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PHOTOSENSITIZING ACTION OF EOSIN Y FOR VISIBLE LIGHT INDUCED HYDROGEN EVOLUTION FROM WATER

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Eosin Y was not photobleached with triethanolamine (TEOA) on visible light irradiation in the presence of methyl viologen (MV^{2+}), and worked as an effective sensitizer to reduce MV^{2+} into $MV^{+\cdot}$ with TEOA in aqueous ethanol. The resulting $MV^{+\cdot}$ reduced water to hydrogen in the presence of colloidal platinum in the same solvent. The quantum yield for $MV^{+\cdot}$ formation was measured to be ca. 0.3.

Currently active efforts have been devoted to achievement of hydrogen evolution from water through visible light irradiation of appropriate sensitizers in suitable electron transferring systems comprized of an electron donor like amines, a mediator like methyl viologen (MV^{2+}), and a redox catalyst like colloidal platinum and hydrogenase.1) Among sensitizers, ruthenium complexes have been the best studied;2) however, a few reports have appeared on utilization of organic dyes.3) Xanthene dyes are known to be irreversibly photobleached in alcoholic solutions under nitrogen into their leuco-forms;4,5) the resulting matters cannot be reconverted to the starting dyes on contact with air. This behavior is in remarkable contrast with thiazine dyes which are reversibly photoreduced under nitrogen in alcoholic solutions into the leuco-forms;4,6) the starting dyes can be recovered on contact with air. However, we have found that Eosin Y (2',4',5',7'-tetrabromofluorescein disodium salt), one of xanthene dyes, is not photobleached in the presence of MV^{2+} and triethanolamine (TEOA) as an electron donor and works as an effective sensitizer for reduction of MV^{2+} into $MV^{+\cdot}$,7) which subsequently reduces water to hydrogen in the presence of colloidal platinum.

In a typical run, irradiation of Eosin Y (1.7×10^{-5} mol/dm^3) in aqueous ethanol (1:1 by volume, 4 ml) containing TEOA (0.05 mol/dm^3) with visible light ($\lambda > 450$ nm) from a 650 W tungsten-bromine lamp resulted in complete bleaching of Eosin Y in 60 s, and the original color of the dye was not recovered at all on introduction of air into the irradiated solution. However, irradiation of an aqueous ethanol solution of Eosin Y and TEOA containing MV^{2+} (5.2×10^{-3} mol/dm^3) under otherwise the same conditions caused growth of a new absorption band around 602 nm due to production of $MV^{+\cdot}$ in an amount of 1.6×10^{-4} mol/dm^3 in 90 s. This means that the electron transfer through Eosin Y was cycled 9 times in this period. On introduction of air into the irradiated solution, the new absorption disappeared completely and the absorption of Eosin Y was

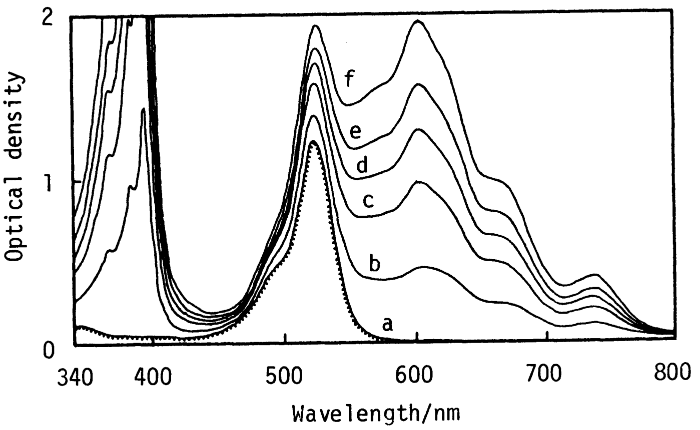

Fig. 1. Spectral change of an aqueous ethanol solution of Eosin Y/MV^{2+}/TEOA on irradiation under N_2(——) and on introduction of air after photolysis(···); irradiation periods as follows: a) 0, b) 15, c) 30, d) 45, e) 60, f) 90 s.

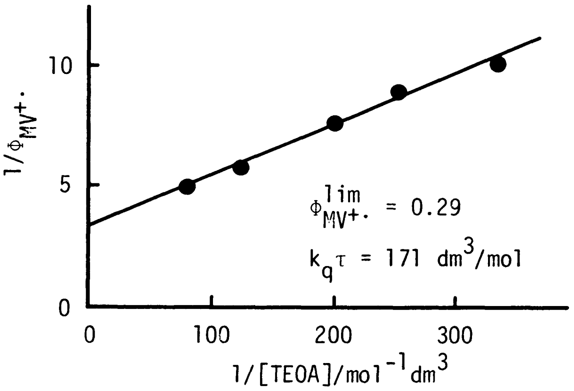

Fig. 2. Stern-Volmer plot for $MV^{+\cdot}$ formation on irradiation of Eosin Y/MV^{2+}/TEOA in aqueous ethanol.

recovered quantitatively (Fig. 1).

