$$D^* + X^\bullet \rightarrow \text{fast decomposition of D} \tag{3}$$

(b) In the presence of reducing agent (XH) and dissolved oxygen:

$$D + h\nu \rightarrow D^* \tag{1}$$

$$D^* + XH \rightarrow DH^\bullet + X^\bullet \tag{2}$$

$$X^\bullet + O_2 \rightarrow X{-}O{-}O^\bullet \tag{4}$$

(formation of less active radical)

$$X{-}O{-}O^\bullet + XH \rightarrow X{-}O{-}OH + X^\bullet \tag{5}$$

(slow reaction)

$D^* + X^\bullet \rightarrow$fast decomposition of D (3), which might be influenced by the following terminating steps:

$$X^\bullet + X^\bullet \rightarrow X{-}X \tag{6}$$

$$X{-}O{-}O^\bullet + X{-}O{-}O^\bullet \rightarrow X{-}O{-}O{-}X + O^2 \tag{7}$$

$$X^\bullet + X{-}O{-}O^\bullet \rightarrow X{-}O{-}O{-}X \tag{8}$$

The present work was aimed at studying the photofading kinetics of two heterobifunctional azoreactive dyes in aqueous solution, in the presence and absence of artificial perspiration, varying simultaneously the concentration of dissolved oxygen in the system from nearly zero to the saturation level. The components of artificial perspiration which might act as XH in a series of reactions leading to dye photodegradation are lactic acid and the binary system of acetic acid and glucose, respectively. Only acidic artificial perspiration was used in the present work, according to the Japanese ATTS standard method (12). An induction period in the photofading process was also observed in the presence of acidic artificial perspiration (1). As the explanation of this phenomenon was a goal of the present work, (Table 2) the same acidic artificial perspiration was used in the associated experiments. Consequently, we chose to avoid making direct comparisons with results obtained in the presence of alkaline artificial perspiration. However, the partial protonation of azo reactive dyes dissolved in acidic artificial perspiration can not be excluded. Likewise, the effect of buffering constituents (Na_2HPO_4, amino acids), and electrolytes (aggregation, suppressed electrolytes dissociation) were also taken into consideration.

2. Materials and methods (Tables 1–3)

2.1. Dyes

Table 1
Heterobifunctional azo reactive dyes used in this study

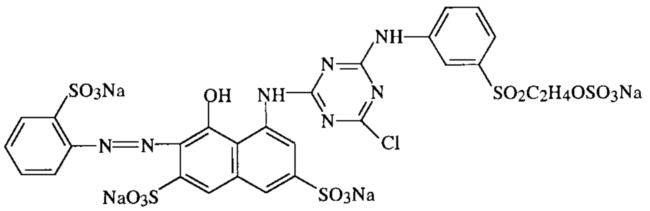
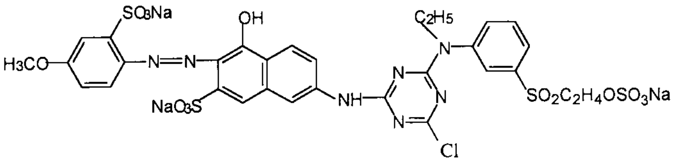
Code	Structure	Molar mass
A (MCT-VS)		983
B (MCT-VS)		938

Table 2
Composition of artificial perspiration [12]

Component	Structure	Concentration (g/litre)
Disodium-hydrogen-phosphate	$Na_2HPO_4 \cdot 12H_2O$	5.0
Sodium chloride	NaCl	5.0
Sodium D-panthotenate	$C_9H_{16}NO_5Na$	5.0
Glucose (anhydrous)	$C_6H_{12}O_6$	5.0
Lactic acid (85%)	CH_3-CHOH-COOH	5.0
L-Histidine monohydrochloride monohydrate	$C_6H_9N_3O_2.HCl.H_2O$	5.0
DL-Aspartic acid	$C_4H_7O_4N$	5.0
Acetic acid	CH_3COOH	(*)[a]

[a] (*) The final pH of the solution should be adjusted to 3.5 by acetic acid.

