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Effects of Organic Solvents on Charge Separation in Photo-induced Electron Transfer from Xanthene Dyes to Methyl Viologen

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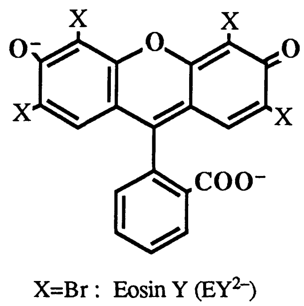
Efficiencies of charge separation in eosin Y- and erythrosine-sensitized reduction of methyl viologen (MV^{2+}) were determined in water-organic solvent mixtures by laser flash photolysis. The $MV^{+\cdot}$ yield increased with increasing fraction of organic solvents, and depended on the type of solvent, increasing in the order of acetonitrile > acetone > dioxane > ethanol > DMSO. The hydrophobic nature of solvents plays an important role in the charge separation.

Recently, very extensive works have been carried out in photo-induced electron transfer to methyl viologen (MV^{2+}),[1] and surfactants are often used to enhance the production of $MV^{+\cdot}$ in aqueous solutions.[2] Previously, we reported that, in eosin Y(EY^{2-})- and erythrosine(ER^{2-})-sensitized reduction of MV^{2+} in aqueous solution, addition of alcohols like methanol, ethanol, and 2-propanol increased the yield of $MV^{+\cdot}$.[3] We now wish to report that the addition of various organic solvents miscible with water generally enhances the production of $MV^{+\cdot}$ and that the extent of enhancement is not directly related to viscosity of the mixed solvents but mostly correlated with a hydrogen-accepting property of the added organic solvents.

EY^{2-} (1.25×10^{-5} mol dm^{-3}) and MV^{2+} ($0-7.0\times10^{-5}$ mol dm^{-3}) were dissolved in mixed solvents containing 0.02 mol dm^{-3} $LiClO_4$[4] of varying ratios of water and organic solvents such as methanol, ethanol, acetonitrile, acetone, dioxane, and dimethylsulfoxide (DMSO). The solutions were deaerated by bubbling with argon, and irradiated at ambient temperature with 520-nm laser pulses (excimer laser-pumped dye laser, coumarin 307)[5] to follow the transient absorption of the resulting species. The initially produced EY^{2-} triplets observed at wavelengths longer than 580 nm was efficiently quenched by MV^{2+} with a diffusion controlled rate constant (k_q, $3-9\times10^9$ mol^{-1} dm^3 s^{-1}), concurrently giving rise to $MV^{+\cdot}$ and the one-electron oxidized dye ($EY^{-\cdot}$) as observed at 395[6] and 405 nm,[7] respectively. These species grew up to afford the stationary concentrations before they finally disappeared.

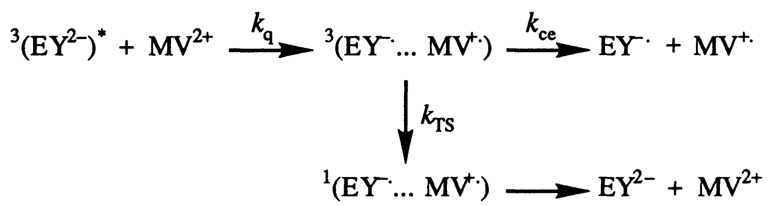


X=Br : Eosin Y (EY^{2-})
X=I : Erythrosine (ER^{2-})

The reaction is reasonably considered to proceed according to Scheme 1. Quenching of EY^{2-} triplets by MV^{2+} gives triplet radical ion pairs of $EY^{-\cdot}$ and $MV^{+\cdot}$ in a solvent cage, which subsequently undergoes either diffusion escaping from the solvent cage to give free $MV^{+\cdot}$ ions or intersystem crossing to singlet radical ion pairs followed by rapid back electron transfer reproducing the ground-state EY^{2-} and MV^{2+}. According to this scheme, the quantum yield for free $MV^{+\cdot}$ production, $\phi_{MV^{+\cdot}}$, is given by Eq. 1.

$$\phi_{MV^{+\cdot}} = \phi_{isc} \times \phi_{q} \times \phi_{ce}, \qquad (1)$$

where ϕ_{isc} is the quantum yield for intersystem crossing of EY^{2-}, $\phi_q = k_q[MV^{2+}]/(k_q[MV^{2+}]+\tau^{-1})$ the quenching efficiency of EY^{2-} triplets (lifetime τ) by MV^{2+}, and $\phi_{ce} = k_{ce}/(k_{ce}+k_{TS})$ the cage escape efficiency of the triplet radical ion pairs.



Scheme 1.

In the presence of a sufficient concentration of MV^{2+}, the EY^{2-} triplets are almost completely quenched by MV^{2+} ($\phi_q \approx 1$), and thus $\phi_{MV^{+\cdot}}$ is mostly governed by ϕ_{isc}, which is slightly dependent on the solvent composition[8] and by ϕ_{ce}. Under these conditions ϕ_{ce} is given by dividing the concentration of produced $MV^{+\cdot}$ by the initial concentration of EY^{2-} triplets. We determined the concentration of the EY^{2-} triplet from depletion of the ground-state absorption (515-530 nm) on laser excitation and that of $MV^{+\cdot}$ from the absorbances at the absorption peak (395-396 nm) by using the reported molar extinction coefficient (ε 42000)[6] (*cf.* Fig. 1).

