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Electron transfer events in solutions of cyanine dyes

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Abstract

Photosensitized reduction of oxygen to superoxide anion by cyanine dyes in dimethyl sulphoxide containing dissolved oxygen has been investigated. The technique of spin trapping has been successfully applied to the detection of the photoinduced formation of the superoxide anion. In aqueous solution the hydroxyl radical observed after irradiation originates from primarily formed O_2^-. The superoxide anion formation is due to photoinitiated electron transfer from the cyanine dyes to dissolved oxygen. The intensities of the electron spin resonance signals of various dyes as photosensitizers of superoxide are correlated with the redox potentials of the dyes.

Keywords: Electron transfer; Cyanine dyes; Photosensitized reduction; Superoxide anion; Dimethyl sulphoxide

1. Introduction

There has been considerable interest in the superoxide anion because it is involved in numerous vital processes [1–3], but in spite of extensive studies, the boundary between its harmful and useful effects is still not clear.

On the other hand, cyanine dyes are efficient photosensitizers not only in the spectral sensitization of silver halide but also in biology, medicine, etc. Since oxygen is a good electron acceptor and abundant in nature, the reaction of dyes in the excited state with dissolved oxygen is usually involved in the primary process of chemical reaction of dyes. From the photochemical point of view there are two possible mechanisms of the interaction of an excited dye molecule with oxygen.

(1) Energy transfer, which leads to the formation of energetically excited singlet oxygen:

$$^3O_2 \xrightarrow[\text{dye}]{h\nu} {}^1O_2(^1\Delta_g) \qquad (1)$$

(2) Electron transfer from the excited dye to oxygen, which leads to the formation of the superoxide anion O_2^- and a dye radical cation:

$$O_2 + dye \xrightarrow{h\nu} O_2^- + dye^+ \qquad (2)$$

Since the lifetime of the superoxide radical anion at room temperature is only 1 μs [4] and the lifetime of singlet oxygen is only about 200 μs [5], the direct detection of them at room temperature by conventional electron spin resonance (ESR) is impossible and their presence as intermediates was not proven until the advent of spin trapping [6,7].

The aim of this paper is to detect the radicals generated in the reactions of 16 dyes with dissolved oxygen upon irradiation using the spin-trapping technique and to elucidate the reaction mechanism.

2. Experimental details

2.1. Materials

The dyes 1-ethyl-3'-methyl-2-thiacyanine bromide (1), 1,1'-diethyl-2,2'-cyanine iodide (2), 5,5'-diethyl-9-methyl-selenacarbocyanine bromide (3), 3,3'-dimethyl-4,5,4',5'-dibenzo-9-ethyl-thiacarbocyanine chloride (4), anhydro-3-sulphopropyl-3'-sulphoethyl-5,5'-diphenyl-9-ethyl-oxacarbocyanine hydroxide (5), 3,3'-diethoxyl-5,5'-dimethoxyl-9-ethyl-thiacarbocyanine chloride (6), anhydro-3-ethoxyl-3'-sulphopropyl-5-methoxyl-5'-chloro-9-ethyl-thiacarbocyanine hydroxide (7) and anhydro-1,1'-diethyl-3,3'-disulphobutyl-5,5'-dicyan-imidazolo-carbocyanine hydroxide (8) were purchased from the No. 1 Film Factory of the Ministry of Chemical Industry, China. The dyes 1,3'-diethyl-2-thiacyanine iodide (9), 1,3'-diethyl-2-selenacyanine iodide (10), 3,3'-diethyl-thiacarbocyanine iodide (11), 3,3'-diethyl-9-methyl-thia-

