ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 116 (1998) 57–62

Journal of Photochemistry and Photobiology A:Chemistry

Triplet-excited dye molecules (eosine and methylene blue) quenching by H_2O_2 in aqueous solutions

V.Yu. Gak [a], V.A. Nadtochenko [a], J. Kiwi [b]

[a] *Institute of Chemical Physics in Chernogolovka RAS, Chernogolovka, Moscow Region 142432, Russian Federation*
[b] *ICP II, EPFL, Lausanne 1015, Switzerland*

Received 15 December 1997; accepted 22 January 1998

Abstract

The quenching of the triplet-excited dyes eosine and methylene blue (MB) by H_2O_2 has been studied by laser and steady-state photolysis. The quenching rate constant of the eosine triplet is $k_q = 2.4 \pm 0.3 \times 10^5$ (M s)$^{-1}$ and rate constant of MB quenching with H_2O_2 was found to be $k_q = 6.5 \pm 0.5 \times 10^5$ (M s)$^{-1}$. The decolorization of both dyes is accelerated upon H_2O_2 addition under steady-state photolysis and the redox reaction mechanism is suggested. The quantum yield for ion–radicals formation obtained were: for eosine 0.01 ± 0.005 and 0.03 ± 0.01 for MB. This latter observation provides the evidence for stability of these dyes under light irradiation in the presence of H_2O_2.

Keywords: Eosine; Methylene Blue; Dye decolorization; Dye oxidation; Hydrogen peroxide; Yield radical-formation

1. Introduction

Oxidative and reductive redox reactions and bleaching of xanthene and thiazine dyes have been the object of recent research [1–3]. Eosine have been studied by flash photolysis [4–10] and by steady-state irradiation [11]. Flash photolysis studies of eosine have shown that the triplet state oxidizes phenol [12], *p*-cresol, tyrosine and tryptophan [13], *p*-phenylenediamine [14], aniline, resorcinol, *p*-sulfanilic acid, *β*-naphtol, and *p*-bromophenol [15]. The bleaching of the eosine and formation of the leuco form has been reported. Electron acceptor like methylviologen oxidizes eosine to the radical-cation [16].

The photochemical properties of the methylene blue (MB) have been widely studied [17–22], and the kinetics of the triplet states of MB have been reported [19]. MB has also been used to measure the lifetime of singlet oxygen in solution [19]. The photoreduction of MB by EDTA has also been reported in detail [20]. The reduced form of MB-semimethylene blue radical has been reported via reduction of triplet MB [23] with diphenylamine in water [14]. Recently, the MB triplet was shown to undergo photo-oxidation by quinones [24]. The photochemistry of MB with biological systems has been investigated. The photodynamic effect with purine nucleotides and amino acids [18] has also been reported.

It is known that in the presence of oxygen, the bleaching of dye molecules occurs with the formation of several oxidative intermediates like: $^1O_2$, D^+, and O_2^-, H_2O_2 is also formed during dye bleaching in the presence of O_2. The H_2O_2 generated in solution seems to attain a steady-state concentration during dye-sensitized auto-oxidation [2]. Photochemical mineralization of the dye proceeds easily via photo-Fenton reactions [25].

But little is known about the reactions of the excited states of eosine and MB with H_2O_2. The quenching of the triplet-excited states of the fluorescein dyes by H_2O_2 was reported by flash photolysis at pH = 9.2 [26]. In the present work, the reactions of excited dyes eosine and MB molecules with H_2O_2 were examined by laser photolysis in anaerobic conditions. The main goal of this work was to study the quenching of the triplet-excited dye molecules of eosine and MB by H_2O_2 in solution at neutral pH.

2. Experimental

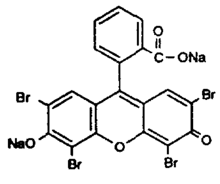
Laser photolysis experiments were done by using the second harmonic of Nd^{3+}-YAG Q-switch laser. The excitation wavelength of the laser pulse was $\lambda = 532$ nm with pulse energy of 5 mJ and the pulse duration of 12 ns. Xe-arc lamp was used for a detection. The data acquisition was carried out by a CAMAC-PC system with the time resolution of 100 ns. The transients were obtained as the average of 60 scans. The

PII S1010-6030(98)00230-5

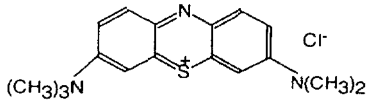
dye solution was circulated during experiments to avoid photodegradation of the dye due to the applied illumination.

Steady-state experiments used Xe-lamp (100 W). This light was cut by optical filters to excite the dye at maximum of the absorption band. The spectral width of filters was 20 nm. Ferrioxalate actinometry was used for measuring the light flux. The absorption spectra of the solution were measured by a Specord spectrophotometer.

The eosine-Y (eosine from now on) or methylene blue solutions were handled prior to photochemical irradiation in tridistilled water, without buffer addition. The oxygen was removed from the solution by three times frozen–melting cycle. Experiments were performed in a 1-cm vacuum silica cell at room temperature.