2.2. Dye solutions

CI

A 5×10^{-5} M dye solution in distilled water containing dissolved oxygen.

CII

A 5×10^{-5} M dye solution in distilled water, saturated with oxygen at room temperature for 60 min, after a 20-min light exposure.

CIII

A 5×10^{-5} M dye solution in distilled water, saturated with oxygen at room temperature for 60 min prior to light exposure.

CIV

A 5×10^{-5} M dye solution in distilled water, deaerated with argon at room temperature for 60 min prior to exposure.

Table 3
Reducing agents

XH	Structure	Molar mass
D-Lactic acid	CH_3-CHOH-COOH	90
D-Maltic acid	COOH-CHOH-CH_2-COOH	134

PI
A 5×10^{-5} M dye solution in artificial perspiration, containing dissolved oxygen.

PII
Similar dye solution to PI, but saturated with oxygen at room temperature for 60 min after a 20-min light exposure.

PIII
Similar dye solution to PI, but saturated with oxygen at room temperature for 60 min prior to light exposure.

PIV
Similar dye solution to PI, from which the majority of dissolved oxygen had been removed by treatment with argon gas at room temperature for 60 min, prior to exposure to light.

2.3. Light exposures

The sealeable quartz cuvette of the optical device (Fig. 1) was filled with dye solution and the solution was exposed to light for 450 min. The absorption spectra of the dye solution were recorded after 5, 10, 15, 20, 30, 50, 60, 100, 120, 300 and 450 min exposures, using an HP UV–vis 8452A diode-array spectrophotometer set at 510 and 502 nm for A (MCT-VS) and B (MCT-VS), respectively.

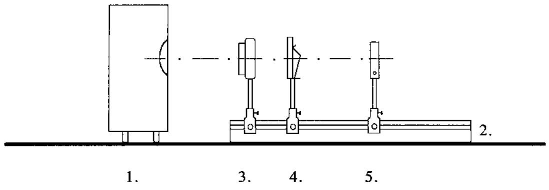


Fig. 1. Device used for light exposures. 1, 250 W high pressure mercury vapour lamp; 2. standard triangular optical bench; 3. quartz lens; 4. filter cell; 5. cuvette holder.

$$a\% = \frac{a_t}{a_0} \times 100$$

a_0 = initial absorbance in advance to exposure
a_t = absorbance after t min of exposure
a% = optical density

3. Results and discussion

3.1. Estimation for the order of the kinetics for the light-induced decomposition of reactive azo dyes in aqueous solution

The kinetics of the light-induced decomposition of the two dyes in aqueous solution could be followed by measuring changes in absorbance (a) as a function of time of exposure. By collecting data at t_{50} (50% drop in absorbance) and t_{80} (80% drop in absorbance), the kinetics of the reaction was estimated.

In the case of first order kinetics, $t=\frac{1}{k}\ln\frac{a}{a-x}$, if $x=0.5a$, and then

$$t_{50}=\frac{1}{k}\ln 2$$

if $x=0.8a$, then

$$t_{80}=\frac{1}{k}\ln 5$$

Table 4
First order kinetic value for t_{80}/t_{50} for the light-induced decomposition of azo dyes A and B

Dye	t_{50} (min)	t_{80} (min)	t_{80}/t_{50}
A (MCT-VS)	120	275	2.29
B (MCT-VS)	101	226	2.22
A (Chr)	82	185	2.23
B (Chr)	99	237	2.39
A (DCT)	105	237	2.26
B (DCT)	113	269	2.38
Ostazin Yellow HA	99	230	2.32
Ostazin Red H3B	124	299	2.41
Remazol Black B	53	125	2.36
Average	–	–	2.32 ± 0.10

hence

$$\frac{t_{80}}{t_{50}} = \frac{\ln 5}{\ln 2} = 2.32.$$

To confirm first order kinetic for the reaction the value for t_{80}/t_{50} has to be 2.32 or very close to it.

The results obtained for nine light exposures are summarized in Table 4.