Table 1
Structural formulae of dyes
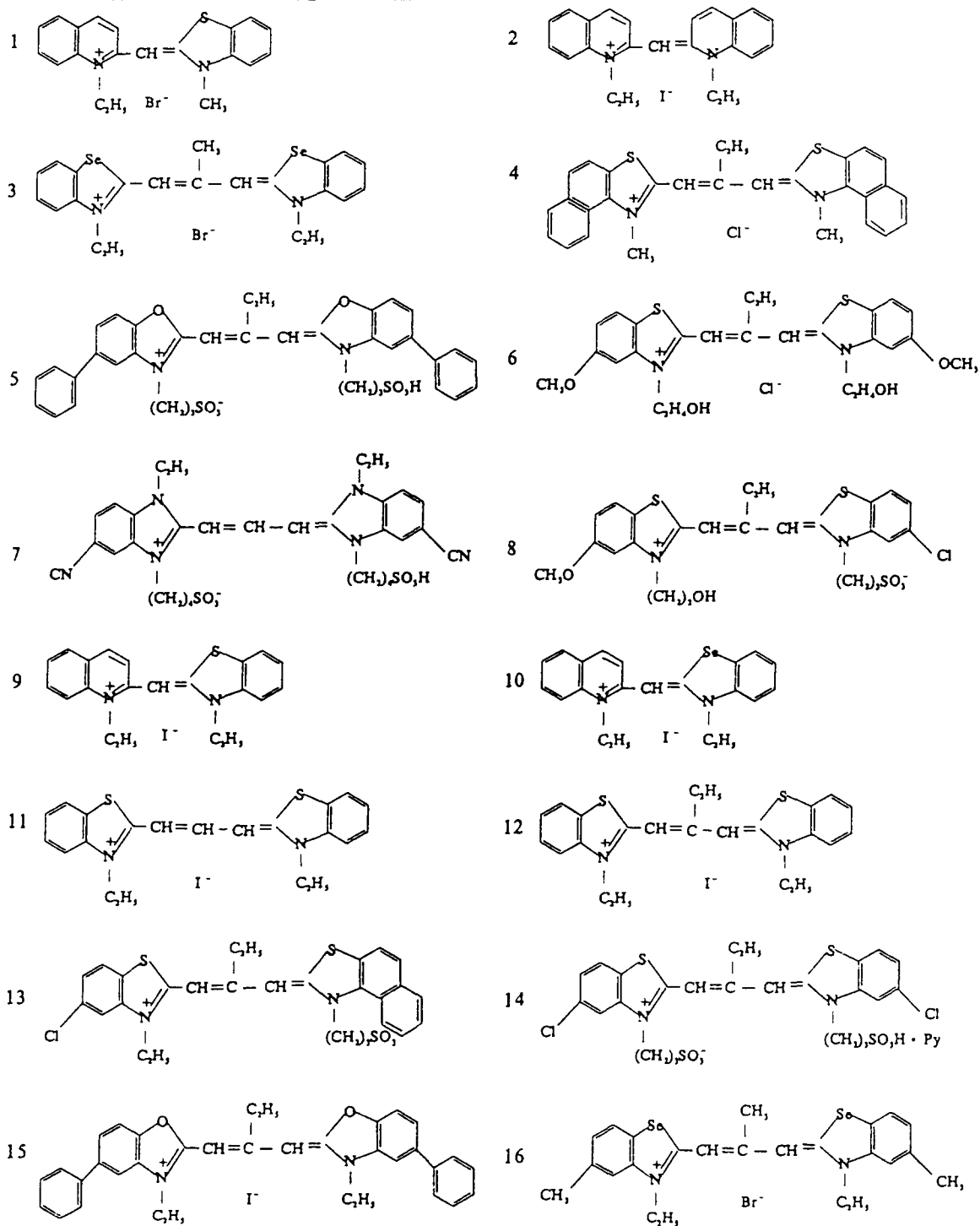
carbocyanine iodide (12), anhydro-3-ethyl-3'-sulpho-propyl-5-chloro-4',5'-benzo-9-ethyl-thiacarbocyanine hydroxide (13), anhydro-3,3'-disulphopropyl-5,5'-dichloro-9-ethyl-thiacarbocyanine hydroxide pyridine salt (14), 3,3'-diethyl-5,5'-diphenyl-9-ethyl-oxacarbocyanine iodide (15) and 3,3'-diethyl-5,5'-dimethyl-9-methyl-se-lenacarbocyanine bromide (16) were purchases from the Nippon Kankoh Shikoh Shikiso Co., Ltd., Japan. The structural formulae of all 16 dyes are given in Table 1. The spin trap 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was purchased from the Experimental Chemical Plant of Najing University. The dimethyl sulphoxide

(DMSO) used was analytical reagent grade and the water was distilled.