Eosine-Y



Methylene Blue

3. Results and discussion

3.1. Laser photolysis results and steady-state photolysis of eosine and MB

Fig. 1 shows the transient absorption spectra under laser photolysis for eosine (Fig. 1a) and for eosine in the presence of H_2O_2 (Fig. 1b). Insets in Fig. 1a,b show the absorption transient at $\lambda = 990$ nm and the bleaching transient observed at $\lambda = 480$ nm. In Fig. 1b, an acceleration of the transient decay takes place between λ values of 390 to 1000 nm due to the added H_2O_2. The bleaching transient recovered back almost to zero level after addition of H_2O_2. Lifetimes of transients decay have been obtained by a one-exponential approximation. The dependence of the reciprocal lifetime k vs. H_2O_2 as a function of concentration for transients of bleaching at $\lambda = 480$ nm and absorption at $\lambda = 990$ nm is shown in the Fig. 2. This dependence is seen to be linear. As seen in Fig. 2, the lifetimes for both transients at $\lambda = 480$ nm and at $\lambda = 990$ nm are the same in experimental error. The quenching rate constant is determined from the slope in Fig. 2. It is $k_{\text{eosine}} = (2.34 \pm 0.08) \times 10^5\ (\text{M s})^{-1}$.

Fig. 3 shows that H_2O_2 addition accelerates the rate of the eosine decolorization under steady-state illumination. This rate increases as the H_2O_2 concentration was increased. In dark experiments, the color remains in the presence of H_2O_2. This indicates that photochemical processes are responsible for the observed eosine decolorization.

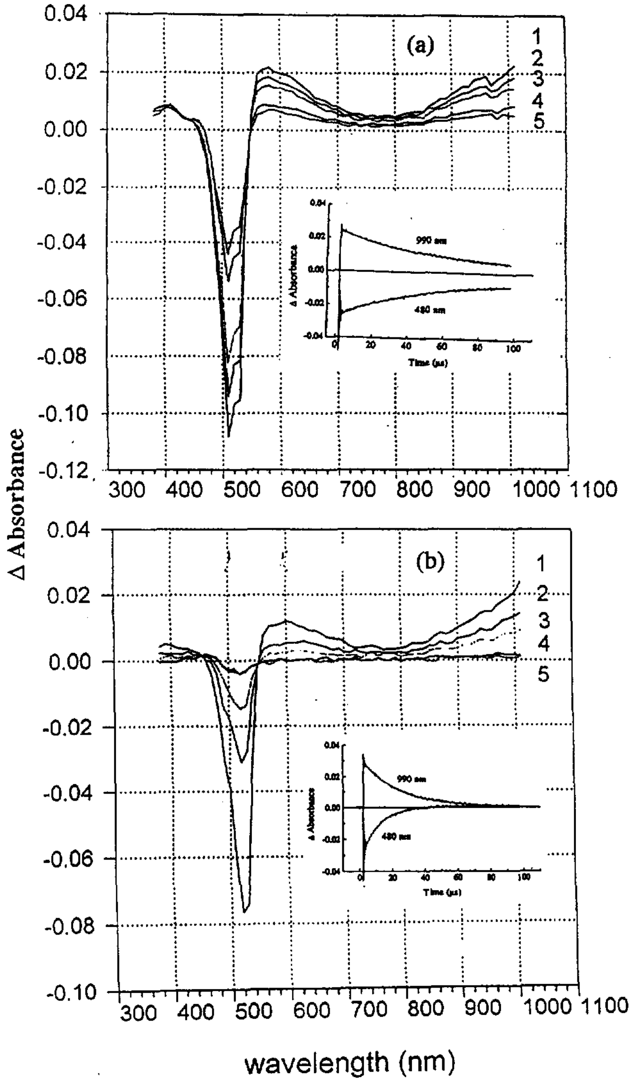


Fig. 1. Differential absorption spectra of eosine $= 2 \times 10^{-5}$ M. Excitation at $\lambda = 523$ nm. (a) $[H_2O_2] = 0$ M, time delay (1) 0 μs; (2) 18 μs; (3) 40 μs; (4) 70 μs; (5) 100 μs; (b) $[H_2O_2] = 0.2$ M, time delay (1) 0 μs; (2) 20 μs; (3) 30 μs; (4) 50 μs; (5) 60 μs.

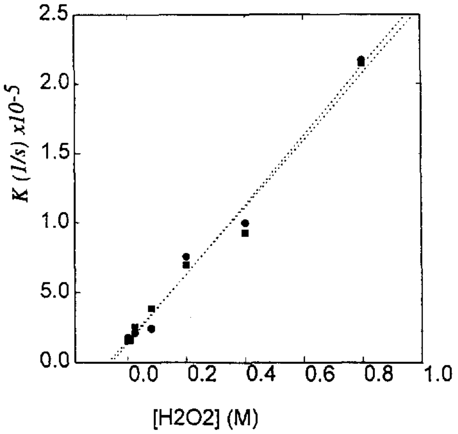


Fig. 2. Dependence of the reciprocal lifetime of transients at $\lambda_{\text{probe}} = 480$ nm (bleaching, squares) and $\lambda_{\text{probe}} = 990$ nm (absorption, circles) vs. H_2O_2 concentration for [eosine] $= 2 \times 10^{-5}$ M.