The average of the t_{80}/t_{50} values was 2.32 ± 0.10, providing good evidence for first order kinetics for the light-induced decomposition reaction of the azo dyes in aqueous solution.

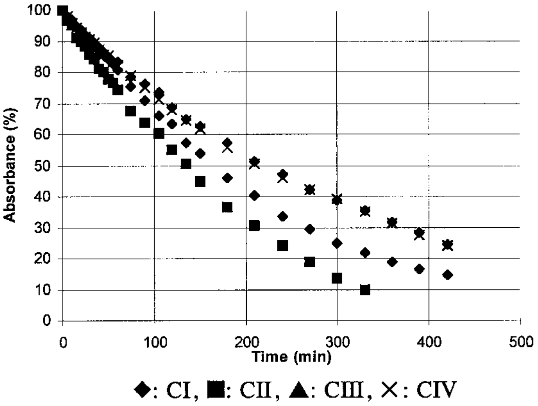


Fig. 2. Kinetics of the light-induced drop in absorbance for A (MCT-VS) in different media (CI, CII, CIII and CIV).

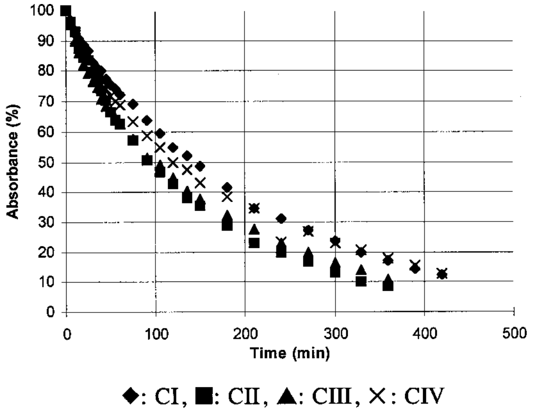


Fig. 3. Kinetics of the light-induced drop in absorbance for B (MCT-VS) in different media (CI, CII, CIII and CIV).

3.2. *Kinetics of the light-induced drop in absorbance of A (MCT-VS) and B (MCT-VS), under different conditions*

In first order reactions, the logarithm of the concentration of the reactant should be linear with respect to time. The slope gives the rate constant (k). Figs. 4, 5, 8 and 9 show the plots we obtained. In some cases a single straight line could be drawn through the data points, while more than one straight line, were possible in others.

3.3. *Kinetics of the light-induced decrease in absorbance for A (MCT-VS) and B (MCT-VS), in various perspiration-containing media (PI, PII, PIII and PIV)*

Based upon the data of Table 5 the following can be concluded:

- The reactions studied in all eight systems followed first order kinetics.
- The reaction rate varied with the changing dissolved oxygen concentration in CII, CIII, PI, PIII and PIV. (Figs. 2, 3, 6 and 7). Near the point of complete consumption of dissolved oxygen, light-induced dye decomposition followed more than one mechanism simultaneously.
- Both dyes were sensitive to oxygen in type C systems. Saturation with oxygen (CII, CIII) enhanced the rate of light-induced decomposition. The rate of photofading of B

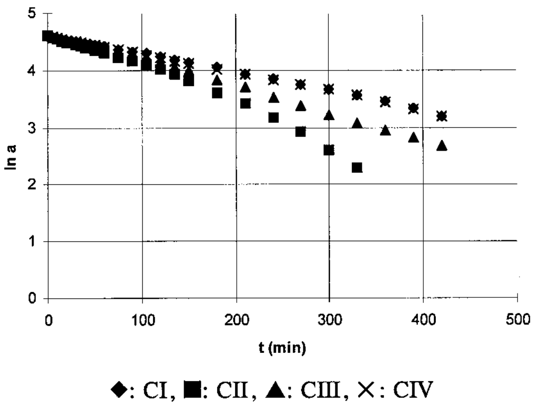


Fig. 4. ln (a) versus *t* for the light-induced decrease in the absorbance of A (MCT-VS) in CI, CII, CIII and CIV.

