Photosensitized Reduction of Methylviologen through the Energy Transfer from Triplet Dyes to 9-Anthracenecarboxylate Anion

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Synopsis. The reaction mechanism for photosensitized reduction of methylviologen, MV^{2+} through the triplet-triplet energy transfer from organic dyes to 9-anthracenecarboxylate, AC^- was investigated. From the kinetic analysis on $MV^{\dot{+}}$ formation, it was estimated that both efficiencies of the energy transfer and of the electron transfer from $^3AC^-$ to MV^{2+} were close to unity.

The mechanistic investigation of highly efficient photosensitized reactions has been required for the utilization of light energy and the application to the optical devices in technology. As for the ideal sensitizer in the reaction, there are three requirments; (a) a light absorption in the wide range of wavelength, (b) an efficient utilization of absorbed light energy and (c) the complete turnover of the light absorber. We have investigated the mechanism of electron-transfer reaction for sensitized formation of methylviologen radical by xanthene dyes, where the initial process is started through electron transfer from triplet dyes, ^{3}Dye to MV^{2+}. This is followed by electron transfer to the resulting semioxidized dyes from triethanolamine, TEOA (oxidation-cycle mechanism for three component system of Dye/MV^{2+}/TEOA).[1,2] The maximum yields for $MV^{\dot{+}}$ formation were equal to 0.16 and 0.045 in case of Eosine Y, $C_{20}H_6O_5Br_4Na_2$ and Erythrosine, Ery, $C_{20}H_6O_5I_4Na_2$ as the sensitizer, respectively. Although this sensitized reaction satisfied the requirement (c), much higher yield was expected by the excitation in the range of visible wavelength, i.e., requirements (a) and (b). In the present paper, attention is focused on the achievement of all requirements of (a)—(c) for the sensitized reaction mentioned above.

Experimental

Materials. Fluorescein, Eosine Y, Erythrosine, Proflavine and Acriflavine were recrystallized three times from ethanol. Methylviologen (Nakarai,G.R.) and triethanolamine (Tokyo kasei,G.R.) were used as received. Each sample was degassed by bubbling argon gas (99.9%) for at least 30 min or by repeating freezing and evacuation 5—7 times under vacuum.

Procedures. A degassed sample in a cell (1 cm×1 cm×4 cm) was irradiated at 25 °C in a steady-light illumination apparatus with a 300 W tungsten lamp. The quantum yield of $MV^{\dot{+}}$ formation was determined by the conventional actinometry using Eosine Y or potassium ferrioxalate solution.[2,3] Laser flash photolysis was carried out by using a pulsed dye laser (Phase R, 2100B; dye G4: excitation 500 nm and dye B1: excitation 440 nm; FWHM of pulse: 500 ns) and a usual monitoring system composed of a light source, a monochromator, and a transient recorder.

Results and Discussion

Using AC^- as a sensitizer instead of xanthene dyes, the steady light irradiation to three component system of AC^-/MV^{2+}/TEOA was carried out. The dependence of the quantum yield of $MV^{\dot{+}}$ formation, Φ^A on MV^{2+} concentration is shown in Fig. 1.
The maximum value of 0.9±0.1 was obtained at MV^{2+} concentration of ca. 1 mM (1 M=1 mol dm^{-3}) in aqueous solution (pH=8.3) and there was no decomposition of AC^- during the irradiation. Although the competitive reactions of $^3AC^-$ with MV^{2+} or with TEOA were considered, the decay rate of $^3AC^-$ was not affected by an addition of 3 mM TEOA in a laser-flash experiment. On the other hand, the rate constant of $^3AC^-$ reacting with MV^{2+} was obtained as 3.1×10^9 M^{-1} s^{-1}. Thus, at the concentrations of MV^{2+} in Fig. 1, the initial process occurred by the electron transfer from $^3AC^-$ to MV^{2+}, which leads to formation of $MV^{\dot{+}}$ and AC· followed by the electron transfer from TEOA (the oxidation cycle mechanism). The kinetical treatment for Φ^A could be performed in a similar manner to that reported in the case of Dye/MV^{2+}/TEOA system, since the linear relationships between $1/\Phi^A$ and $1/[MV^{2+}]$, and between $1/\Phi^A$ and 1/[TEOA] were held, respectively.[2] Then, Φ^A can be written in the following equation:

$$\Phi^A = \phi_{st}{}^A \frac{\alpha_2 k^r_{qA}[MV^{2+}]}{k_{dA} + k_{qA}[MV^{2+}]} \frac{k_2'[TEOA]}{k_2 + k_2'[TEOA]} \tag{1}$$

