The Mechanism of Electron Transfer Reaction for Xanthene Dye-Sensitized Formation of Methyl Viologen Radical

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Sensitized reduction of methyl viologen, MV^{2+}, occurs efficiently through electron transfer from triplet xanthene dyes to MV^{2+} followed by electron transfer to the resulting semioxidized dyes from a reductant like triethanolamine. Unreactive ion pair complexes between these dyes and MV^{2+} are formed (formation constant: $1.2\times10^3\,M^{-1}$ for Eosine Y and MV^{2+} in 50% aqueous ethanol solution). The quantum yield for the reduced methyl viologen radical depends on the concentrations of MV^{2+} and the amine and on the ionic strength of solution. The efficiency of the electron transfer from triplet dyes to MV^{2+} is increased by addition of alcohol, and solvent effects on the reaction mechanism are discussed.

Active efforts have recently been devoted to the hydrogen liberation from water through visible light irradiation on an appropriate sensitizer in a suitable electron transferring system comprising an electron donor like amine, a mediator like methyl viologen, and a redox catalyst like colloidal platinum or hydrogenase.[1–5)]

Although various sensitizers of ruthenium complexes have been well studied, only a few reports have appeared on utilization of organic dyes, and mechanistic studies on such reaction systems are required to increase the reaction yield.[6–16)]

We reported that a photosensitized reaction of Eosine Y (EY^{2-}) induced hydrogen evolution from water under the irradiation of visible light on a mixed solution of methyl viologen (MV^{2+}), triethanolamine (TEOA), and colloidal platinum. The maximum quantum yield for the formation of semireduced radical ($MV^{+}\cdot$) was measured to be ca. 0.3.[17)] For the three-component system, the yield of $MV^{+}\cdot$ is dependent on such a mechanism as may be switched over from an initial process of electron transfer from $^3EY^{2-}$ to MV^{2+} to that from TEOA to $^3EY^{2-}$. Further it has been observed that an ion pair complex is formed between xanthene dye and MV^{2+}, and that the complex formation is sensitive to the composition of solution.

In the present paper, attention is focused on determination of the efficiency of electron transfer processes from triplet dye to MV^{2+} and on the solvent effect in aqueous alcohol solution, in order to increase the yield of $MV^{+}\cdot$. To elucidate the reaction mechanism, we have mainly investigated effects of the concentrations of TEOA and MV^{2+} and the ionic strength and solvent composition of alcohol–water mixtures on the yield of $MV^{+}\cdot$ by kinetic analysis.

Experimental

Materials. Fluorescein, Eosine Y (2′,4′,5′,7′-tetrabromofluorescein), and Erythrosine (2′,4′,5′,7′-tetraiodofluorescein) were recrystallized three times from ethanol. Methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dichloride, Nakarai, G. R.) and triethanolamine (Tokyo Kasei, G. R.) were used as received. Methanol, ethanol, and 2-propanol (Kanto, G. R.) were used without further purification. Phosphate and borate buffer solutions were prepared by dissolving the respective salts (Kanto, G. R.) in redistilled water. Sodium perchlorate (Kanto, G. R.) was used to control the ionic strength of sample solutions. Each sample was deaerated by bublling argon gas (99.9%) for at least 30 min or by repeating freezing and evacuation 5—7 times under vacuum before irradiation.

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 experimental procedure used to determine the quantum yield of $MV^{+}\cdot$ formation was similar to that previously described.[18,19)] Laser flash photolysis was carried out by using a pulsed dye laser (Phase R, 2100B; dye, G4; excitation, 500 nm; FWHM of pulse, 500 ns) and a usual monitoring system composed of a light source, a monochromator, and a transient recorder. For the ns-laser excitation, pulsed nitrogen laser was used (excitation; 337 nm FWHM of pulse, 7 ns). The yield of $MV^{+}\cdot$ for the dye-laser flash excitation was determined by the conventional actinometry using Reinecke's salt.