(MCT-VS) exceeded that of A (MCT-VS). k_B/k_A was between 1.45 and 1.50 in CI and CIV, whereas it was between 1.25 and 1.35 in CII and CIII.

- Saturation with oxygen 20 min after the start of light exposure (CII) resulted in a 2-fold increase of k_A and a 1.4-fold increase of k_B.
- Oxygen (at rather high concentration) showed only detectable increase in the rate constants in CII and CIII. The little change in oxygen concentration for CI versus CIV did not cause a difference in the shape of the fading curves.
- The presence of artificial perspiration in aqueous dye solutions significantly accelerated the light-induced dye decomposition. Dissolved oxygen, however, markedly retarded that reaction.

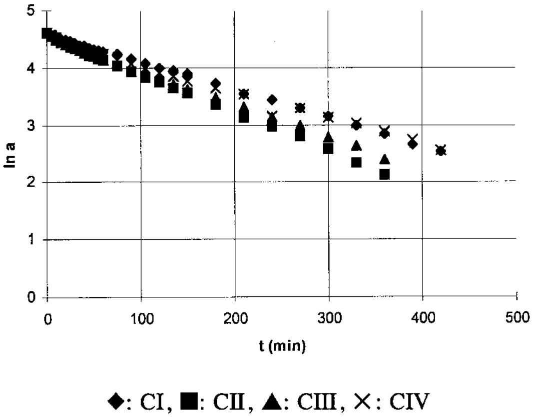


Fig. 5. ln (a) versus *t* for the light-induced decrease in the absorbance of B (MCT-VS) in CI, CII, CIII and CIV.

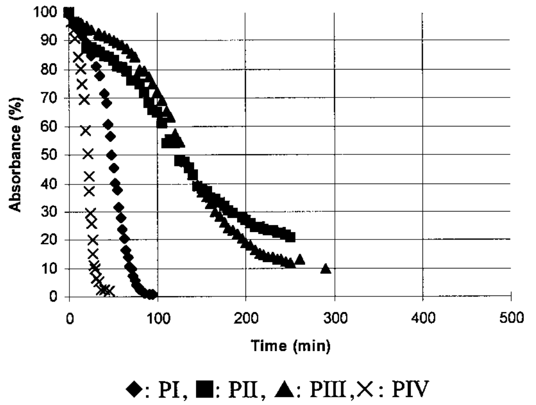


Fig. 6. Kinetics of the light-induced drop in absorbance for A (MCT-VS) in PI, PII, PIII and PIV.

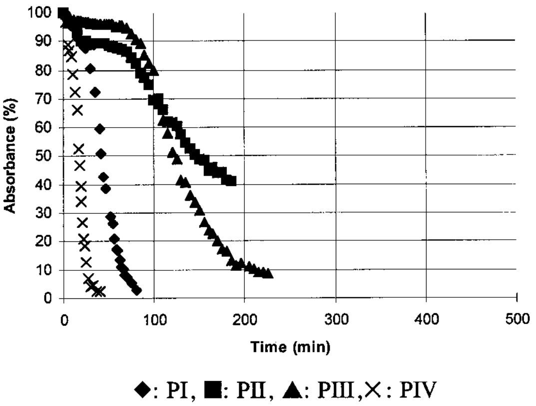


Fig. 7. Kinetics of the light-induced drop in absorbance for B (MCT-VS) in perspiration-containing media.

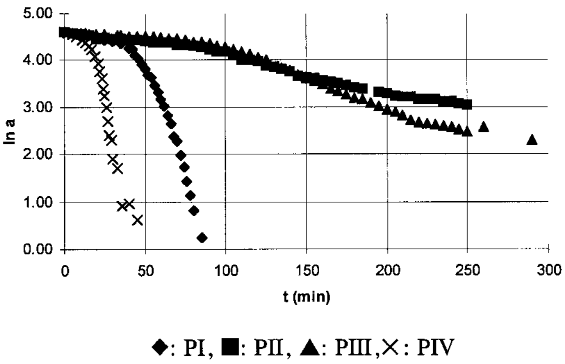


Fig. 8. ln (a) versus *t* for the light-induced decrease in absorbance for A (MCT-VS) in PI, PII, PIII and PIV.