2.2. Equipment

ESR spectra were recorded on a Bruker ESP 300 spectrometer in the X band at room temperature in quartz cells. The samples were irradiated by a GCQ-200 high pressure mercury lamp using a band filter transmitting above 350 nm. The samples were as a rule exposed to air; in some cases they were saturated with oxygen. Check experiments were carried out in a nitrogen atmosphere. In experiments the concentration of DMPO was 10^{-2} mol l^{-1} and the dye concentration in water or DMSO was 10^{-3} mol l^{-1}.

The redox potentials of dyes **9**, **10**, **12**, **13**, **14** and **16** were measured according to Ref. [8]. Data on the redox potentials of the other dyes were taken from Refs. [8–10].

3. Results and discussion

After addition of DMPO to an aqueous solution of dye **5**, a very weak ESR signal was observed. This background was due to the sample being manipulated in scattered daylight. However, when the aqueous solution of dye **5** in the presence of DMPO was irradiated for 15 min, a strong signal which included a quartet with relative intensities 1:2:2:1 and hyperfine splitting value $a_N = a_H = 1.49$ mT appeared (Fig. 1). This signal is attributed to the hydroxyl adduct (DMPO–OH)·. Irradiation of aqueous solutions of the other dyes containing DMPO also gives rise to the same signal of (DMPO–OH)· without any contribution of DMPO–O_2^-, since the superoxide O_2^- is unstable in aqueous solution. The dismutation of O_2^- to H_2O_2 and O_2 proceeds very quickly:

$$O_2^- + H^+ \longrightarrow HO_2^· \qquad (3)$$

$$H_2O + HO_2^· + O_2^- \longrightarrow H_2O_2 + O_2 + OH^- \qquad (4)$$

$$H_2O_2 + O_2^- \longrightarrow OH^· + OH^- + O_2 \qquad (5)$$
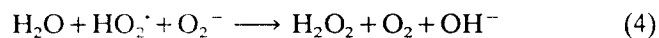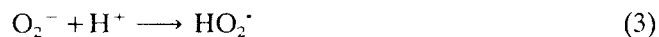

Fig. 1. ESR spectrum of the (DMPO–OH)· adduct generated in dye 5 aqueous solution containing DMPO by irradiation for 15 min.

Further, since the ratio of the rate constants of the DMPO reaction with OH· and O_2^- radicals is of the order of 10^5, it is apparent that the reaction between DMPO and OH· will significantly prevail over the DMPO reaction with O_2^- even when the concentration of O_2^- is high [11]. Although O_2^- radicals were produced in experiments, we could only observe the ESR signal of the (DMPO–OH)· adduct.

In order to provide evidence for the formation of O_2^- photosensitized by cyanine dyes, we performed the same experiment using DMSO as solvent, where no free hydrogen ions (H^+) necessary for the dismutation of O_2^- are accessible, instead of water. After 20 min of irradiation of dye **5** solution in DMSO containing DMPO, the ESR spectrum observed was as shown in Fig. 2. It is characterized by three coupling constants which are due to the interactions of unpaired electrons with the nitrogen atom and two hydrogen atoms in the β and γ positions in DMPO–O_2^- respectively. The determined constants $a_N = 1.29$ mT, $a_H{}^\beta = 1.04$ mT and $a_H{}^\gamma = 0.14$ mT are in good agreement with those published in Ref. [12].

Since Eq. (2) is a reaction of consumed oxygen, it is expected that the concentration of O_2^- photosensitized by the dyes will be affected by the concentration of dissolved oxygen in DMSO. The change in concentration of the DMPO–O_2^- adduct during excitation wavelength irradiation of dye **5** solution in DMSO saturated with oxygen vs. irradiation time is shown in Fig. 3. The concentration of the DMPO–O_2^- adduct
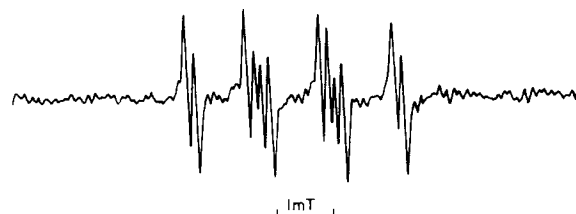

