Dyes and Pigments, Vol. 37, No. 3, pp. 213-222, 1998

PII: S0143-7208(97)00059-4
0143-7208/98 $19.00 + 0.00

Study on the Photooxidation of a Near-infrared-absorbing Benzothiazolone Cyanine Dye

Ping Chen,[a]* Jun Li,[a] Zhiguo Qian,[a] Deshui Zheng,[a]
Tsuneki Okasaki[b] & Masaaki Hayami[b]

[a]Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101,
People's Republic of China.
[b]Nippon Kankah-Shikiso Kenkyusho, Okayama 701, Japan

(Received 29 April 1997; accepted 3 June 1997)

ABSTRACT

The direct photooxidation mechanism of a near-infrared-absorbing benzothiazolone cyanine dye has been studied by UV-Vis absorption spectroscopy and electron spin resonance. The results shows that the rate of the photooxidation reaction follows first-order kinetics in acetonitrile. The technique of spin trapping was successfully applied to the detection of the photoinduced formation of singlet oxygen ($^1O_2$)*and superoxide* (O_2^-). *It was found that both singlet oxygen and superoxide anion were responsible for the photofading of the cyanine dye. The main photooxidation products of the cyanine dye were identified by NMR* (^1H) *and fast atom bombardment (FAB) mass spectrometry. © 1998 Elsevier Science Ltd*

Keywords: photooxidation, benzothiazolone cyanine dye, NIR-absorbing dyes.

INTRODUCTION

In recent years, some near-infrared (NIR)-absorbing dyes have become more important as the use of semiconductor lasers has grown, for information, reading and writing [1, 2]. It has been reported that NIR-absorbing cyanine dyes as recording media for optical disk possess a series of advantages, i.e. high absorbance and reflectance at laser diode wavelength and a sufficient

---

*Corresponding author.

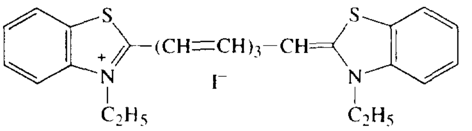
solubility in organic solvents. Therefore, high recording sensitivity and a favorable signal to noise ratio can be obtained in practice [3].

However, cyanine dyes as sensitizers used in optical recording information media, have a drawback, in that they are readily photooxidized. It is therefore, very significant to study the photooxidation of cyanine dyes [4]. Recent studies have led to a rapid increase in the understanding of the photooxidation mechanism [5].

We have made a systematic study on the photofading of some functional cyanine dyes [6, 7]. In this present paper, the direct photooxidation of an NIR-absorbing *N*-ethyl benzothiazolone cyanine dye was investigated, and the photooxidation mechanism examined in detail using electron spin resonance (ESR). The major products of the photooxidation of the dye were also identified.

EXPERIMENTAL

The dye employed was supplied by Nippo Shikiso Kenkysho CO. Ltd; its structure and spectral characteristic are depicted as follows:



DETC

3,3-diethyl-2,2'-thiatricarbocyanine iodide
^{CH_3CN} (ε) = 756 nm (1.72×10^5 mol^{-1} l cm)

The spin trapper, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidone (TEMP) were purchased from Aldrich Chemical Co. Acetonitrile was redistilled before used. Dimethyl sulfoxide-d_4 (DMSO-d_4) was obtained from the Beijing Chemical Works.

Absorption spectra were measured with a Hitachi 330 spectrometer. ESR spectra were recorded on a Varian E-109 spectrometer in the X band at room temperature in quartz cells. The samples were irradiated by a 300 watt iodine-tungsten lamp. The samples were saturated with dioxygen and the control experiments were carried out in a nitrogen atmosphere. In the experiments the concentrations of DMPO and TEMPO were 10^{-2} mol l^{-1}, and the dye concentration was 10^{-3} mol l^{-1}.