Results and Discussion

Formation of Ionic Complex between EY^{2-} and MV^{2+} in the Ground State. It was observed that the absorption spectrum of EY^{2-} changed with an isosbestic point at 537 nm by addition of MV^{2+} in 50 v/v% aqueous ethanol solution, in such a manner that the maximum wavelength (λ_{max}) of EY^{2-} was shifted from 526 to 528 nm with the maximum extinction coefficient at λ_{max} decreased to 7.6×10^4 from 9.4×10^4 $M^{-1}\,cm^{-1}$ (1 M=1 mol dm^{-3}).[17)] Also, the fluorescence of EY^{2-} was remarkably quenched by addition of 1.0×10^{-3} M MV^{2+}, but the fluorescence lifetime in solution was not affected at all. Increasing the alcohol content (95%) in the mixture made the fluorescence from EY^{2-} hardly observable. The degree of the change in absorption spectra and fluorescence intensities depended on the ionic strength, (μ) of solution and the solvent composition of alcohol–

Table 1. Formation Constants of the Ion-Pair Complex, $EY^{2-}\cdots MV^{2+}$ in 50 v/v% Ethanol

μ	K/M^{-1}
0.005	1.5×10^{3}
0.020	1.0×10^{3}
0.050	6.0×10^{2}
0.090	2.1×10^{2}

water mixture. In a mixed solvent with a molar fraction of ethanol (χ_{EtOH}) of 0.80, the maximum absorption and fluorescence intensities of EY^{2-} with 0.05 mM MV^{2+} were increased by the factors of 1.5 and 50, respectively, with increase in μ from 0 to 0.05. These phenomena mean that EY^{2-} forms a non fluorescent ionic complex with MV^{2+} and that the equilibrium, Eq. 1 is shifted to the right by increase in the molar fraction of ethanol or decrease in the ionic strength:

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

From an analysis of the results of absorption and fluorescence spectra, values of the formation constant (K) for the complex were estimated at several values of ionic strength, as shown in Table 1.

Effects of MV^{2+} Concentration and Ionic Strength on the Quantum Yield of $MV^{+}\cdot$ Formation. For the three-component system of EY^{2-}/MV^{2+}/TEOA, either the initial electron transfer from triplet eosine Y ($^{3}EY^{2-}$) to MV^{2+} or that from TEOA to $^{3}EY^{2-}$ needs to be considered. The competitive reactions can be switched over between each other depending on the rate constants and the concentrations of TEOA and MV^{2+}.[20] The rate constant of the $^{3}EY^{2-}$ quenching with MV^{2+} or with TEOA was obtained as 3.2×10^{9} (k_Q) or $3.0\times10^{6}\ M^{-1}\,s^{-1}$ in a laser-flash experiment, respectively ($[EY^{2-}]=10\ \mu M$, $\mu=0.05$, 50 v/v% ethanol-water mixture). The rate constant of the $MV^{+}\cdot$ formation was also obtained as $3\times10^{9}\ M^{-1}\,s^{-1}$ (k'_Q) in the $^{3}EY^{2-}$ reaction with MV^{2+} and was approximately the same as the quenching rate constant. Thus, at an MV^{2+} concentration of about 1 mM and a TEOA concentration of 10 mM, the photosensitized reduction of MV^{2+} is to be initiated by the efficient electron transfer from $^{3}EY^{2-}$ to MV^{2+}, which leads to formation of $EY^{-}\cdot$ followed by the electron transfer from TEOA.

In the laser flash experiment with an aerated solution of EY^{2-} and MV^{2+} where $MV^{+}\cdot$ was scavenged by oxygen, only transient absorption of $EY^{-}\cdot$ was observed after about 30 μs. The decay rate of free radical $EY^{-}\cdot$ ($\lambda_{max}=462$ nm) was increased by the addition of TEOA, and the rate constant (k) of the electron transfer from TEOA to $EY^{-}\cdot$ was obtained as $k=1.5\times10^{7}\ M^{-1}\,s^{-1}$.