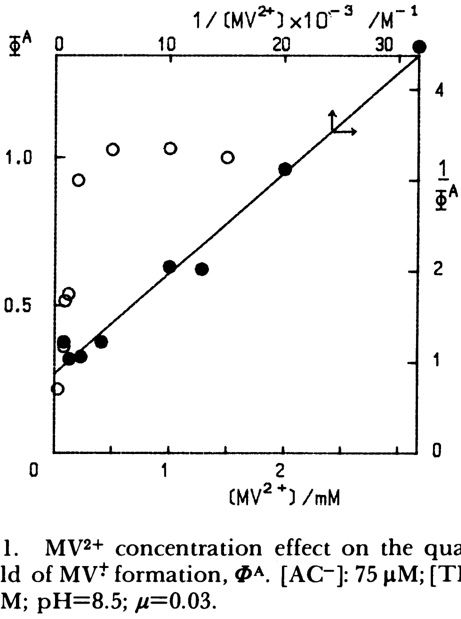

Fig. 1. MV^{2+} concentration effect on the quantum yield of $MV^{\dot{+}}$ formation, Φ^A. [AC^-]: 75 μM; [TEOA]: 3 μM; pH=8.5; μ=0.03.

where α_2 represents the formation efficiency of $MV^{\dagger}$. k_{dA}, k^r_{qA} (k_{qA}), k_2 and k_2' are the rate constants for $^3AC^-$ decay, for the genuine (and total) reaction between $^3AC^-$ and MV^{2+}, for AC· decomposition and for the electron transfer reaction between AC· and TEOA, respectively. Maximum value of Φ^A was close to the values of an intersystem crossing probability to $^3AC^-$, $\phi_{st}{}^A$. From the fact, it seems that the electron transfer from $^3AC^-$ to MV^{2+} occurred without any deactivation i.e., $k^r_{qA}=k_{qA}$ and that the production efficiency of radicals of $MV^{\dagger}$ and AC· separated from its radical pair complex was unity, approximately i.e., $\alpha_2=1$.[4] The reaction system of AC^-/MV^{2+}/TEOA satisfies requirements, (b) and (c).

In order to achieve the requirement, (a), it is very useful to introduce the concept of an energy transfer from organic dyes. Many studies about triplet–triplet energy transfer have been carried out. Concerning the present system, the kinetical investigations on energy transfer from the triplet dyes to several anthracene derivatives have been reported.[5–7] The quantum yield of $MV^{\dagger}$ formation through the energy transfer, Φ^T on four-component system of Dye/AC^-/MV^{2+}/TEOA by steady-light illumination increased both with MV^{2+} concentration and with AC^- concentration. For the AC^- concentration effect, an effective enhancement in about 16-fold on Φ^T was observed by the addition of 0.78 mM AC^- using Erythrosine as a sensitizer. The results on Φ^T are shown in Fig. 2 (Sens: Ery). The essential mechanism in Fig. 3 can be proposed which is applicable to the present system by referring to the results in Figs. 1 and 2. Depending on the concentrations of MV^{2+} and AC^-, the electron transfer from triplet dyes to MV^{2+} competes with the energy transfer.[1,2] Therefore, the quantum yield of free radical formation of $MV^{\dagger}$ is given as follows:

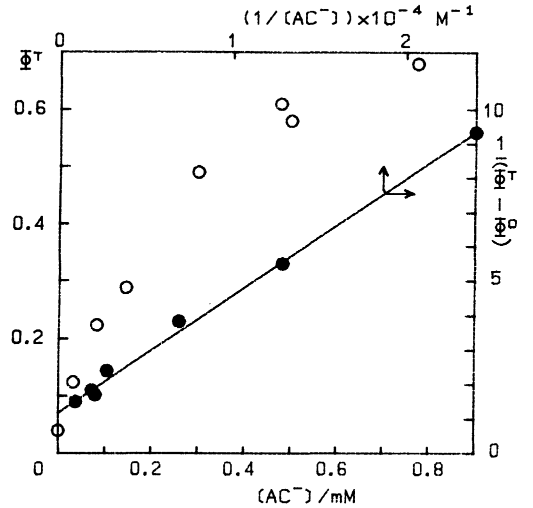

Fig. 2. AC^- concentration effect on the quantum yield of $MV^{\dagger}$ formation through the energy transfer from $^3Ery^{2-}$ to AC^-, Φ^T. [Ery^{2-}]: 5 μM; [MV^{2+}]: 0.1 mM; [TEOA]: 3 mM; pH=8.5; μ=0.1.