Photooxidation of cyanine dye in solution

The preparative photooxidation of the cyanine dye was performed in a photochemical reactor.

Sample solution (1×10^{-4} mol l^{-1}) was prepared in acetonitrile and saturated with O_2; the solution was irradiated in a 500 watt iodine-tungsten lamp with magnetic stirring at room temperature. The qualitative photooxidation of DETC was examined with a Hitachi-300 spectrometer, until the reaction was complete. The dye solution after photooxidation was then concentrated using a rotor evaporator.

The photooxidated products of the dye were evaluated using NMR and fast atom bombardment mass spectrometry. NMR analysis of the photooxidation products were performed in d_4-DMSO. Equipment used was a Varian Gemini 300 NMR Spectrometer and a KYKY-ZH-P-5 FAB Mass Spectrometer.

RESULTS AND DISCUSSION

Photofading of the cyanine dye

The absorption spectrum of DETC in solution saturated with N_2 showed little change under irradiation about 30 min and those saturated with oxygen was also stable in the dark for a long period of time. However, an extremely rapid decrease of the absorbance for DETC was observed when irradiated, which indicates that the photofading of the cyanine dye may be caused by self-sensitizing photooxidation (as shown in Fig. 1).

In Fig. 1, it can be seen that, whilst the dye absorbance decreased rapidly, a new broad absorption band appeared at lower wavelength and gradually increased with the radiation time, indicating the appearance of new photoproducts.

The kinetics of the photo-oxidation of DETC was studied spectrophotometrically by monitoring the decrease in the 756 nm peak absorbance with irradiation time (Fig. 1). The kinetic analysis results shows that a plot of $\ln(A_0/A_t)$ vs illumination time was linear in acetonitrile (Fig. 2). This linear

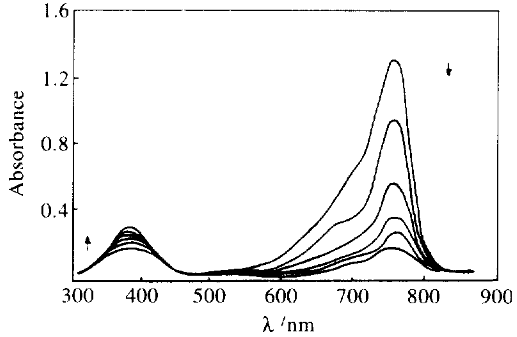


Fig. 1. Absorption spectra of DETC at various stages or irradiation time (Δt between curves was 0.5 min).

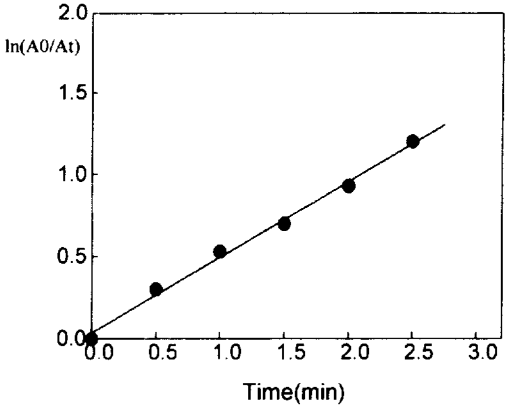


Fig. 2. Plot of ln (A_0/A_t) vs illumination times.

relationship indicates the rate of the photooxidation obeyed first-order kinetics, for which the calculated rate constant (kg) value was about 0.39 min^{-1}.