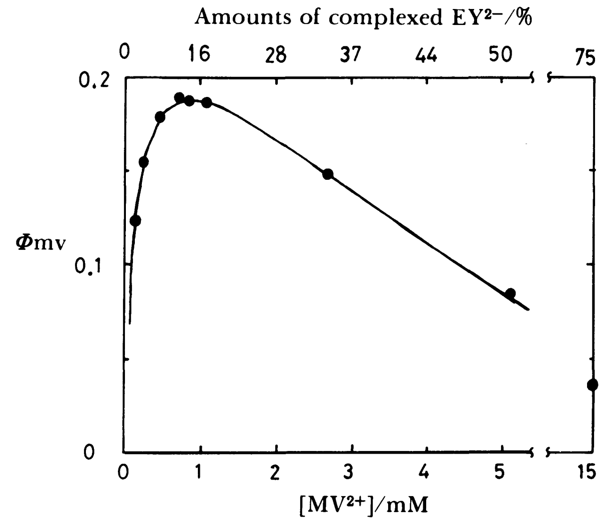


Fig. 1. Effect of MV^{2+} concentration on the quantum yield of $MV^{+}\cdot$ formation. $[EY^{2-}]=17\ \mu M$, $[TEOA]=10$ mM, $\mu=0.08$, pH=11.7, in 40% Ethanol-water mixture.

For a steady light irradiation, the dependence of the quantum yield for $MV^{+}\cdot$ radical formation (Φ_{mv}) on the MV^{2+} concentration showed a maximum of 0.2 at an MV^{2+} concentration of ca. 1 mM in aqueous ethanol with a constant ionic strength and a fixed concentration of TEOA (Fig. 1). The concentration of the EY^{2-} complexed with MV^{2+} noted on the upper abscissa in Fig. 1 was calculated from the K values in Table 1. It can be considered that the decreasing tendency of Φ_{mv} values at higher concentrations of MV^{2+} (> ca. 3 mM) is due to the fact that EY^{2-} forms an ion-pair complex with MV^{2+} and that this complex is unreactive. Actually, the transient absorption of $MV^{+}\cdot$ was scarcely observed by the μs-laser flash excitation of the complex.

In an air saturated solution of EY^{2-} and MV^{2+} ($[EY^{2-}]=4.85\ \mu M$, $[MV^{2+}]=0$—5 mM, $[O_2]=220\ \mu M$, pH=5, $\mu=0.004$, 50 v/v% ethanol-water mixture), the photobleaching of EY^{2-} was accelerated by the addition of MV^{2+}. Considering that the $MV^{+}\cdot$ radical produced by the electron transfer from $^{3}EY^{2-}$ is fairly reactive to the dissolved oxygen ($MV^{+}\cdot + O_2 \rightarrow MV^{2+} + O_2^{-}\cdot$; $k'=6\times10^{8}\ M^{-1}\,s^{-1}$),[21] the reverse electron transfer to the resulting $EY^{-}\cdot$ from $MV^{+}\cdot$ can be taken to be prohibited. Thus, it is supposed that the acceleration of EY^{2-} bleaching is attributed to the irreversible decomposition of semioxidized radical, $EY^{-}\cdot$.[20] The dependence of the bleaching yield on the MV^{2+} concentration was the same as that shown in Fig. 1, and the contribution of the unreactive ionic pair complex is supposed similar. Figure 2 shows the pH effect on Φ_{mv} which is enhanced in alkaline solution. The production yield of $^{3}EY^{2-}$ does not seem to undergo a significant change in the pH region.[20] We also confirmed that the equilibrium of the ionic complex of Eq. 1 was not affected by the change in pH because similar K values were obtained in the pH region from 5.4 to 11.4 (μ=0.05, 50 v/v% ethanol-water mixture). Judging from the property of TEOA that electron donation is effective in its basic form (pK_a (protonated TEOA)=7.76), the curve in Fig. 2 seems to match the result on the dissociation of protonated TEOA.

Figure 3 shows the effect of ionic strength, μ, on Φ_{mv} at two MV^{2+} concentrations. In the case where EY^{2-} and MV^{2+} exist free at the lower concentration of MV^{2+} (0.2 mM), the decrease in Φ_{mv} in Fig. 3 is due to a neutral salt effect on the competetive reactions between $^3EY^{2-}$ and MV^{2+} since the rate constant decreases with increasing μ.[22] At the higher concentration of $MV_2{}^+$ (5.7 mM) where 50% of EY^{2-} forms the ion-pair complex, it was suspected that the Φ_{mv} value increased as a result of the dissociation of the unreactive complex to the free EY^{2-} and MV^{2+} caused by increase in μ as shown in Table 1. Considering both of the opposite effects, i.e., the neutral salt effect and the dissociation of the ion-pair complex, the small effect observed at the MV^{2+} concentration of 5.7 mM can be interpreted in terms of the mutual compensation of these effects.

