ELSEVIER

Dyes and Pigments, Vol. 37, No. 3, pp. 249–254, 1998

Printed in Great Britain
PII: S0143-7208(97)00081-8 0143-7208/98 $19.00 + 0.00

Photocatalytic Degradation of Acid Azo Dyes in TiO_2 Colloidal Suspension III. Spectral Characterization of Excited State

Haoqiang Zhan & He Tian*

Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, People's Republic of China

(Received 27 June 1997; accepted 31 July 1997)

ABSTRACT

Azo dyes derived from H-acid and K-acid can be degraded by TiO_2 photoassisted catalysis. The triplet state lifetimes of these dyes in TiO_2 colloidal suspension now investigated. The lifetime of triplet state is almost independent on the presence of TiO_2, which implies that the triplet state of the dyes does not react with $^{\bullet}OH$ and $O_2^{-\bullet}$. © 1998 Elsevier Science Ltd

INTRODUCTION

Large volumes of azo dyes are manufactured annually worldwide and used in a variety of applications such as textiles, paper, foodstuffs, and cosmetics. The photocatalytic decolorization approach of some textile azo dyes [1, 2] and acid azo dyes [3, 4] have been investigated, and have potential application in the treatment of dye wastewater. Some azo dyes are resistant to aerobic degradation (without TiO_2 photoassistant) [3, 4], which is a desirable property in commercial applications. However, the relationship between the photostability and the excited states of these acid azo dyes is an important factor in the design of more photostable azo dyes. It has shown the light fastness of dyes can be evaluated using kinetic parameters determined in the

*Corresponding author.

liquid phase [5]. Kuramoto and Kitao [6] have studied the effect of substituents on the photofading of some naphthols in air-saturated methanol, and observed that, with the exception of a nitro substituent, the relative rate of photofading increased with the replacement of electron-releasing substituents in the aryl ring. In this paper, laser flash photolysis technique was used to investigate the triplet excited state properties of several acid azo dyes. We attempt to elucidate a correlation between the light fastness of H/K acid azo dyes synthesized and the decay lifetimes of triplet state, a factor which may be useful in the molecular design of new azo dyes.

EXPERIMENTAL

Dyes

Several azo dyes derived from H-acid or K-acid have been previously synthesized by us, and their structures confirmed [7] (Table 1). The concentration of the aqueous solutions of dyes used in this study is 2.5×10^{-5} M. Three metal complex dyes were supplied by BASF research center and used without further punfication.

Preparation of TiO_2 suspension

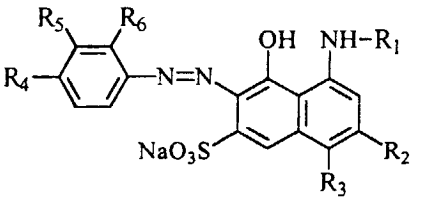
Colloidal TiO_2 suspension was prepared via hydrolysis of $TiCl_4$ in aqueous solution [5]. The solution was passed through an ion exchanger in the OH^- form [6]; transparent TiO_2 solution was obtained, which has a sharp absorption band in the UV region [7].

Experiment and apparatus

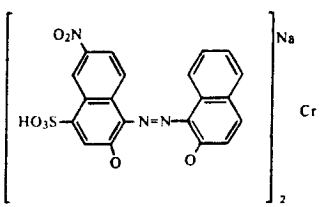
Absorption spectra were measured using a Shimadzu UV-260 UV–VIS spectrophotometer. The time-resolved absorption decay kinetics was measured by laser flash kinetic spectrophotometer. The solutions (in 2 cm × 2 cm quartz cells) were excited at 337 nm (nitrogen gas laser with a 6–7 ns pulse wide, Radiant Dyes Laser Acce. GmbH), and transient optical density ($\triangle$OD) at 488 nm (Ar ion laser, 5500 AWC, Ion Laser Technology) and at 632.8 nm (He-Ne laser as monitoring light) were detected using a fast response diode (DET2-Si, Thorlabs Inc.) and displayed on a digital storage oscilloscope (Tektronix TDS 420). In the measurements, "O_2 aerated" means that the solutions were saturated by bubbling with oxygen gas for 20 min. All measurements were performed at room temperature.