Fig. 4 shows the transient absorption spectra for MB. The inset to Fig. 4 shows two transients: (a) the absorption transient at $\lambda = 820$ nm and the bleaching transient at $\lambda = 620$ nm. The lifetime of the absorption transient at the 820 nm is 65 μs. This value is in good agreement with the literature value

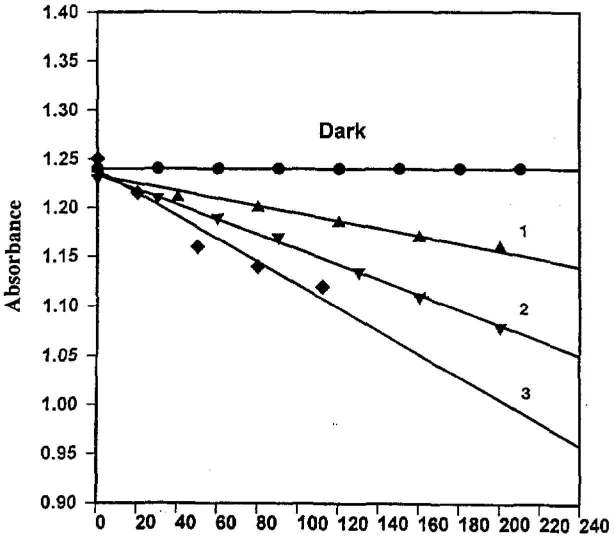


Fig. 3. Kinetics of the eosine bleaching under steady-state illumination at $\lambda = 530$ nm at different $[H_2O_2]$ concentrations: (1) $[H_2O_2] = 0.04$ M; (2) $[H_2O_2] = 0.08$ M; (3) $[H_2O_2] = 0.16$ M. $[H_2O_2] = 0.4$ is used in dark control experiment.

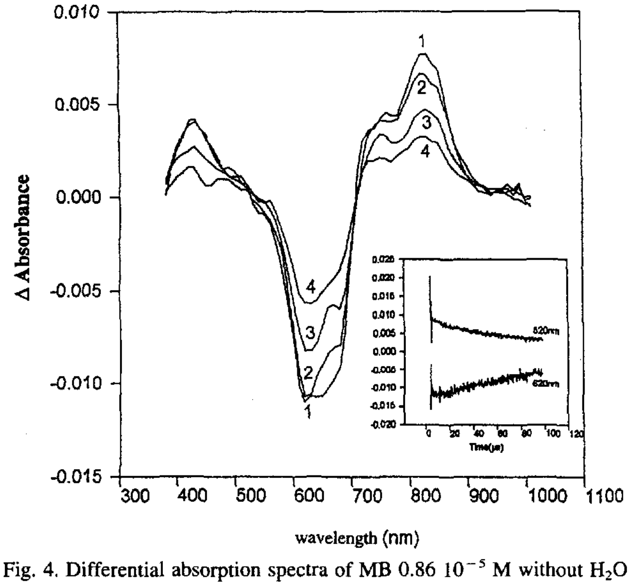


Fig. 4. Differential absorption spectra of MB 0.86 10^{-5} M without H_2O_2. Times delay: (1) 0 μs; (2) 10 μs; (3) 40 μs; (4) 85 μs. Inset shows the kinetics of bleaching ($\lambda = 620$ nm) and absorption ($\lambda = 820$ nm) of the transient spectra.

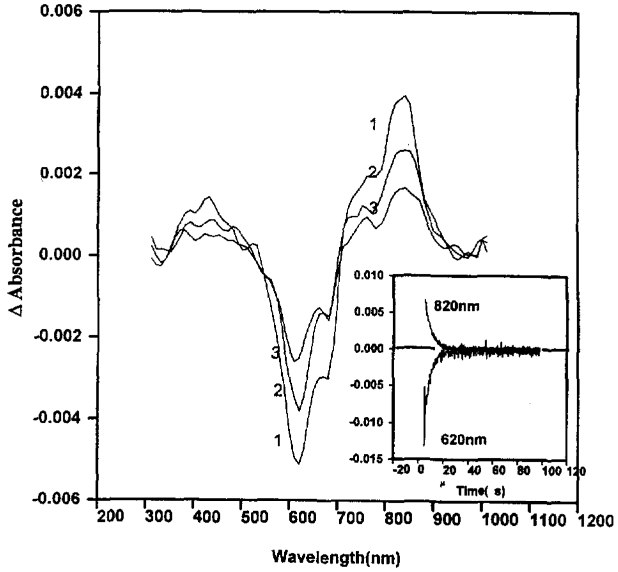


Fig. 5. Differential absorption spectra of MB 0.86×10^{-5} M without $[H_2O_2] = 0.08$ M. Times delay: (1) 0 μs; (2) 2 μs; (3) 4 μs. Inset shows the kinetics of bleaching ($\lambda = 620$ nm) and absorption ($\lambda = 820$ nm) of the transient spectra.