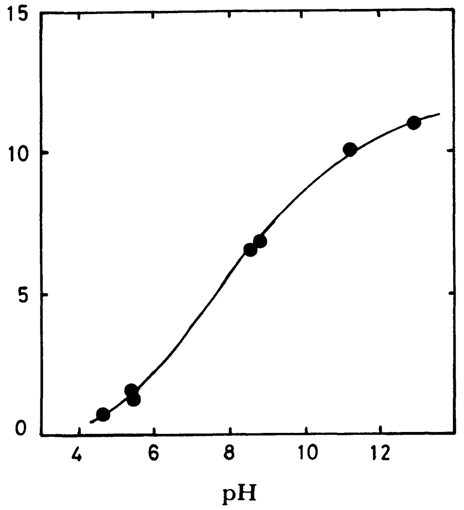


Fig. 2. Effect of pH on the quantum yield of $MV^{+\cdot}$ formation. $[EY^{2-}]$=17 μM, $[MV^{2+}]$=5.7 mM, [TEOA]= 10 mM, in 40% Ethanol-water mixture.

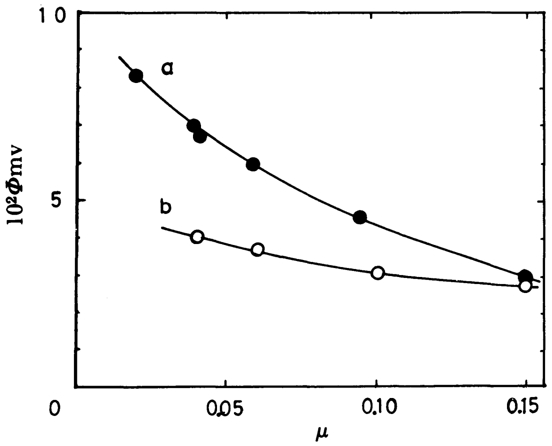
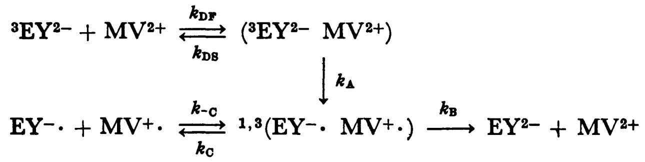


Fig. 3. Effect of ionic strength on the quantum yield of $MV^{+\cdot}$ formation. (a) $[MV^{2+}]$=0.2 mM, (b) $[MV^{2+}]$=5.7 mM. $[EY^{2-}]$=17 μM, [TEOA]=10 mM, in 40% Ethanol-water mixture.

Efficiency of Electron Transfer from Triplet Eosine Y to Methyl Viologen. Kinetic investigations for the efficiency of the initial electron transfer from $^3EY^{2-}$ to MV^{2+} existing in the free form were carried out to increase the sensitization yield. Scheme 1 shows the electron-transfer mechanism proposed as applicable to the present system by reference to the investigations reported by Harriman et al.[12,22–25]



$$ {}^3EY^{2-} + MV^{2+} \underset{k_{DS}}{\overset{k_{DF}}{\rightleftarrows}} ({}^3EY^{2-}\ MV^{2+}) $$

$$ \downarrow k_A $$

$$ EY^{-\cdot} + MV^{+\cdot} \underset{k_{C}}{\overset{k_{-C}}{\rightleftarrows}} {}^{1,3}(EY^{-\cdot}\ MV^{+\cdot}) \xrightarrow{k_B} EY^{2-} + MV^{2+} $$

$$ k_Q{}^r = \frac{k_{DF}k_A}{k_A + k_{DS}} \qquad (2) $$

$$ k_b = \frac{k_{-C}k_B}{k_B + k_C} \qquad (3) $$

Scheme 1.