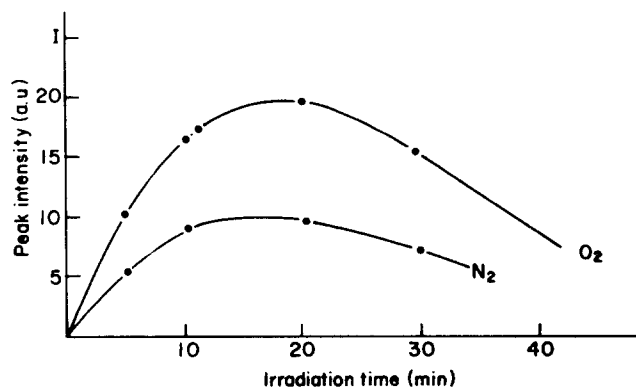Fig. 2. ESR spectrum of the O_2^- adduct of DMPO generated by irradiation of dye 5 solution in DMSO containing DMPO.

Fig. 3. Production of the spin adduct DMPO–O_2^- during irradiation of dye 5 solution in DMSO saturated with oxygen and in a nitrogen atmosphere.

is highest after 20 min of irradiation and then drops with time. Likewise, when the concentration of dissolved O_2 is diminished by the introduction of nitrogen, the concentration of $DMPO-O_2^-$ is decreased considerably.

Similar results were obtained upon irradiation of the other 15 dyes in DMSO containing DMPO. The intensities of the ESR signals of the various dyes as photosensitizers of superoxide are correlated with the redox potentials of the dyes (Fig. 4). Since the redox potential of O_2 is -0.15 V (NHE) (normal hydrogen electrode) [4] and the redox potentials of the dyes used are all less than that of molecular oxygen, the electron transfer from the dye to the dissolved oxygen with the formation of superoxide radical is energetically favourable. Furthermore, the free-energy change ΔG of the electron transfer reaction (2) can be evaluated by the following simplified Rehm–Weller relation in the case where the electronically excited molecule is the electron donor (dye*) [13]:

$$\Delta G = 23.06[E(\text{dye}^+/\text{dye}) - E(O_2/O_2^-)]$$

$$- E_{\text{dye}} \cdot \text{kcal mol}^{-1} \qquad (6)$$

where $E[(dye^+/\text{dye})]$ (V) is the oxidation potential of the dye, $E(O_2/O_2^-)$ (V) is the reduction potential of O_2 and E_{dye} (kcal mol^{-1}) is the energy of the electronically excited state of the dye molecule. The calculated ΔG values listed in Table 2 are negative, so that under our experimental conditions the electron transfer from dye* to O_2 may compete successfully with other pathways of deactivation of dye*.

It is interesting that when the solvent is a mixture of water and DMSO ($H_2O:DMSO = 1:1$), irradiation of the solution of dye 5 containing DMPO saturated with oxygen gives rise to the ESR signal of a triplet of doublets besides the ESR signal of the $(DMPO-O_2^-)^\cdot$ adduct. However, only the signal of the triplet of doublets
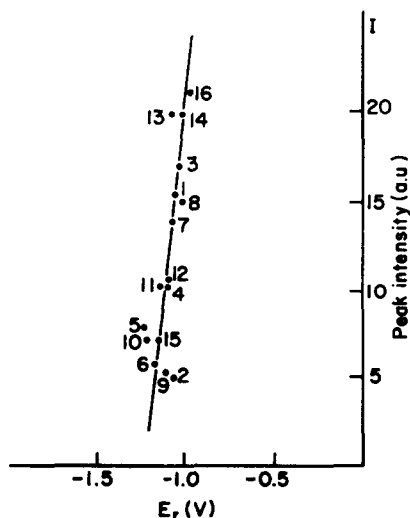

Fig. 4. Intensity of the ESR signal of various dyes as a function of the dye redox potential.