reported for the triplet lifetime of 70–90 μs [27]. Fig. 5 shows the transient absorption spectra for MB in the presence of H_2O_2. The inset shows the transients at the same λ's as in the inset in Fig. 4. From Figs. 4 and 5, it is readily seen that the quenching of the MB transients species takes place in solution by H_2O_2. In the presence of H_2O_2, the MB bleaching signal recovers to the zero level in Fig. 5. This means that H_2O_2 effectively promotes the recovery of excited MB to the ground state.

Fig. 6 presents the reciprocal lifetimes of the transients decay at two wavelengths: $\lambda = 820$ nm and $\lambda = 620$ nm as a function of the concentration of H_2O_2 added in solution. A linear dependence between these two variables is observed. The measured lifetime for the bleaching at $\lambda = 620$ nm corresponds to the absorption trace observed at $\lambda = 820$ nm. From the slope of the dependence presented in Fig. 6, the quenching constant of excited MB by H_2O_2 was found to be $k_{MB} = 6.9 \pm 0.6 \times 10^5$ $(\mathrm{M\ s})^{-1}$.

Fig. 7 shows the effect of H_2O_2 on the decolorization rate of MB. This indicates that at higher H_2O_2 concentrations, the decay of the MB in solution is more pronounced. The initial color is conserved when this run was carried out in the dark.

3.2. Eosine: acid–base equilibria and assignment of the nature of the excited states quenched by H_2O_2

The acid–base equilibrium of eosine molecules in ground and triplet-excited state have been reported with $pK_{gs} = 4.3$ and $pK_T < 4$ [28]. Therefore, eosin exists in the deprotonated form in both the ground and triplet state (pH = 6). Triplet–triplet (T–T) absorption predominates in eosine above 550 nm and up to 700 nm [1,6–11]. An additional band is observed in Fig. 1 from 800 to 1000 nm. This band is attributed to T–T absorption because the observed decay proceeds with the same rate as observed for the band of 550–700 nm. The lifetime of the transient at $\lambda = 990$ nm was 51 ± 2 μs, the lifetime of the transient at $\lambda = 600$ nm was 50 ± 2 μs and the bleaching transient at $\lambda = 480$ nm was 48 ± 2 μs. The quenching of the triplet-excited state of eosine can be determined from either the bleaching band at 480–570 nm or from the absorption transients at 580–750 nm and 800–1000 nm. Absorption of ion–radicals of eosine below 480 nm have been reported in the literature with (a) a maximum band for the eosine semi-reduced radical at $\lambda = 405$ nm [1,6–11] and (b) a maximum for the eosine semi-oxidized radical at $\lambda = 460$ nm [11]. At $\lambda < 480$ nm, the absorption of triplet states and

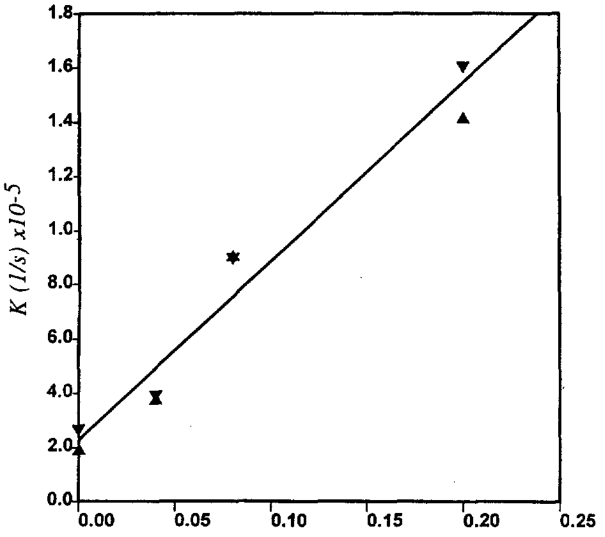


Fig. 6. Dependence of the reciprocal lifetime of transients at $\lambda_{probe} = 650$ nm (bleaching, inverted triangles) and $\lambda_{probe} = 50$ nm (absorption, normal triangles) vs. H_2O_2 concentration for [MB] $= 0.86 \times 10^{-5}$ M.