The formation of an encounter complex ($^3EY^{2-}$ MV^{2+}) is to be a diffusion controlled process (k_{DF}), which is reversible (k_{DS}). The complex undergoes an electron transfer to form a geminate radical pair of $^{1,3}(EY^{-\cdot}\ MV^{+\cdot})$, which can be regarded as an exciplex with a radical-pair-like electronic structure.[24,25] This complex may collapse either to give the radical ions through a separation (k_C) followed by a recombination (k_{-C}), or to reform the ground states of EY^{2-} and MV^{2+} (k_B). The yield of free radical $MV^{+\cdot}$ or $EY^{-\cdot}$ (ϕ_{mv}) is given by[23,24]

$$ \phi_{mv} = \phi_{st}\phi_Q\phi_S \qquad (4) $$

where ϕ_{st}, ϕ_Q, and ϕ_s refer to the probabilities of the intersystem crossing to $^3EY^{2-}$ (0.64),[26,27] the quenching of $^3EY^{2-}$ by MV^{2+} to give the geminate radical pair with $\phi_Q = k_Q^r[MV^{2+}]/(k_Q[MV^{2+}]+\tau_T^{-1})$, and the formation of the free radicals from $^{1,3}(EY^{-}\cdot MV^{+}\cdot)$ with $\phi_s = k_C/(k_C + k_B)$, respectively. The lifetime of $^3EY^{2-}(\tau_T)$ is equal to 220 μs at $[EY^{2-}]$=10 μM. On the assumption that the rate constant $k_Q{}^r$ ($=k_{DF}k_A/(k_A+k_{DS})=3.0\times10^9\ M^{-1}\ s^{-1}$) as obtained from the ns laser experiment corresponds to the process of $^{1,3}(EY^{-}\cdot MV^{+}\cdot)$ formation, ϕ_Q can be estimated to be 0.94 for the present condition ($[MV^{2+}]$=0.05 mM) from the observed values of k_Q^r, k_Q, and τ_T, where k_Q^r and k_Q

are the rate constants for the genuine and total reactions between $^3EY^{2-}$ and MV^{2+}, respectively. These rate constants are numerically almost equal to each other as described in a previous section (i.e., $k_Q{}^r \approx k_Q$). The absorption by $MV^{+}\cdot$ observed in the μs and ms time regions will arise from the free species of $MV^{+}\cdot$ dissociated from $^{1,3}(EY^{-}\cdot\ MV^{+}\cdot)$. Since $EY^{-}\cdot$ is completely reduced by the addition of 10 mM TEOA and $MV^{+}\cdot$ does not decrease, ϕ_{mv} can be obtained from the concentration of $MV^{+}\cdot$ produced per laser pulse. Thus, we can estimate the value of ϕ_s (=0.53) from Eq. 4 and the ratio of k_C/k_B(=1.1) by using the value of the maximum yield of the sensitized $MV^{+}\cdot$ formation (0.32) in 50 v/v% ethanol and water mixture. On the other hand, assuming the diffusion controlled process with k_{-C}(=1.2×10^{10} $M^{-1}\,s^{-1}$) and substituting the rate constant k_b (=2.9×10^{9} $M^{-1}\,s^{-1}$) from the recombination kinetics of the free $EY^{-}\cdot$ and $MV^{+}\cdot$ radicals into the equation of $k_b = k_{-C}/(1+(k_C/k_B))$ we obtain a similar value for the ratio of k_C/k_B(=1—3). These results mean that $^{1,3}(EY^{-}\cdot\ MV^{+}\cdot)$ complex dissociates to the free radicals or to the molecules of ground state to a comparable extent.