TABLE 1

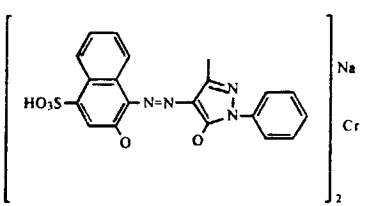
The Structures of the Dyes used in this Study, and Absorption Data of them in Aqueous Solutions



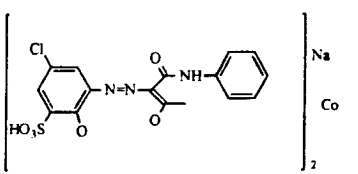
Dye	R_1	R_2	R_3	R_4	R_5	R_6	λ_{max} *(nm)*	$\varepsilon(\times 10^{-4})$ *(1. mol^{-1} cm^{-1})*
D-13	COPh	H	$-SO_3Na$	H	H	$-SO_3Na$	506.6	1.876
D-5	$COCH_3$	$-SO_3Na$	H	$-NO_2$	H	H	532.2	2.223
D-7	COPh	$-SO_3Na$	H	H	$-NO_2$	H	499.4	1.819
D-3	COPh	$-SO_3Na$	H	$-NO_2$	H	H	515.8	1.426



Dye-1



Dye-2



Dye-3

λ_{max} *(nm)* ε 10^{-4} *(1 mol^{-1} cm^{-1})*		λ_{max} *(nm)* ε 10^{-4} *(1 mol^{-1} cm^{-1})*		λ_{max} *(nm)* ε 10^{-4} *(1 mol^{-1} cm^{-1})*	
570	2.065	523.2	1.907	453.4	2.866

RESULTS AND DISCUSSION

The transient absorption decay kinetic data at 488 nm and 632.8 nm of the dyes in different solvents are shown in Tables 2 and 3. In ethanol, the dyes have transient absorption at 488 nm under aerated and O_2-saturated conditions, but in aqueous solution the dyes show no detectable transient signal at 488 nm. Compared with data for the decay lifetimes in aerated and O_2-saturated case, the decay lifetime was very sensitive to oxygen. This implies that the decay lifetime as experimentally measured could be equatable to the lifetime of the triplet state of the dyes, since singlet oxygen is a very effective quencher for the triplet state of dyes. In ethanol, the dyes are adsorbed on the surface of TiO_2 particles [8]. When irradiated by UV light, TiO_2 is excited and the excited energy is transferred to the adsorbed dyes. When the concentration of TiO_2 was lower, the transient $\triangle$OD at 488 nm for the dyes in ethanol could not be detected. Parallel experiment on the TiO_2 photocatalytic degradation of the H/K acid azo dyes used in this study indicates the light-fastness of the dyes (Table 4). As seen in Table 4, even complexes, which have a high light fastness in dyeing applications, can be degraded by TiO_2. The photocatalytic degradation of H/K acid azo dyes in aqueous TiO_2 suspension follows apparent first-order kinetics. Compared with the photosensitive degradation, homogeneous photocatalysis appears to be a rapid

TABLE 2

Kinetic Data of Transient $\triangle$OD at 488 nm for the Dyes in Ethanol (2×10^{-5}M). $[TiO_2]=0.02$ mol litre^{-1}

	Dyes	*D-3*	*D-5*	*D-7*	*D-13*	*Dye-1*	*Dye-2*	*Dye-3*
τ	($\pm0.2\,\mu$s) aerated	8.4	9.1	7.9	12.9	4.4	4.1	9.9
τ	($\pm0.2\,\mu$s) O_2-saturated	6.2	5.3	5.9	3.9	0	4.0	4.1

TABLE 3

Kinetic Data of Transient $\triangle$OD at 632.8 nm for the Dyes in Different Solvents (2×10^{-5}M). $[TiO_2]=0.04$ mol litre^{-1}

	Dyes	*D-3*	*D-5*	*D-7*	*D-13*	*Dye-1*	*Dye-2*	*Dye-3*
τ	($\pm0.2\,\mu$s) in EtOH aeated	7.0	5.8	7.1	7.3		6.1	
τ	($\pm0.2\,\mu$s) in EtOH O_2-saturated	6.2	5.3	5.9	3.9		3.6	
τ	($\pm0.2\,\mu$s) in H_2O aerated	11.6			10.1	7.0	6.0	6.1
τ	($\pm0.2\,\mu$s) in H_2O aerated (without TiO_2)	8.4	10.1	6.8	8.3	7.1	8.8	7.6

TABLE 4

Photosensitive k_1 and Photocatalytic k_2 Degradation Rates of the Dyes in Tetraborate Buffering Solution of pH 9.2 and Photosensitive Degradation Rate k_3 in Ammonium Buffering Solution of pH 9.2

Dyes	$k_1(min^{-1} \times 10^4)$	$k_2(min^{-1} \times 10^3)$	*Fastness*	$k_3(min^{-1} \times 10^4)$
D-13	0.12	3.396	excellent	4.766[a]
Dye-1	3.80	24.6		
Dye-2	6.53	27.56		
Dye-3	14.08	31.42		
D-5	21.15	6.31		25.41[a]
D-7	29.85	8.78		33.82
D-3	215.5	28.83	bad	185.2

[a]Because organic compounds can form hydrogen bonds with amines, the intramolecular hydrogen bond in *o*-arylazonaphthols is destroyed and it is easily attacked by the electrophilic oxidant.

way of evaluating light-fastness of azo dyes. The results, therefore, on the photocatalytic degradation by non-toxic titanium dioxide, may be of value in the context of the degradation of the water-soluble azo dyes in dyeing and dye-manufacturing wastewater. Comparing the data of light fastness (Table 4) and the transient absorption decay lifetimes, it was found that those dyes having a shorter triplet lifetime in O_2-saturated case have usually good light fastness.