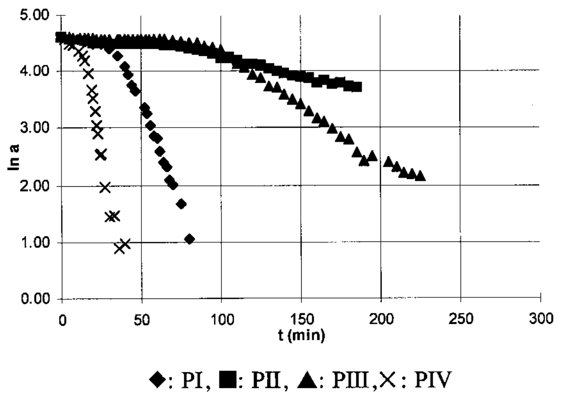


Fig. 9. ln (a) versus *t* for the light-induced decrease in absorbance for B (MCT-VS) in PI, PII, PIII and PIV.

Table 5
Rate constants for the light-induced decrease in absorbance for A (MCT-VS) and B (MCT-VS) in different media

		Period		
System	Rate constant	First 0–20 min	Second 20–60 min	Final > 60 min
CI	k_A h^{-1}	0.193	0.193	0.193
	k_B h^{-1}	0.289	0.289	0.289
CII	k_A h^{-1}	0.193	0.295	0.295
	k_B h^{-1}	0.289	0.403	0.403
CIII	k_A h^{-1}	0.281	0.281	0.281
	k_B h^{-1}	0.348	0.348	0.348
CIV	k_A h^{-1}	0.282	0.282	0.282
PI	k_A h^{-1}	0.249	20–40 40–60 0.249 6.978	0.978
	k_B h^{-1}	0.267	20–40 40 – 60 0.267 4.308	4.308
PII	k_A h^{-1}	0.246	20 – 80 0.162	> 80 0.552
	k_B h^{-1}	0.264	0.048	0.408
PIII	k_A h^{-1}	0.114	0.114	0.822
	k_B h^{-1}	0.120	0.120	1.158
PIV	k_A h^{-1}	0.900	13.920	–
	k_B h^{-1}	1.260	12.078	–

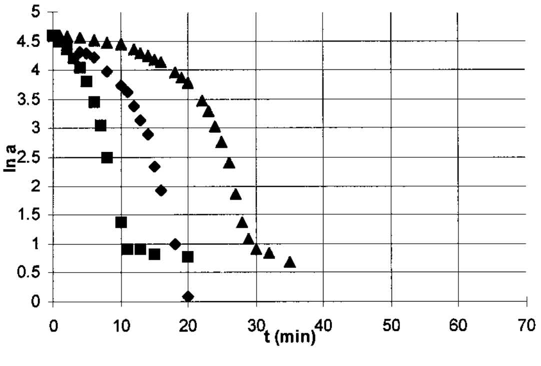
- Comparing the rate constants in CI and PI, the initial slight (1.3-fold) increase of k_A PI increased to 36-fold in the final period of light exposure. The corresponding difference in k_B was negligible initially and "only" 15-fold at the end.
- Saturation with oxygen caused significant deceleration in the light-induced decomposition of both dyes in PII and PIII at the early stages of exposure, when compared with the results in CII and CIII. Rate constants for both dyes became three times higher in the P-media than in C media, in the final stages of exposure and after the consumption of dissolved oxygen.
- k_A increased in PIV to 71-fold of the value in CIV, in the final stages of exposure. The increase in k_B was 42-fold under the same conditions. The presence of a small amount of dissolved oxygen delayed this large acceleration at the early stages of light exposure.
- The final k_A in PIV was 56 times higher than the k_A in PI. The corresponding ratio of k_B values was "only" 45:1.
- k_A became 90 times lower in PII versus PI, 40 min after the start of the light exposure. A 45 times lower k_B value was obtained under identical conditions. This was the most convincing evidence for the retarding effect of the dissolved oxygen on the light-induced and perspiration assisted-decomposition of the dyes studied.