In the presence of colloidal platinum carried by poly(vinyl alcohol) as a redox catalyst, irradiation of the Eosin/MV^{2+}/TEOA system led to hydrogen evolution. However, high concentration of MV^{2+} tended to suppress the production of hydrogen. Thus, when Eosin Y (1.5×10^{-5} mol/dm^3) was irradiated for 15 h with a 1 kW xenon lamp ($\lambda >$ 450 nm) in aqueous ethanol (1:1, 20 ml) containing TEOA (0.01 mol/dm^3) and colloidal platinum (6.6×10^{-5} mol/dm^3), the volumes of hydrogen evolved were 40, 1100, 70, and 0 μl in the presence of MV^{2+} in 0, 4.8×10^{-4}, 4.5×10^{-3}, and 4.5×10^{-2} mol/dm^3, respectively.

Quantum yields were determined on irradiation of sample solutions in a mixture (1:1 by volume, 4 ml) of ethanol and water adjusted to pH 5 with phthalate buffer with 490 nm light obtained through a monochromator (slit width: 20 nm) from a 500 W xenon lamp employing potassium tris(oxalato)ferrate(III) actinometry. The quantum yield for disappearance of Eosin Y (8.6×10^{-5} mol/dm^3) in the presence of TEOA [(3.-12.0) $\times 10^{-3}$ mol/dm^3] alone (two-component system) was determined by following the decrease of absorption of Eosin Y at 480 nm. The reciprocal of quantum yield showed linear Stern-Volmer relationships against the reciprocal of concentration of TEOA. The limiting quantum yield, the quantum yield extrapolated to infinite concentration of TEOA, was 0.11.

The quantum yield of $MV^{+\cdot}$ production in the three-component system was determined by measuring absorption of the resulting $MV^{+\cdot}$ on similar irradiation of Eosin Y (8.6×10^{-5} mol/dm^3) in the presence of a fixed concentration of MV^{2+} (1.0×10^{-3} mol/dm^3) and varying concentrations of TEOA [(3.0-12.0) $\times 10^{-3}$ mol/dm^3]. The results fit Stern-Volmer relationships as depicted in Fig. 2 with the limiting quantum yield of 0.29.

On the other hand, on irradiation of Eosin Y (8.6×10^{-5} mol/dm^3) with a fixed concentration of TEOA (0.01 mol/dm^3) and varied concentrations of MV^{2+} (1.0×10^{-5} - 1.0×10^{-3} mol/dm^3) the quantum yield for $MV^{+\cdot}$ production was almost unchanged with

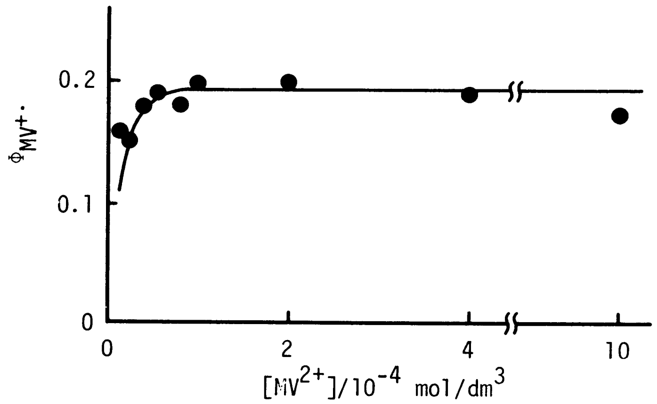

Fig. 3. Quantum yields for $MV^{+\cdot}$ formation as a function of MV^{2+} concentration on irradiation of Eosin Y/MV^{2+}/TEOA in aqueous ethanol.

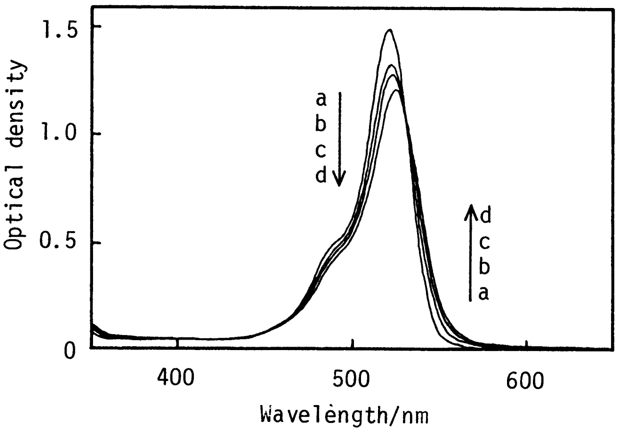

Fig. 4. Spectral change of Eosin Y in aqueous ethanol on addition of MV^{2+}; MV^{2+} concentrations as follows: a) 0, b) 1.51×10^{-4}, c) 5.02×10^{-4}, d) 5.02×10^{-3} mol/dm^3.