Kinetic data for the transient $\triangle$OD at 632.8 nm for the dyes in different solvents are shown in Table 3. When an aqueous solution of the dyes without TiO_2 was irradiated at 337 nm, the transient absorption was also detected at 632.8 nm. This implies that the lifetime of the triplet state of the dyes in aqueous solution is almost independent of the presence of TiO_2. In aqueous solution, photoassisted catalytic degradation of the dyes is caused by the active oxygen produced on the surface of TiO_2 [7–12]. Photo-generated holes oxidized the pre-adsorbed H_2O to generate $^{\bullet}OH$ free radicals, a powerful electrophilic oxidant. Photo-generated electrons reduced the pre-adsorbed dissolved oxygen to produce the superoxygen anionic free radical $O_2^{-\bullet}$. The lifetime of the triplet state of the dyes is almost independent of the presence of TiO_2 (at least it is not obviously dependent thereon), which implies that the triplet state of the dyes does not react with $^{\bullet}OH$ and $O_2^{-\bullet}$. The degradation of dye in aqueous solution may be due to combination factors, which include two reactions, viz., (a) between the triplet state and singlet oxygen; and (b) between dyes and $^{\bullet}OH$ and $O_2^{-\bullet}$. TiO_2 acts as a strong photosensitizer for $^{\bullet}OH$ and $O_2^{-\bullet}$ radicals which are highly reactive towards azo dyes:

$$TiO_2 \xrightarrow{h\nu} TiO_2(h_{VB}^{+} \ldots e_{CB}^{-})$$

$$H_2O + h_{vB^+} \rightarrow {}^{\bullet}OH + H^+$$

$$O_2 + e^-_{CB} \rightarrow O_2^{-\bullet}$$

CONCLUSIONS

The triplet state lifetimes of azo dyes derived from H-acid and K-acid in TiO_2 colloidal suspension has been investigated. The lifetime of the triplet state is almost independent of the presence of TiO_2, which implies that the triplet state of the dyes does not react with $^{\bullet}OH$ and $O_2^{-\bullet}$. The degradation of the dye in aqueous solution may be due to dual factors, which include two reactions: (1) between the triplet state and singlet oxygen and (2) between the dyes and $^{\bullet}OH$ and $O_2^{-\bullet}$, since TiO_2 acts as a strong photosensitizer for $^{\bullet}OH$ and $O_2^{-\bullet}$ radicals which are highly reactive towards azo dyes.

ACKNOWLEDGEMENTS

This project was financially supported by BASF AG/ Germany. The authors also thank Drs G. Paul, G. Seybold, Y. H. Cheng and L. Hauessling, and Professor Kongchang Chen and Bingkui Wang.

REFERENCES

1. Zollinger, H., *Color Chemistry*, 2nd edn. VCH, NY, 1991.
2. Moser, J. and Gratxel, M., *J. Am. Chem. Soc*, 1984, **106**, 6557.
3. Mathews, R. W., *J. Chem. Soc., Faraday Trans. I*, 1989, **85**(6), 1291.
4. Mathews, R. W., *Water Res.*, 1991, **48**, 413.
5. Sirbiladze, K. J., Vig, A., Anyisimov, V. M., Anyisimava, O. M., Krichovskiy, G. E. and Russznak, I., *Dyes and Pigments*, 1990, **14**(1), 23.
6. Kuramoto, N. and Kitao, T., *J. Soc. Dyers Color*, 1992, **108**(3), 150.
7. Zhan, H. and Tian, H., *Dyes and Pigments*, 1998, **37**, 231.
8. Tian, H., Zaitsev, N. K. and Galashin, A. E., *J. Photochem. Photobio. A: Chem.*, 1992, **65**, 399.
9. Bahnemann, D., *Isr. J. Chem.*, 1993, **33**(1), 115.
10. Henglein, A. and Gutierrez, M., *Ber. Bunsenges. Phys. Chem.*, 1983, **87**, 852.
11. Noda, H., Oikawa, K. and Kamada, H., *Bull. Chem. Soc. Jpn.*, 1992, **65**, 2505.
12. Cai, R., Bala, R., Hashimoto, K., Kubota, Y. and Fujishima, A., *J. Electroanal. Chem.*, 1993, **360**, 237.