It can be assumed that the mechanism of light-induced dye decomposition was radical oxidative in the C media but radical reductive in P media. To confirm the latter assumption, the rate increasing role of the reducing XH component of artificial perspiration (lactic acid) had to be demonstrated. The results are shown in Figs. 10–13 and in Table 6.

These data show the kinetics for the photofading of A (MCT-VS) and B (MCT-VS) in 0.05 M aqueous solution of XH, at various initial dissolved oxygen levels.

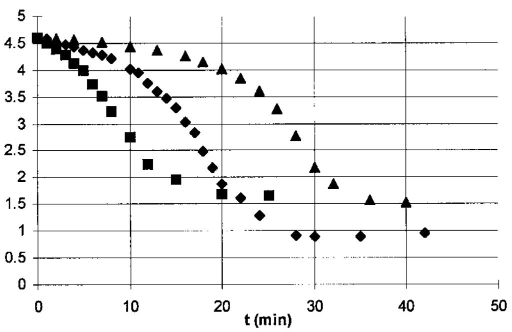
The data of Table 6 permitted the following conclusions:

- The light-induced decomposition of both dyes in 0.05 M XH followed first order kinetics.
- The rate of the reaction decreased with increasing dissolved oxygen levels.
- In agreement with the observations involving perspiration, A (MCT-VS) is more sensitive to light than B (MCT-VS) in aqueous XH.
- The rate of decomposition in systems of low oxygen content was 3–10 times higher than in oxygen saturated systems.



◆: malic acid, ■: malic acid + Ar, ▲: malic acid + O_2

Fig. 10. Kinetics of the light-induced decrease in ln a (absorbance) of A (MCT-VS) in aqueous malic acid at various initial dissolved oxygen levels.



◆: malic acid, ■: malic acid + Ar, ▲: malic acid + O_2

Fig. 11. Kinetics of the light-induced decrease in ln a (absorbance) of B (MCT-VS) in aqueous malic acid at various initial dissolved oxygen levels.

4. Possible mechanisms of the light-induced dye decomposition

1. Photofading in distilled water

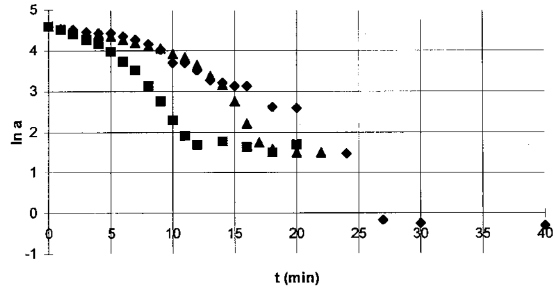
$$D \xrightarrow[k_1]{h_\nu} D^* \tag{1}$$

$$D^* \xrightarrow{k_2} \text{decomposition products} \tag{2}$$

If $[D^*] < < [D]$ the light-induced dye decomposition follows first order kinetics:

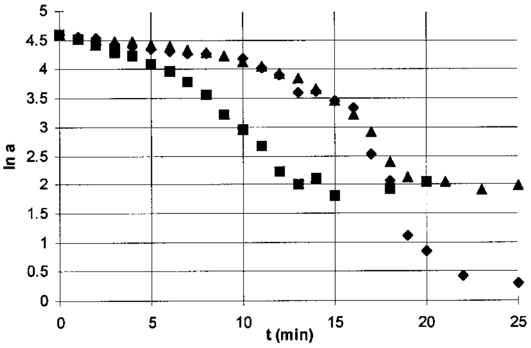
$$v = k_1[D] \tag{3}$$

where k_1 is proportional to the intensity of the incident light.