MV^{2+} concentration as shown in Fig. 3; the quantum yield increased from 0.15 to 0.20 with increasing concentration of MV^{2+} from 1.0×10^{-5} to 1.0×10^{-4} mol/dm^3, and then remained nearly 0.20 despite increase in MV^{2+} concentration up to 1.0×10^{-3} mol/dm^3.

This relative insensitivity of quantum yield to MV^{2+} concentration must be related with formation of a complex between Eosin Y and MV^{2+} as depicted in Fig. 4, which shows the spectral change of Eosin Y with MV^{2+} concentration. Also, MV^{2+} effectively quenched fluorescence of Eosin Y in intensity but did not affect the fluorescence lifetime at all. These facts mean that Eosin Y forms a non-fluorescent complex with MV^{2+} in the ground state but singlet excited Eosin Y is not quenched with MV^{2+}. From the measurements of absorption and fluorescence spectra the equilibrium constant for complex formation was estimated to be nearly 1200 dm^3/mol in aqueous ethanol (1:1).

The present results show that among sensitizers for MV^{2+} reduction, Eosin Y (EY^{2-}) works as a fairly good sensitizer with a quantum yield of 0.2-0.3. The mechanism for the present reaction has not thoroughly been explored. However, it is worth noting that the efficient sensitizing action of Eosin Y can be attributed to the highly cathodic electrochemical potential of its one-electron reduced form [$E_{1/2}(EY^{2-}/EY^{3-\cdot}) = -1.56$ V in CH_3CN vs. Ag/$AgNO_3$]; the Eosin Y triplet is reduced by TEOA to give $EY^{3-\cdot}$, which subsequently undergoes electron transfer to MV^{2+} resulting in formation of $MV^{+\cdot}$ and recovery of EY^{2-} (Eqs. 1-4).[8] Concurrently, electron transfer from excited states of EY^{2-} to MV^{2+} within the complex may contribute in part to the MV^{2+} reduction (Eqs. 5-7).

$$EY^{2-} + MV^{2+} \rightleftarrows (EY^{2-}\cdots MV^{2+}) \tag{1}$$

$$EY^{2-} \xrightarrow{h\nu} {}^1(EY^{2-})^* \longrightarrow {}^3(EY^{2-})^* \tag{2}$$

$${}^3(EY^{2-})^* + TEOA \longrightarrow EY^{3-\cdot} + TEOA^{+\cdot} \tag{3}$$

$$EY^{3-\cdot} + MV^{2+} \longrightarrow EY^{2-} + MV^{+\cdot} \tag{4}$$

$$(EY^{2-}\cdots MV^{2+}) \xrightarrow{h\nu} [(EY^{2-})^{*}\cdots MV^{2+}] \qquad (5)$$

$$[(EY^{2-})^{*}\cdots MV^{2+}] \longrightarrow EY^{-\cdot} + MV^{+\cdot} \qquad (6)$$

$$EY^{-\cdot} + TEOA \longrightarrow EY^{2-} + TEOA^{+\cdot} \qquad (7)$$

The detailed mechanism for the present reaction is now under investigation through transient spectroscopy and will be reported elsewhere.

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7) Methylene blue, one of thiazine dyes, behaved in a way contrasting with Eosin Y. Irradiation of Methylene blue (1.5×10^{-5} mol/dm^3) with visible light (λ>550 nm) from a 650 W tungsten-bromine lamp in aqueous ethanol (1:1) containing TEOA (0.01 mol/dm^3) resulted in rapid bleaching of the dye, and introduction of air into the irradiated solution caused quick recovery of the starting dye. Irradiation of Methylene blue/TEOA in aqueous ethanol containing MV^{2+} under nitrogen led to bleaching of the dye and formation of only a small amount of $MV^{+\cdot}$ (1.5×10^{-5} mol/dm^3) in 8 min.

8) A possibility cannot be ruled out that the Eosin Y triplet may undergo electron transfer to MV^{2+} producing $MV^{+\cdot}$ and $EY^{-\cdot}$ followed by reduction of $EY^{-\cdot}$ by TEOA to recover EY^{2-}.

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