Mechanism of photooxidation

Some cyanine dyes are efficient sensitizers and oxygen is a good electron acceptor, therefore the reaction of the dye with oxygen under irradiation usually involves a primary photochemical process. Organic dye molecules are converted to reactive electronic excited states on absorption of light. From the photochemical point of view, there are two possible mechanisms of the interaction of an excited sensitizer with oxygen [8, 9]:

(i) Energy transfer, which leads to the formation of energetically excited singlet oxygen $({}^1\Delta_g)$

$$\mathrm{Dye} + h\nu \rightarrow {}^3\mathrm{Dye}^* \qquad (1)$$

$${}^3\mathrm{Dye}^* + \mathrm{O}_2 \rightarrow \mathrm{Dye} + {}^1\mathrm{O}_2^*\ ({}^1\Delta_g) \qquad (2)$$

$${}^1\mathrm{O}_2^* + \mathrm{Dye} \rightarrow \mathrm{Dye{-}O_2}\ (\mathrm{Fading}) \qquad (3)$$

Scheme 1

(ii) Electron transfer from the excited dye to oxygen, which leads to the formation of the superoxide anion($\mathrm{O_2}^-$) and a dye radical cation.

$$\mathrm{Dye} + h\nu \rightarrow \mathrm{Dye}^* \qquad (4)$$

$$\mathrm{Dye}^* + \mathrm{O}_2 \rightarrow \mathrm{Dye}^+ + \mathrm{O}_2^- \qquad (5)$$

$$\mathrm{O}_2^- + \mathrm{Dye} \rightarrow \mathrm{Fading} \qquad (6)$$

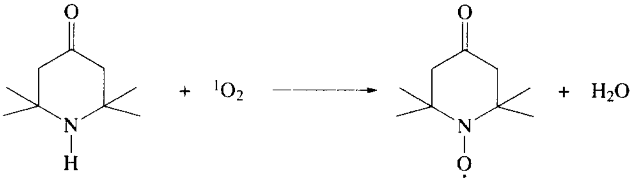
Scheme 2

It is well known that the singlet oxygen and superoxiode anion are the most reactive oxygen species, and dyes may be oxidized by these species. Therefore, if $^1O_2$ and O_2^- could be confirmed, we should expect that the photofading of the cyanine dye follows the above mechanism mentioned earlier.

Because the lifetime of the superoxide radical anion at room temperature is only 1 μs and the lifetime of $^1O_2$ is only about 200 μs [10], the direct detection of them at room temperature by conventional ESR is impossible. In this experiment, we used the spin-trapping technique for proving their presence in the reaction process.

Examination of $^1O_2$

In order to provide evidence for the formation of $^1O_2$ in the photosensitisation by the cyanine dye, we used TEMP as spin-trapper of $^1O_2$, which involves reaction with $^1O_2$, following Scheme 3 [11].



Scheme 3

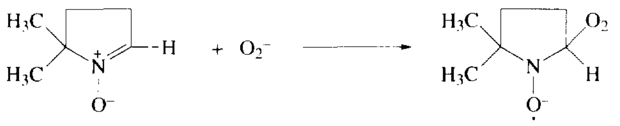
After addition of TEMP to solution of DETC under irradiation, a strong ESR signal of the spin adduct TEMP-O$^\cdot$ was observed. The formation of $^1O_2$ was thus confirmed through examination of the resonance signal of TEMP-O$^\cdot$ (Fig. 3).

The determined constants $\alpha N = \alpha H = 1.55\,mT$, the values of the coupling constants are in good agreement with those found in the literature [11].

Fig. 3. Light induced ESR signal of DETC adduct of TEMP.

Examination of O_2^-

As a spin-trapper of O_2^-, DMPO can react with O_2^-, as shown in Scheme 4. The strong ESR signal of DMPO-O_2^- was produced immediately when the DETC solution containing DMPO was irradiated; the ESR spectrum observed is shown in Fig. 4. The ESR spectrum is characterized by three coupling constants, which are due to the presence of the nitrogen atom and two hydrogen atoms in the β and γ positions in DMPO-O_2^- adduct. The determined constants $\alpha N = 1.23$ mT, $\alpha_H^\beta = 1.17$ mT and $\alpha_H^\gamma = 0.14$ mT, which were in good agreement with those previously reported [12].