◆: lactic acid, ■: lactic acid + Ar, ▲: lactic acid + O_2

Fig. 12. Kinetics of the light-induced decrease in ln a (absorbance) of A (MCT-VS) in aqueous lactic acid at various initial



◆: lactic acid, ■: lactic acid + Ar, ▲: lactic acid + O_2

Fig. 13. Kinetics of the light-induced decrease in ln a (absorbance) of B (MCT-VS) in aqueous lactic acid at various initial dissolved oxygen levels.

Table 6
The effect of 0.05 mol/L^{-1} XH and initial dissolved oxygen level on the light-induced decrease in absorbance for solution of A (MCT-VS) and B (MCT-VS)

XH	Saturated with	Rate constant	Initial period (0–t_1 min)	Main period (t_2–t_3 min)	t_2–t_1 (min)
Malic acid	–	k_A h^{-1}	3.888	25.518	0
			(0–6)	(6.20)	
		k_B h^{-1}	2.916	15.072	4
			(0–10)	(14–22)	
	Ar	k_A h^{-1}	9.510	31.302	0
			(0–5)	(5–12)	
		k_B h^{-1}	6.552	14.406	0
			(0–4)	(4.15)	
	O_2	k_A h^{-1}	0.984	21.612	0
			(0–12)	(12–30)	
		k_B h^{-1}	1.098	14.304	8
			(0–16)	(24–32)	
Lactic acid	–	k_A h^{-1}	2.634	8.952	0
			(0–5)	(5–20)	
		k_B h^{-1}	3.520	24.440	5
			(0–10)	(15–20)	
	Ar	k_A h^{-1}	6.846	20.754	0
			(0–5)	(5–12)	
		k_B h^{-1}	6.342	18.426	0
			(0–6)	(6–15)	
	O_2	k_A h^{-1}	2.146	25.140	2
			(0–12)	(14–20)	
		k_B h^{-1}	2.346	20.910	5
			(0–10)	(15–20)	

2. If radical reductive photofading became likely in the presence of perspiration, due to its XH component, dissolved and/or retrieved oxygen might interact either with XH, or X*, or with both.

$$D \xrightarrow[k_1]{h\nu} D^* \qquad (1)$$

$$D^* + XH \xrightarrow{k_3} X^\bullet + DH^\bullet \rightarrow \text{decomposition products (fast radical reaction)} \qquad (4)$$

If $k_3 \neq 0$, the decomposition of D* has to be accelerated by XH. The acceleration is significant if $k_3 > k_2$

$$X^\bullet + O_2 \xrightarrow{k_4} X - O - O^\bullet \text{ (less reactive radical)} \qquad (5)$$

$$X^\bullet + D^* \xrightarrow{k_5} \text{decomposition products (fast reaction)} \qquad (6)$$

Dissolved and particularly blown in oxygen may oxidize XH, preventing its interaction with D*, or it may form X–O–O$^\bullet$ radicals that are less reactive than X$^\bullet$ [Eq. (5)]. If perspiration-containing dye solution was saturated with oxygen (PII and PIII systems) XH was oxidized for 60 min and only its remaining proportion could interact with D* in the final period of exposure. This phenomenon might explain the significantly lower rate constants in the final period in PII or PIII, versus PI.

5. Final conclusions

- The light-induced decomposition of two heterobifunctional reactive azo dyes, dissolved

in water, perspiration and aqueous hydroxyacid (XH) solution, follows first order kinetics.
- The rate of decomposition is influenced by the concentration of dissolved oxygen.
- Dye decomposition in aqueous solution, in the absence of perspiration or XH, is accelerated by dissolved oxygen. A radical oxidative mechanism can be assumed.
- Dye decomposition in perspiration and XH solution, was decelerated by dissolved oxygen. The anticipated reductive radical mechanism is inhibited by oxygen, converting aggressive X• radical species to milder X-OO• species and/or oxidizing XH molecules.
- Higher dissolved oxygen levels caused longer deceleration in photofading in P systems. Its influence on the rate constant decrease is small.
- The initial "induction period" in the fading rate curve for light-induced dye decomposition in perspiration is caused by the consumption of dissolved oxygen.

Acknowledgements

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