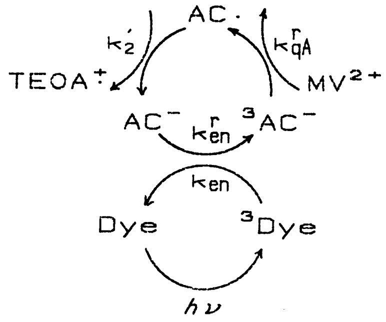

Fig. 3. The proposed reaction scheme for the sensitized reduction of MV^{2+} through the energy transfer from triplet dyes to AC^-.

$$\Phi^T = \phi_{st}{}^D \frac{1}{k_{dd} + k_q[MV^{2+}] + k_{en}[AC^-]} \left(\gamma_1 k^r_q[MV^{2+}] + \gamma_2 \frac{k^r_{qA}[MV^{2+}]}{k_{dA} + k_{qA}[MV^{2+}]} k^r_{en}[AC^-] \right) \tag{2}$$

and

$$\gamma_1 = \alpha_1 k_1'[TEOA]/(k_1 + k_1'[TEOA])$$

$$\gamma_2 = \alpha_2 k_2'[TEOA]/(k_2 + k_2'[TEOA])$$

where γ_1 and γ_2 refer to the reaction efficiency through the processes of dye-sensitized electron transfer and to that through the process of AC^- sensitized one, respectively. $\phi_{st}{}^D$ represents the intersystem crossing probability of dye. k_{dd}, $k^r_q(k_q)$, k^r_{en} (k_{en}), k_1 and k_1' are the rate constants for ^{3}Dye decay, for the genuine (and total) reaction of electron transfer between ^{3}Dye and MV^{2+}, for the genuine (and total) reaction of energy transfer from ^{3}Dye to AC^-, for $Dye^{\dagger}$ decomposition and for the electron transfer reaction between $Dye^{\dagger}$ and TEOA, respectively. Putting Φ^T at $[AC^-]=0$ as Φ^0, the approximate equation, Eq. 3, is obtained under the condition of $k_{dd} \ll k_q[MV^{2+}]$, $k_{en}[AC^-]$ and $k_{dA} \ll k_{qA}[MV^{2+}]$ in Eq. 2:

$$\Phi^T - \Phi^0 = \phi_{st}{}^D \frac{(\gamma_2 k^r_{en} k^r_{qA}/k_{qA} - \gamma_1 k_{en} k^r_q/k_q)[AC^-]}{k_q[MV^{2+}] + k_{en}[AC^-]} \tag{3}$$

The linear relationship between $1/(\Phi^T-\Phi^0)$ and $1/[AC^-]$ is obtained as shown in Fig. 2. The values of interception are 1.7 and 1.1 for Eosine Y ($\phi_{st}{}^D=0.64$) and Erythrosine ($\phi_{st}{}^D \approx 1$) sensitization, respectively. Since the interception equals to the value of $1/\phi_{st}{}^D$, the relation of $k^r_{en}=k_{en}$ is suggested. This means that the

Table 1. Maximum Quantum Yield of $MV^{\dagger}$ Formation (Φ^T_{max}) through the Energy Transfer from Dyes to AC^- and the Rate Constants of the Energy Transfer (k_{en})

Dyes(concentration/μM)	Φ^T_{max}	$k_{en}/M^{-1}\,s^{-1}$
Fluorescein(10)	0.045	4.5×10^9
Eosine Y(10)	0.55	4.7×10^9
Erythrosine(10)	0.77	3.2×10^9
Proflavine(22)	0.23	2.7×10^9
Acriflavine(17)	0.28	7.4×10^9

energy transfer from triplet dye to AC^- occurs without any deactivation as is shown in Fig. 3.

Under the higher concentrations of AC^-, the following approximate equation can be derived from Eq. 2 and the effect of MV^{2+} concentration on Φ^T is analyzed.

$$\Phi^T = \phi_{st}{}^D \frac{k^r_{en}}{k_{en}} \frac{k^r_{qA}[MV^{2+}]}{k_{dA} + k_{qA}[MV^{2+}]} \quad (4)$$

From the interception of linear relationship between $1/\Phi^T$ and $1/[MV^{2+}]$, k^r_{en}/k_{en} values was also estimated to be unity using $\phi_{st}{}^D$ value of sensitizer. This result coincides with the fact ($k^r_{en}=k_{en}$) obtained from AC^- concentration effect on Φ^T.

Using xanthene dyes and acridine dyes as energy donors, the observed values of maximum yield of $\Phi^T{}_{max}$ and the values of the rate constant, k_{en} are summarised in Table 1. These reaction systems of Dye/AC^-/MV^{2+}/TEOA satisfy all requirements of (a), (b), and (c) since a light absorption extends in the range of wavelength from 370 nm to 550 nm.

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