The decay processes through the recombination of the free radical ions $EY^{-}\cdot$ (λ_{max}=462 nm, ε_{max}=5.5×10^4 $M^{-1}\,cm^{-1}$)[28] and $MV^{+}\cdot$ (λ_{max}=395 nm, ε_{max}=4.2×10^4 $M^{-1}\,cm^{-1}$)[29] followed by the dissociation of $^{1,3}(EY^{-}\cdot\ MV^{+}\cdot)$ complex, were monitored under various reaction conditions in a laser flash experiment in the μs region and analyzed in terms of the second-order reaction kinetics to evaluate k_b for the $EY^{-}\cdot$ decay as 4.7×10^9 $M^{-1}\,s^{-1}$ and that for the $MV^{+}\cdot$ decay as 5.1×10^9 $M^{-1}\,s^{-1}$ (in 60 v/v% CH_3OH-H_2O, μ=0.02). There was no permanent production of $MV^{+}\cdot$ or $EY^{-}\cdot$ radical in the EY^{2-}/MV^{2+} system by irradiation. Incidentally, it was ascertained that the observed decay process did not correspond to the recombination to the geminate radical pair $^3(EY^{-}\cdot\ MV^{+}\cdot)$, because the decay data hardly satisfy the root equation for the kinetical treatment on the geminate pair in the μs-region.[30]

Values of k_b depend on the solvent composition of binary mixtures of methanol-water, ethanol-water, 2-propanol-water, and ethylene glycol-water, in such a manner that the k_b values decrease initially in regard to the molar fraction of alcohol and then increase gradually. As shown in Fig. 4, the plot of k_b against the reciprocal of solvent viscosity (η) satisfies a linear relationship. Even if the processes designated the rate constants of k_B and k_C result from the local diffusion of each paired radical in a cage to the bulky phase, this viscosity effect will be cancelled out in the expression of Eq. 3 so as to be negligible for the k_b value itself. On the other hand, the polarity effect of solvent is supposed to be in corporated in the k_B value, which will be discussed in a later section. It is known that there is no considerable change in the solvent polarity of dielectric constant or in the empirical solvent parameters such as Kosowar's Z-value for such a mixture of methanol and ethylene glycol. However, since the linear relationship between k_b and η^{-1} in the methanol and ethylene glycol mixture is the same as that for the alcohol and water mixture, and since the polarity change in the latter mixture is not so large in the region $\chi_{alc} < 0.7$, it is considered that the diffusional recombination process between $EY^{-}\cdot$ and $MV^{+}\cdot$ with k_{-C} (=$8RT/3000\eta$) will reflect the viscosity effect on k_b values in the expression of $k_b = k_{-C}/(1+(k_C/k_B))$. Such linear relationships were observed with the Eosine Y-MV^{2+}, Erythrosine-MV^{2+}, and fluorescein-MV^{2+} systems. This result seems to confirm that the observed decay processes correspond to the diffusional recombinations between the free radical ions.

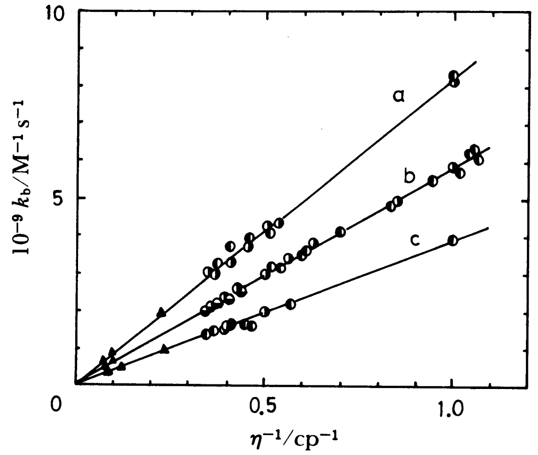


Fig. 4. Solvent viscosity effect on k_b values. (a): Erythrosine/MV^{2+} system, (b): Eosine Y/MV^{2+} system, (c): Fluorescein/MV^{2+} system([NaOH]=0.5 mM). [Dye]=10 μM, [MV^{2+}]=0.05 mM, μ=0.02; Methanol-water mixture(◑), Ethanol-water mixture(◐), 2-Propanol-water mixture(◒), Ethylene glycol-methanol mixture(▲).

Solvent Effect on ϕ_{mv} Values. Since the quantum yield of hydrogen evolution for the three-component system with a catalyst was increased by the addition of methanol or ethanol, the dependence of ϕ_{mv} after the laser excitation (about 30 μs) on the concentration of methanol, ethanol, or 2-propanol was investigated. ϕ_{mv} values are increased by the addition of each alcohol as shown in Figs. 5a and 5b. The yield for $EY^{-}\cdot$ increased in a similar manner.