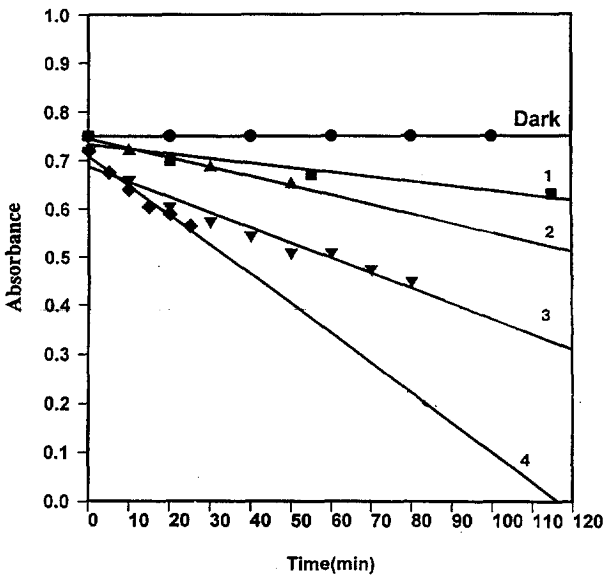


Fig. 7. Kinetics of the MB bleaching under steady-state illumination at $\lambda = 650$ nm at different $[H_2O_2]$ concentrations: (1) $[H_2O_2] = 0.002$ M; (2) $[H_2O_2] = 0.004$ M; (3) $[H_2O_2] = 0.04$ M; (4) $[H_2O_2] = 0.4$. The $[H_2O_2] = 0.4$ M is used in dark control experiment.

radicals has been reported to overlap [1,6–11], whereas in the region at $\lambda > 480$ nm, it was possible to follow the signals of the triplet quenching by H_2O_2.

Fig. 1 indicates that in the case of H_2O_2 addition, a decay is observed for the transients between 390 nm to 1000 nm, even in the domain below 480 nm, where ion radical absorption band exists. The bands were seen in this figure to decay with the same rate. This means that only one species is decaying in solution. Therefore, the quenching constant $k_{eosine} = (2.34 \pm 0.08) \times 10^5$ (M s)$^{-1}$ found for eosine originates from the quenching of the eosine triplet-excited state. No meaningful long-lived transients were observed in the presence of H_2O_2 below 480 nm, the region of ion–radical absorption. The disappearance for (a) the bleaching band and (b) the absorption of the transient spectra in Fig. 1b indicated that no meaningful amount of products were formed between H_2O_2 and the triplet-excited state of eosine.

3.3. Methylene Blue (MB) acid–base equilibria and assignment of the nature of the excited states quenched by H_2O_2

The acid–base equilibria existing in the MB ground state have been reported as: $pK(MBH^{2+} \leftrightarrow MBH^+ + H^+) < 1$ and $pK(MBH^+ \leftrightarrow MBH + H^+) > 11$. In the present work, the form of MB present in solution is MBH^+, since this study has been carried out at pH = 6. For the triplet MB: $pK_T(^3MBH_2^{2+} \leftrightarrow {}^3MBH_2^+ + H^+) \sim 7$ [29,30]. Therefore, protonation in the triplet-excited state can occur at pH = 6. The pK_a of the semi-methylene blue $MBH_2^{+\bullet}$ has been reported as 1.9 [22]. In the present experiments, semi-reduced radical MB exists in the deprotonated form MBH^+.

The literature has reported an absorption of MB with T–T peaks at 415 nm and 820 nm [18,31,32]. The semi-reduced radical $MBH_2^{2+\bullet}$ [31,32] is reported with an absorption at 420 nm. The semi-reduced radical $MBH^{+\bullet}$ have two maxima at 410 nm with $\epsilon_{410} = 9800$ (M cm)$^{-1}$ and at 880 nm with $\epsilon_{880} = 33000$ (M cm)$^{-1}$ [22]. The semi-oxidized radical $MB^{+\bullet}$ was detected at 520 nm [32]. Despite the significant overlap of the T–T absorption band with the ion–radical absorption, it is possible to identify the MB species quenched by H_2O_2 and decide whether it is a triplet or an ion–radical. The bleaching transient at $\lambda = 620$ without H_2O_2 shown in the inset of Fig. 4 has a non-exponential form suggesting the excited triplet of MB partially being converted into radical–ions. In the presence of H_2O_2, the decay kinetics is exponential. In the inset to Fig. 5, the transient absorption at $\lambda = 820$ nm has the same form as the bleaching at $\lambda = 620$ nm. The similarity of the transient for absorption and bleaching indicates that during the quenching of the MB triplet by H_2O_2, the last process was in competition with concentration quenching reactions of the MB triplet. Fig. 5 shows that the excited triplet and the bleaching transient of MB recovered to the ground state. As in the case of eosine, there was no indication on the formation of the long-lived intermediates during MB quenching by H_2O_2. Moreover, the radicals of eosine and MB dyes have been reported to have a low absorption in the spectral domain of the dye absorption in the ground state [22]. Therefore, if these radicals are formed they should be seen along the bleaching transients. This indicates a low yield of ion–radicals due to the triplet dye quenching by H_2O_2. On the other hand, if radicals are formed due to the triplet state quenching of MB or eosine, their yield would not exceed 3–5%. This is in the accuracy range of the bleaching amplitude measurements.

Since the radical yield is low, it is impossible to follow in detail the reaction of the ion–radical with H_2O_2 by laser photolysis.