In order to further confirm the formation of O_2^-, the photosensitized reaction of DETC with O_2 in CH_3CN-H_2O solution was investigated with ESR, because the superoxide anion is known to be relatively stable in aprotic solvents. When the aqueous solution of DETC was irradiated in the presence of DMPO, the produced O_2^- was rapidly converted to H_2O_2 and O_2 (Scheme 5), and thus only the ESR signal of DMPO-OH$^\cdot$ was observed and no direct ESR signal of O_2^- under this condition was apparent.

$$\cdot O_2^- + H^+ \rightarrow HO_2^\cdot \quad (1)$$

$$H_2O + HO_2^\cdot + O_2^- \rightarrow H_2O_2 + O_2 + OH^- \quad (2)$$

$$H_2O_2 + \cdot O_2^- \rightarrow OH^\cdot + OH + O_2 \quad (3)$$

$$OH^\cdot + DMPO \rightarrow (DMPO\text{-}OH)^\cdot \quad (4)$$

Scheme 5

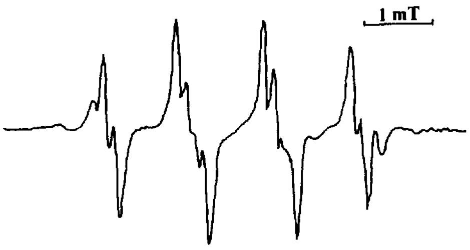


Fig. 4. Light induced ESR signal of DETC adduct of DMPO.

The spectrum of DMPO-OH (Fig. 5) was recorded under irradiation of DETC in CH_3CN-H_2O solution containing DMPO, and it is characterized by two coupling constants corresponding to the non-zero nuclear spins of the nitrogen atom and the hydrogen atom in the β position: $\alpha_N = \alpha_H^\beta = 1.49$ mT. Both coupling constants were identical, which gives rise to a spectrum consisting of four peaks with an intensity ratio 1:2:2:1. The values obtained agree well with the those found in the literature [12, 13].

The above results provide indisputable evidence for the presence of singlet oxygen and superoxide in the process of photooxidation of cyanine dye with dissolved oxygen.

The investigation of the photoproduct of thiacarbocyanine

The photoproduct of the self-sensitized oxidation of thiacarbocyanine was investigated. It was difficult to isolate the photoproduct, even in small quantity by conventional techniques, so we used NMR and fast atom bombardment mass spectrometry to directly examine the reaction mixtures.

A little of the DETC sample and its photoproduct were dissolved in DMSO-d_4 and examined by their NMR spectra; the results are shown in Fig. 6. Comparison of the NMR spectra of DETC before and after photooxidation revealed that the N-ethylbenzothiazolone (I), the ionic acid (II), and the ionic aldehyde (III) were the principal products, and the quantity of III was relatively small in the photoproducts . Therefore, we inferred that the photooxidation of DETC followed Scheme 6.

Additional evidence was obtained by examining the mass spectrometry of the photoproduct using a fast atom bombardment mass spectrometer. The mass spectra of the main photoproducts (I, II, III) were in good agreement with the assigned structures, yielding parent ions at m/e = 270, m/e = 179, m/e = 286, respectively.

The initial products of the photooxidation of the carboncaynine were analogous to the photoproducts obtained from oxidation of 8,10-dimethyl-

Fig. 5. Light induced ESR signal of DETC in CH_3CN-H_2O solution adduct of DMPO.