The results shown in Figs. 5a—c refer to the solvent effect on ϕ_{mv} and the second shows the difference in ϕ_{mv} among the dye sensitizers. On the basis of the fact that the effect of alcohol addition on ϕ_{st} is negligible[20,26,27] and on the assumption that the effect on ϕ_Q is negligible, the first effect could result from the ϕ_s in Eq. 4. From the view point that the free radicals are produced by the separation of the

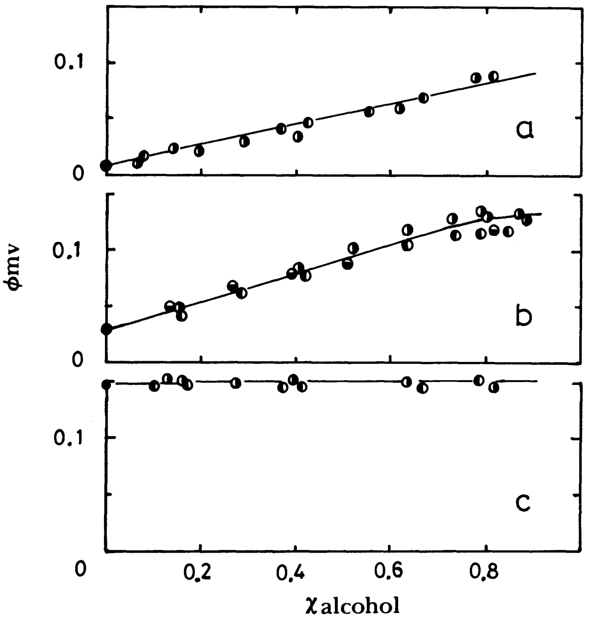


Fig. 5. Effect of molar fraction (χ) of alcohol on the yield of $MV^{+\cdot}$, ϕ_{mv}. (a) Erythrosine/MV^{2+} system, (b) Eosine Y/MV^{2+} system, (c) Fluorescein/MV^{2+} system([NaOH]=0.5 mM). [Dye]=10 μM, [MV^{2+}]= 0.05 mM, μ=0.02; Methanol-water mixture (◑), Ethanol-water mixture(◐), 2-Propanol-water mixture(◒).

geminate radical pair in competition with the decay process as discussed in respect of Scheme 1, a similar explanation as reported by Winter and Steiner can be applied in terms of the solvent polarity dependence of the energy gap between the exciplex and the corresponding Franck-Condon ground state.[32] Thus, the observed effect on ϕ_{mv} is determined by two decay constants for the exciplex as

$$\phi_{mv} = \phi_{st}\phi_{Q}\frac{k_C}{k_B+k_C} \tag{5}$$

$$= \phi_{st}\phi_{Q}\left(1+\frac{F_{el}F_{FC}}{k_C}\right)^{-1} \tag{6}$$

where k_b is a product of a factor F_{el} (the electronic coupling strength) and a factor F_{FC} which is determined mainly by the Franck-Condon weighted density of vibrationally excited ground state levels isoenergitic with the exciplex; $k_B=F_{el}F_{FC}$. If the analysis for ϕ_{mv} discloses no significant influence of solvent on k_C, the radical yield ϕ_{mv} may be concluded to be determined mostly by the factor F_{FC}.

Since the explanation for the polarity dependence in the presence of alcohol added calls for F_{FC} or k_B to be small, it may be expected that ϕ_{mv} becomes large because of the lesser polarity of alcohol. As shown in Fig. 5, such solvent effects are found in the systems of EY^{2-} and MV^{2+} and of Erythrosine and MV^{2+}. In the system of fluoresceine and MV^{2+} shown in Fig. 5c, the solvent effect is little observed and ϕ_{mv} value are larger than those in the other systems.