3.4. The mechanism of triplet-excited state of eosine and MB quenching by H_2O_2

The observed quenching cannot be ascribed to energy transfer from the eosine T (1.84 eV) or MB (1.36 eV) to H_2O_2 (2.07 eV). The quenching may proceed, therefore, via a redox quenching mechanism. The free energy for the electron transfer reactions from the triplet excited state of a dye molecule is known as

$$\Delta G_a = E_{1/2}(D/D^{+\cdot}) - E_{1/2}(OH^{\cdot}/H_2O_2) - E(D^{T_1}) \quad (1)$$

$$\Delta G_b = E_{1/2}(H_2O_2/HO_2^{\cdot}) - E_{1/2}(D^{-\cdot}/D^{+\cdot}) - E(D^{T_1}) \quad (2)$$

The redox potentials for H_2O_2 and dye are seen below in Table 1.

The experiment was carried out at pH = 6

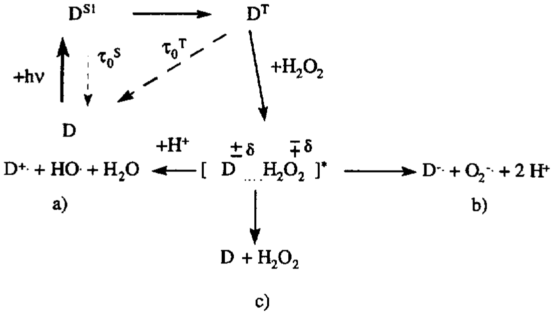
$$\Delta G_a(\text{eosine}) = 0.89 - (-0.106) - 1.84 - 0.059 \times 6 \ (\text{pH}=6) = -1.2$$

$$\Delta G_b(\text{eosine}) = 0.95 - (-1.09) - 1.84 - 0.059 \times 2 \ (2 \text{ protons}) \times 6 \ (\text{pH}=6) = -0.51$$

$$\Delta G_b(\text{MB}) = 0.95 - (-0.23) - 1.36 - 0.059 \times 2 \ (2 \text{ protons}) \times 6 \ (\text{pH}=6) = -0.89$$

Scheme 1 can be considered as the general scheme in excited dye (eosine or MB) quenching by H_2O_2. The reaction of the triplet quenching by H_2O_2 shows three possible channels: (a) the electron transfer from the excited dye molecule to the quencher with the formation of the dye radical cation and OH, (b) the electron transfer from the quencher to the dye molecule with the formation of the dye radical anion and $HO_2^{\cdot}$ radical and finally (c) the quenching of the triplet-excited state of the dye by H_2O_2 without the formation of products. Reaction (c) can be considered as the excited charge transfer (exciplex) state between dyes with H_2O_2 relaxing subsequently to the ground state.

The yield of radicals in reaction (Scheme 1) can be estimated from the measurements of the rate of dye decolorization during steady-state experiments. An increase in the rate of the decolorization with increasing H_2O_2 was experimentally observed. Assuming the free radical reaction mechanism, it is possible to estimate the radical yield due to the triplet dye quenching by H_2O_2 in the following way. The rate of the dye decolorization during the initial degradation:



Scheme 1.

Table 1

	$E_{1/2}$-$(D/D^{+\cdot})$ eV	$E_{1/2}$-$(D^{-\cdot}/D)$ eV	E-(D^{T_1}) eV	$E_{1/2}$-(OH/H_2O_2) eV	$E_{1/2}$-(H_2O_2/HO_2) eV
Eosine	0.89	−1.09	1.84	–	–
MB	–	−0.23	1.36	–	–
H_2O_2	–	–	–	−0.106*	0.95**

*A redox potential is for $H_2O_2 \xrightarrow{-e^-} O_2^{-\cdot} + 2H^+$ at pH = 0; a reaction $D^T + H_2O_2 \rightarrow [D^{-\delta} \cdots H_2O_2{}^{+\delta}] \rightarrow D^{-\cdot} + O_2^{-\cdot} + 2H^+$ is considered.

**A redox potential is for $H_2O_2 \xrightarrow{+e^-, +H^+} HO^{\cdot} + H_2O$ at pH = 0; a reaction $D^T + H_2O_2 \rightarrow [D^{+\delta} \cdots H_2O_2{}^{-\delta}] \xrightarrow{+H^+} D^{+\cdot} + HO^{\cdot} + H_2O$ is considered (Courtesy of Atlas of Electrochemical Equilibria in Aqueous Solutions by Marcel Pourbaix National Association of Corrosion Engineers, Houston, Texas, USA, Brussel, 1974).

$$\frac{d[D]}{d[t]} = -k_r \cdot [D^{T_1}] \cdot [H_2O_2] = -\frac{k_r \cdot \phi \cdot I}{(k_r + k_q) \cdot [H_2O_2] + 1/\tau_0^T} \cdot [H_2O_2] \quad (3)$$

$$[D^{T_1}] = -\frac{\phi \cdot I}{(k_r + k_q) \cdot [H_2O_2] + 1/\tau_0^T} \quad (4)$$

D^{T_1} is the stationary concentration of the excited dye molecules during steady-state photolysis; k_r corresponds to the reaction (a) or (b); k_q corresponds to the reaction (c); $\tau_0{}^T$ is the lifetime of the excited dye without H_2O_2; ϕ—quantum yield of the triplet formation; I—absorbed photon flux.