Table 2
Redox potentials [a] and spectral data [b] of dyes and calculated ΔG values for electron transfer from dyes to oxygen

| Dye	E_{ox} (V)	E_{red} (V)	λ_{max} (nm) (E (eV))		ΔG (kcal mol^{-1})
1	1.00	−1.07	485	(2.56)	−33.43
2	0.99	−1.03	523	(2.34)	−28.59
3	0.76	−1.06	553	(2.23)	−31.36
4	0.60	−1.12	580	(2.13)	−32.74
5	1.02	−1.30	500	(2.51)	−31.82
6	0.66	−1.12	570	(2.18)	−32.51
7	0.94	−1.10	565	(2.21)	−26.74
8	0.62	−1.02	550	(2.23)	−34.12
9	1.00	−1.07	485	(2.56)	−33.43
10	1.01	−1.28	491	(2.50)	−32.74
11	0.76	−1.15	561	(2.22)	−31.13
12	0.76	−1.10	544	(2.27)	−32.28
13	0.67	−1.13	568	(2.21)	−32.97
14	0.81	−1.10	565	(2.21)	−29.74
15	0.83	−1.20	562	(2.21)	−29.28
16	0.62	−1.02	562	(2.21)	−34.12

[a] E_{ox} and E_{red} vs. Ag/AgCl.
[b] λ_{max} (nm), wavelength of absorption band of dyes.

Fig. 5. ESR spectrum of the $(DMPO-CH_3)$. adduct generated by irradiation of a solution ($H_2O:DMSO = 1.1$) of dye 5 containing DMPO in a nitrogen atmosphere.

with $a_N = 1.58$ mT and $a_H = 2.26$ mT (Fig. 5) was observed during irradiation of the solution in a nitrogen atmosphere. It can be assigned to a $(DMPO-CH_3)^\cdot$ adduct. This result can be ascribed to the reaction of DMSO with the $\cdot$OH radical produced in Eq. (7), resulting in the formation of the methyl radical [14].
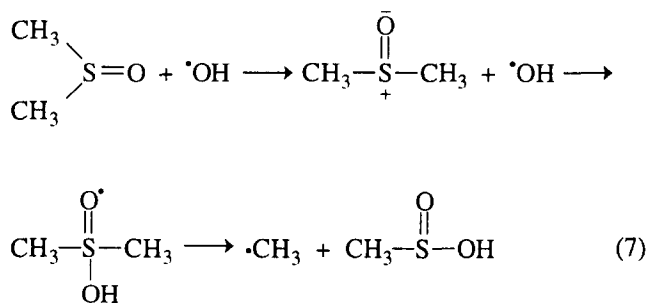
In the ESR spectra there was no evidence whatsoever of the spin adduct formed by the reaction of singlet oxygen with DMPO (nine lines, $a_N = 0.70$ mT and $a_H = 0.35$ mT) [15]. Hence singlet oxygen is not formed in a measurable amount.

The above results provide indisputable evidence for the electron transfer mechanism of the interaction of an excited dye with oxygen.

Acknowledgments

References

[1] W.J. Cooper and R.G. Zika, *Science, 220* (1983) 711.

[2] E. Lee-Ruff, *Chem. Soc. Rev.,* (1977) 195.

[3] J.R. Harbour and J.R. Bolton, *Photochem. Photobiol., 28* (1986) 231.

[4] J.R. Harbour and M.L. Hair, *Adv. Colloid Interface Sci., 24* (1986) 103.

[5] N.J. Turro, *Modern Molecular Photochemistry,* Benjamin–Cummings, New York, 1978.

[6] J.R. Harbour, V. Chew and J.R. Bolton, *Can. J. Chem., 52* (1974) 3549.

[7] J.R. Harbour and J.R. Bolton, *Biochem. Biophys. Res. Commun., 64* (1975) 803.

[8] T. Shen, *Ganguang Kexue Ye Kuang Huaxue,* (1984) 20.

[9] J. Guo and X. Wang, *Ganguang Kexue Yu Kuang Huaxue,* (1987) 8.

[10] T.L. Penner and P.B. Gilman Jr., *Photogr. Sci. Eng., 19* (1975) 102.

[11] K. Lang, D.M. Wagnerova, P. Stopka and W. Damerau. *J. Photochem. Photobiol. A: Chem., 67* (1992) 187.

[12] J.R. Harbour and M.L. Hair, *J. Phys. Chem., 82* (1978) 1397.

[13] D. Rehm and A. Weller, *Isr. J. Chem., 8* (1970) 259.

[14] E.G. Janzen, *Acc. Chem. Res., 4* (1971) 31.

[15] E. Ben-Hur, A. Carmichael, P. Riesz and I. Rosenthal, *Int. J. Radiat. Biol., 48* (1985) 837.