In the systems of EY^{2-}/MV^{2+} and Ery^{2-}/MV^{2+}, the correlations of ϕ_{mv} with the solvent parameter of Kosowar's Z are similar to each other in both the methanol-water and ethanol-water mixtures. In relation to the solvent dependence on the ionic photodissociation yield in the singlet exciplex state (for example, pyrene and *N,N*-dimethylaniline), the radical yield increased with the solvent dielectric constant (ε) and a quantitative analysis for the mechanism was carried out.[33] In the present case, ϕ_{mv} decreases with ε values of alcohol-water mixtures and the mechanism differs from the case involving the singlet excited state. From a variation of solvent viscosity in the range 1—3 cp effected by mixing methanol, ethanol, or 2-propanol with water, the viscosity dependence may be expected to appear on k_C and accordingly on ϕ_{mv}. However, the effect of viscosity was observed as a decrease in ϕ_{mv} beyond ca. 4 cp.

A second effect on ϕ_{mv} values in Fig. 5 may be derived by making a comparison between the heavy-atom-substituted sensitizers (Br, I). A similar heavy atom effect was reported with thiopyronine reduction by substituted electron donors (Br, I).[32] In the present case, ϕ_{mv} values are 0.12 for fluorescein, 0.090 for Eosine Y, and 0.055 for Erythrosine ([MV^{2+}]=0.05 mM, μ=0.02, χ_{MeOH}=0.5). It is known that ϕ_{st} values of dyes increase in the order: $\phi_{st}(Ery^{2-})>\phi_{st}(EY^{2-})>\phi_{st}(Fl^{2-})$.[20] To interpret the order: $\phi_{mv}(Ery^{2-})<\phi_{mv}(EY^{2-})<\phi_{mv}(Fl^{2-})$ as obtained from Figs.5a—c at a given molar fraction of alcohol on the basis of Eq. 2, ϕ_s values of dyes must taken to be in the same order with more decrease than the change in the respective ϕ_{st} values: $\phi_s(Ery^{2-})<\phi_s(EY^{2-})<\phi_s(Fl^{2-})$. Since the k_b values for the Ery^{2-}/MV^{2+}, EY^{2-}/MV^{2+}, and Fl^{2-}/MV^{2+} systems decrease in the order listed, k_C/k_B and then ϕ_{mv} values should increase in the same order, in conformity with the above results on ϕ_{mv} values. However, further investigations for the effects of solvent viscosity and polarity and the heavy atom associated with spin conversion on the dissociation of $^{1,3}(Dye^{-\cdot}\ MV^{+\cdot})$ are required for quantitative interpretation.

Electron Donation to Semioxidized Eosine. In an alkaline deaerated aqueous solution of EY^{2-} and MV^{2+} without TEOA, sensitized production of $MV^{+\cdot}$ was observed by means of stationary illumination, although the yield was very low as shown in Table 2. The electron donative reaction from OH^- ion to $EY^{-\cdot}$ may be possible to produce an adduct $EYOH^{2-\cdot}$ from $OH\cdot$ and EY^{2-}, since $EY^{-\cdot}$ is a strong oxidant ($E^0(EY^{-\cdot}/EY^{2-})$=1.1 V NHE).[34-37] The possibility of the above process is experimentally suggested from: (i) the decay rate of $EY^{-\cdot}$ is enhanced by the addition of OH^- ion and the rate constant is about $10^5\ M^{-1}\ s^{-1}$; (ii)

Table 2. Quantum Yield of $MV^{+}\cdot$ Formation in Alkaline Solution[a)]

[NaOH]/mM	χ_{CH_3OH}	Φ_{mv}
10	0	0.0021
10	0.23	0.0058
50	0.40	0.042
100	0.51	0.067

a) $[EY^{2-}]=10\,\mu M$ and $[MV^{2+}]=0.05\,mM$. χ_{CH_3OH}: mole fraction of methanol.

a transient spectrum (λ_{max}=600 nm, $\tau_{1/2}$=4.4 ms) is observed which is similar to that of $EYOH^{2-}\cdot$ reported by Grossweiner et al. as a result of pulse radiolysis experiment;[38)] (iii) the spectrum of $EYOH^{2-}\cdot$disappeared after reaction with methanol, with simultaneous increase in the permanent yield of $MV^{+}\cdot$, Φ_{mv}. The above phenomenon (iii) suggests that the competetive recombination between $EYOH^{2-}\cdot$ and $MV^{+}\cdot$ is prohibited by the addition of methanol, and thus that the reaction process of $EYOH^{2-}\cdot$ with methanol causes the yield to increase as shown in Table 2.

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