Eq. (5) predicts the linear dependence of reciprocal decolorization rate on the reciprocal H_2O_2 concentration

$$\frac{1}{\text{Q.Y.}} = \frac{I_0}{d[D]/dt} = \frac{(k_r + k_q)}{k_r \cdot \phi} + \frac{1}{\tau_0^T \cdot k_r \cdot \phi} \cdot \frac{1}{[H_2O_2]} \quad (5)$$

Fig. 8a (MB) and Fig. 8b (eosine) show a linear dependence of the reciprocal rate of the dye's disappearance vs. H_2O_2 concentration plotted according to Eq. (5). The rates of dye decolorization were obtained from the data shown in Fig. 3 for eosine and Fig. 7 for MB. In Fig. 8a,b a linear dependence is observed. The intercept A and slope B is for MB ($A = 45 \pm 15$; $B = 0.37 \pm 0.05$ M); eosine ($A = 184 \pm 90$; $B = 84 \pm 7$ M). According to the (5) intercept A equals $(k_r + k_q)/(k_r)$. Taking the known values for the intersystem crossing of 0.68 (eosine) and 0.54 (MB) the yield of the radical formation $k_r/(k_q + k_r)$ can be estimated from steady-state measurements to be 0.01 ± 0.005 for eosine and 0.033 ± 0.01 for MB. These values show that the bleaching transients in the laser photolysis to the zero level is in agreement with low yields for the reaction product. According to this consideration, the values of radical yield are the upper limit of the radical yield due to the triplet quenching by H_2O_2, because $OH^{\cdot}$ radicals should react with the dye molecules effectively increasing the observed yield. The $k_r + k_q$ is equals to the value of the quenching rate constant obtained by laser

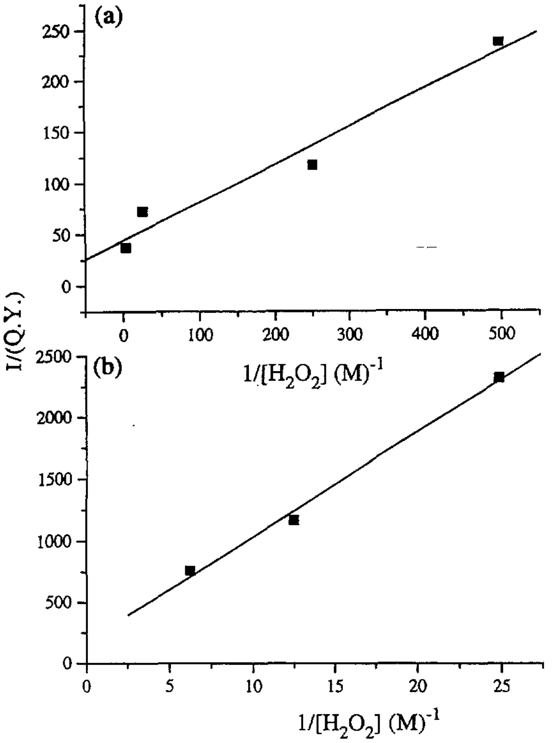


Fig. 8. Dependence of the reciprocal bleaching rate of the dye vs. reciprocal H_2O_2 concentration in steady-state illumination: (a) MB, (b) eosine.

photolysis experiments. These values are $2.4 \pm 0.3 \times 10^5$ $(\mathrm{M\ s})^{-1}$ for eosine and $6.5 \pm 0.5 \times 10^5$ $(\mathrm{M\ s})^{-1}$ for MB. According to Eq. (5), the ratio of the intercept to slope A/B is $\tau_0^{\mathrm{T}}(k_r + k_q)$. The last relation allows to estimate the dye triplet quenching constant $(k_r + k_q)$ from steady-state experiments. This value is found to be 3×10^5 $(\mathrm{M\ s})^{-1}$ for eosine, and 2×10^6 $(\mathrm{M\ s})^{-1}$ for MB. Steady-state experiments for MB give the rate constant value three times more than laser photolysis. Taking the simplified kinetics of steady-state decolorization, these rate constants from the steady-state and laser photolysis experiments are in fairly good agreement. Reaction (c) is the main channel for eosine and MB quenching. A mechanism involving an exciplex could be suggested. The quenching of the dye triplets by H_2O_2 cannot compete with the quenching by O_2 dissolved in the solution. At the very high H_2O_2 (1 M) the triplet lifetime should be about 4 μs for the eosine and 1.5 μs for the MB. These lifetimes are significantly longer than the triplet lifetime in air-saturated aqueous solution, which was observed to be less than 1 μs, because the quenching constant for the triplet state is close to the diffusion-controlled value [3].