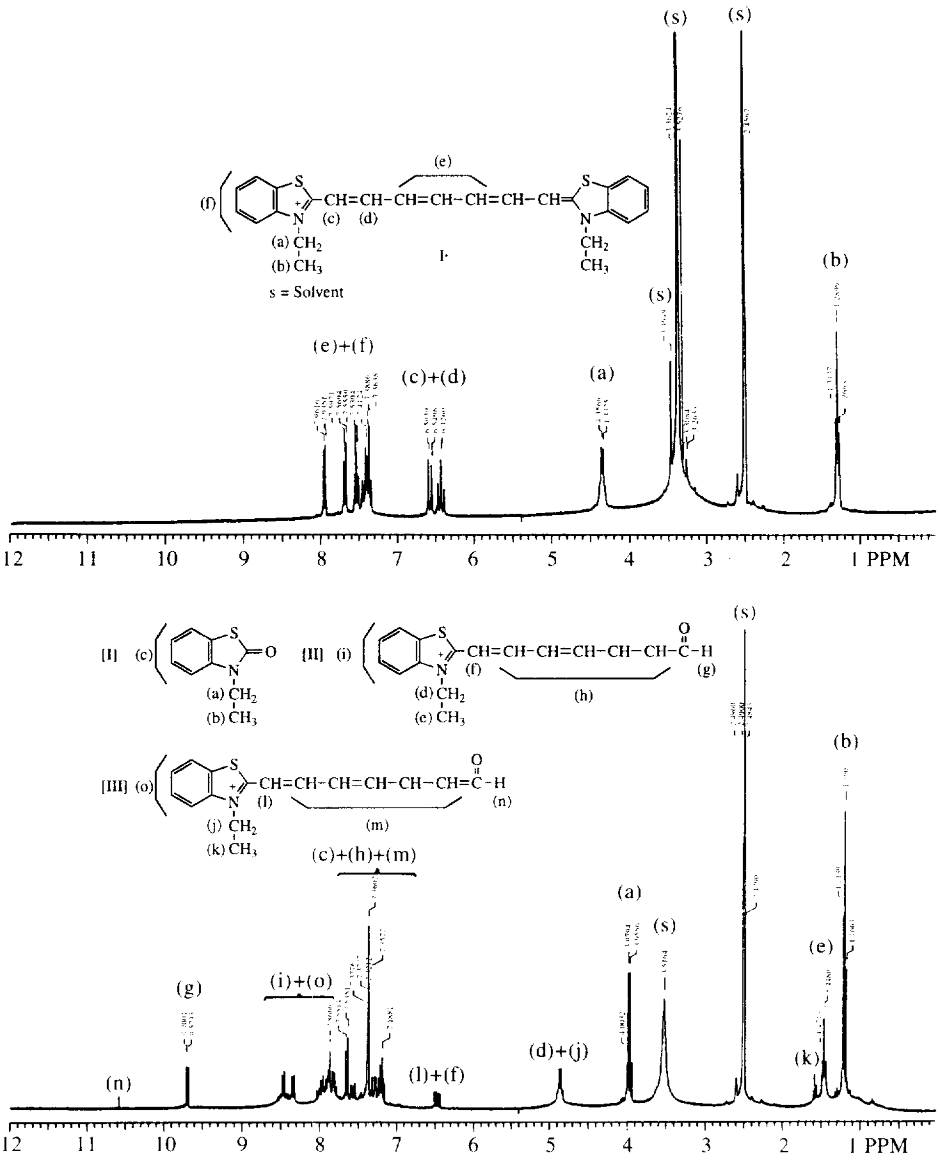
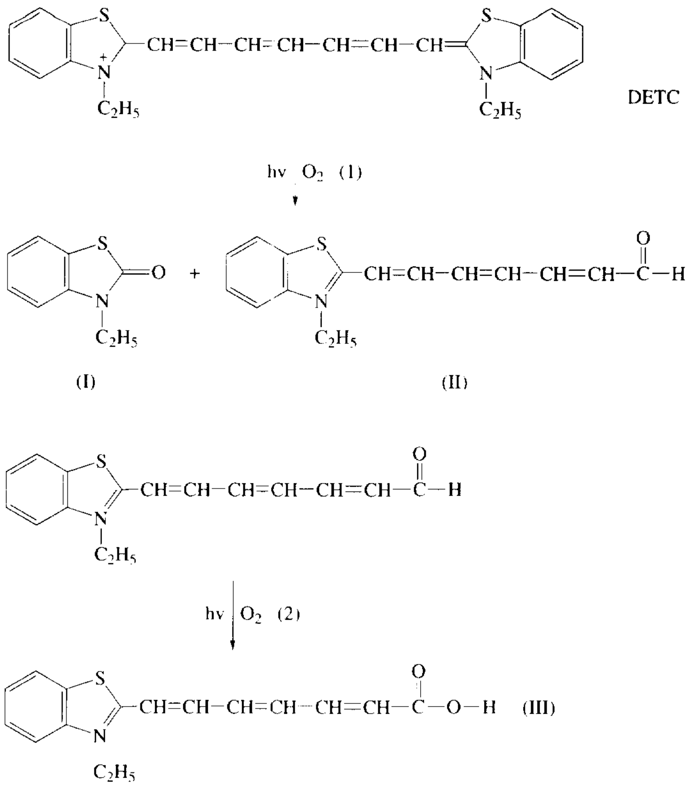