4. Conclusion

The triplet state of the eosine and MB dyes are quenched by H_2O_2 with rate constants equal to $2.4 \pm 0.3 \times 10^5$ $(\mathrm{M\ s})^{-1}$ and $6.5 \pm 0.5 \times 10^5$ $(\mathrm{M\ s})^{-1}$ respectively. Decolorization of both dyes under steady-state illumination was observed in the presence of H_2O_2. The dependence of the decolorization rates vs. H_2O_2 concentration agrees with the observed quenching of the triplet states of the dyes by H_2O_2. The estimation of the free energy of reaction shows that (a) photoinduced electron transfer from the eosine triplet-excited to H_2O_2 with formation of $OH^{\bullet}$ radical and (b) that the oxidation of H_2O_2 by MB triplet state is possible with the formation $HO_2^{\bullet}$ radicals in thermodynamically allowed. The yield of radicals formation is estimated to be (~3% reactions) in agreement with previously reported observations obtained by steady-state and laser photolysis experiments.

Acknowledgements

The financial support of the INTAS contract 94-0642 and from the European Communities Environmental Program NEV-NEV-0064 (NEV N 96.0350, Bern) is duly appreciated.

References

[1] A. Nev, H. Freeman, Environmental Chemistry of Dyes and Pigments, Wiley-Interscience, New York, 1996.
[2] H. Zollinger, in: Synthesis, Properties and Applications of Organic Dyes and Pigments, VCH Publishers, New York, 1992.
[3] A.K. Chibisov, Russ. Chem. Rev. 50 (1981) 616.
[4] V. Kasche, Photochem. Photobiol. 6 (1967) 643.
[5] L. Lindqvist, Arkiv Kemi 16 (1960) 79.
[6] V. Kashe, L. Lindqvist, J. Phys. Chem. 68 (1964) 923.
[7] L. Lindqvist, Acta Chem. Scand. 20 (1960) 2967.
[8] F. Zwicker, L.I. Grossweiner, J. Phys. Chem. 67 (1962) 549.
[9] J. Crysochoos, J. Ovadia, L.I. Grossweiner, J. Phys. Chem. 71 (1967) 1629.
[10] P.G. Bowers, G. Porter, Proc. R. Soc. A (London) 297 (1967) 348.
[11] A.G. Kepka, L.I. Grossweiner, Photochem. Photobiol. 14 (1971) 621.
[12] L.I. Grossweiner, E.F. Zwicker, J. Phys. Chem. 34 (1961) 1411.
[13] L.I. Grossweiner, E.F. Zwicker, J. Phys. Chem. 39 (1963) 2774.
[14] V. Kashe, L. Lindqvist, Photochem. Photobiol. 4 (1965) 923.
[15] N. Chrysochoos, L.I. Grossweiner, Photochem. Photobiol. 8 (1968) 193.
[16] V.A. Nadtochenko, I.V. Rubtsov, T.S. Dzhabiev, Chem. Phys. 11 (1983) 1515 in Russian.
[17] M. Nemoto, H. Kokubun, M. Koizumi, Bull. Chem. Soc. Jpn. 42 (1972) 2464.
[18] D. Dunn, H.L. Vivian, I.E. Kochevar, Photochem. Photobiol. 53 (1991) 47.
[19] P.B. Nilsson, M. Merkel, D.R. Kearns, Photochem. Photobiol. 16 (1972) 109.
[20] P. Bonneau, Fornier de Violet, J. Joussot-Dubien, Photochem. Photobiol. 19 (1974) 129.
[21] H.E. Jacob, Photochem. Photobiol. 96 (1974) 133.
[22] P.V. Kamat, N. Lichtin, Photochem. Photobiol. 33 (1981) 109.
[23] T. Ohno, T.L. Osif, N.N. Lichtin, Photochem. Photobiol. 30 (1979) 541.
[24] M. Misran, D. Matthews, P. Valente, A. Hope, Aust. J. Chem. 47 (1994) 209.
[25] V. Nadtochenko, J. Kiwi, J. Chem. Soc., Faraday Trans. 93 (1997) 2373.
[26] K.J. Youtsey, L.I. Grossweiner, J. Phys. Chem. 73 (1969) 447.
[27] J.P. Keene, E.J. Land, A.J. Swallow, A Pulse Radiolysis Study of Methelene Blue, Pulse Radiolysis, p. 227.
[28] V.E. Korobov, A.K. Chibisov, Russ. Chem. Rev. 52 (1983) 27.
[29] H. Fisher, Z. Phys. Chem. N.F. 43 (1964) 177.
[30] F. Faurej, R. Bonneau, J. Joussot-Dubien, Photochem. Photobiol. 6 (1967) 331.
[31] S. Matsumoto, Bull. Chem. Soc. Jpn. 37 (1964) 491.
[32] S. Kato, M. Morita, M. Koizumi, Bull. Chem. Soc. Jpn. 37 (1964) 117.