Fig. 6. Spectra (^{1}H NMR) of DETC in DMSO-d$_4$ before and after photooxidation.

thiatricarbocyanine as reported in the literature [14]. It is conceivable that cyanines are capable of self-sensitizing $^3O_2$ and are more susceptible to reactive oxygen, and the intermediates once formed might lead to some of the observed complex reaction mixtures.



DETC	M = 417.6	
[I]	M = 179.24	m/e = 179
[II]	M = 270.37	m/e = 270
[III]	M = 286.66	m/e = 286

Scheme 6

CONCLUSION

The photofading of NIR benzothiazolone cyanine dye is caused mainly by the oxidation mechanism. It was found from ESR that the self-sensitized photooxidation of the cyanine dye involved singlet oxygen and superoxide anion as intermediates, which indicates that the energy transfer mechanism and electron transfer mechanism of the interaction of excited cyanine dye with oxygen occurred simultaneously. Based on kinetics analysis, it was shown that the rate of the photooxidation obeyed first-order kinetics with a rate constant (kg) about 0.39 min^{-1}.

ACKNOWLEDGEMENT

Financial support from the National Natural Science Foundation of China is gratefully acknowledged.

REFERENCES

1. Nakazumi, H., *J. Soc. Dyes Colour*, 1988, **104**, 121.
2. Tatsuske, K., *Jpn. Kokai Tokkyo Koho JP*. 07,70,453.
3. Oba, H., Abe, M. *et al.*, *Appl. Opt.*, 1986, **25**, 4023.
4. Zeng, W., Chen, P. *et al.*, *Science in China* (Series B), 1995, **38**, 128.
5. Kuramoto, N. and Kitao, T., *J. Soc. Dyes Colour*, 1982, **98**, 334.
6. Chen, P., Zhang, H. P. *et al.*, *Chinese Chem. Lett.*, 1994, **5**, 667.
7. Li, J., Chen, P. *et al.*, *Chinese Chem. Lett.*, 1996, **7**, 1121.
8. Turro, N. J., *Pure Appl. Chem.*, 1977, **49**, 405.
9. Lang, K. *et al.*, *J. Photochem. Photobiol. A: Chem.*, 1992, **67**, 187.
10. Harbour, J. R. and Hair, M. L., *Adv. Colloid Interface Sci.*, 1986, **24**, 103.
11. Ben-Hur, E. *et al.*, *Int. J. Radiat. Biol.*, 1985, **48**, 837.
12. Harbour, J. R. and Hair, M. L., *J. Phys. Chem.*, 1978, **82**, 1397.
13. Chen, C. *et al.*, *J. Photochem. Photobiol. A: Chem.*, 1995, **89**, 25.
14. Byers, G. W., Gross, S. and Henrichs, P. M., *Photochemistry and Photobiology*, 1976, **23**, 37.