The ϕ_{ce} values were determined in EY^{2-} and MV^{2+} concentrations of 1.25×10^{-5} and $5\text{-}7\times10^{-5}$ mol dm^{-3}, respectively, in the mixtures of varying ratios of water and organic solvents, 100/0, 70/30, 50/50, and 25/75 v/v%. Figure 2 plots ϕ_{ce}'s as a function of mole fraction (x) of organic solvents. In Fig. 2 ϕ_{ce} increases almost

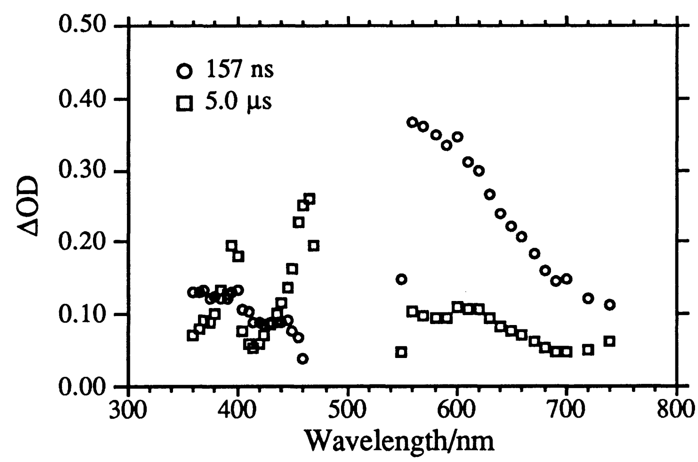


Fig. 1. Transient absorption spectrum on 520-nm laser excitation of EY^{2-} in a mixture of water and acetonitrile (x 0.24).

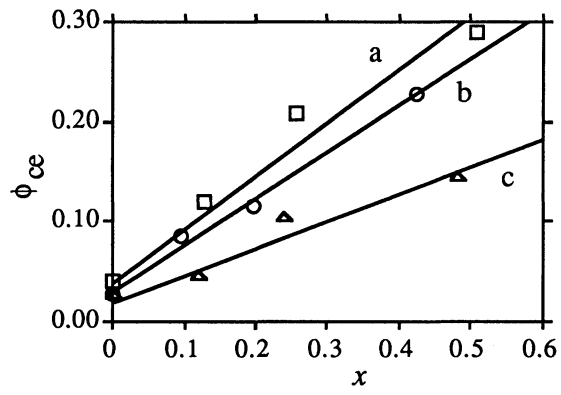


Fig. 2. Plots of cage escape yields (ϕ_{ce}) of $MV^{+\cdot}$ in EY^{2-}-sensitized reduction of MV^{2+} as a function of mole fraction of organic solvents in mixed aqueous solvents; a) acetonitrile, b) acetone, and c) ethanol.

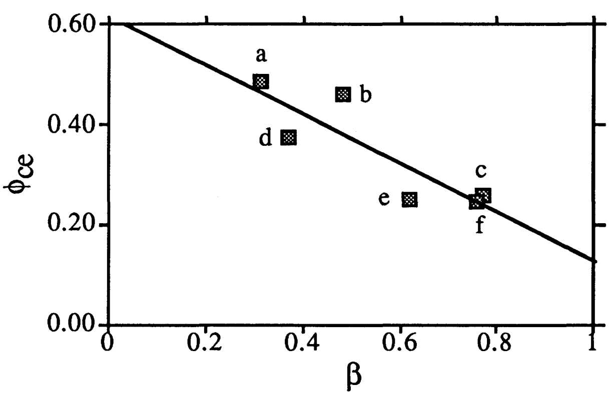


Fig. 3. Correlation of enhancing efficiencies of organic solvents (ϕ_{ce}/x) in $MV^{+\cdot}$ production with hydrogen-accepting property of the solvents, Taft's β; a) acetonitrile, b) acetone, c) ethanol, d) dioxane, e) methanol, and f) DMSO.

linearly with increasing x, and the slope (ϕ_{ce}/x) can be interpreted as an enhancing efficiency of the organic solvent. The slopes decrease in the order of acetonitrile, acetone, dioxane, ethanol, methanol, and DMSO. Similar enhancing effects of these organic solvents were observed in erythrosine (ER^{2-})-sensitized reduction of MV^{2+};[9] however, the efficiencies were lower than in EY^{2-} sensitization.[10] In Fig. 2 it is remarkable that the addition of acetonitrile in a 0.5 mole fraction to water, as an example, increased ϕ_{ce} nearly ten times; this effect may be somehow comparable to that caused by the addition of surfactants.[2] Moreover, it is noticeable that the above observations are in contrast with the well-accepted concept that the increase in polarity and decrease in viscosity of the solution accelerate the charge separation.[11] In the present reaction, however, ϕ_{ce} tends to increase with decreasing dielectric constant and with increasing viscosity on addition of organic solvents.

In a solution of a high mole fraction of acetonitrile (ϕ_{ce}=0.3), if k_{ce} can be assumed to be 5×10^{8} s^{-1},[12] k_{TS} is estimated as nearly 10^{9} s^{-1} for the triplet pair of $EY^{-\cdot}$ and $MV^{+\cdot}$. The subsequent back electron transfer in the singlet radical ion pair might proceed with a rate constant of nearly 10^{9} s^{-1} [13] since it is accompanied by the free energy change estimated as −1.55 eV.[14]

Inspection of the results enables us to correlate the effect of various organic solvents with their hydrogen-accepting property. Figure 3 plots the slopes for solvents in Fig. 2 as a function of Taft's parameter β,[17] a parameter for hydrogen-accepting property (hydrophilicity) of solvents. Figure 3 indicates that the enhancing effect tends to decrease with increasing β. The stabilization of organic solvent molecules by hydration decreases in the order of alcohols > acetone >> acetonitrile, as recently determined by adiabatic expansion of liquid jets.[18]

The less hydrogen-accepting, *i.e.*, more hydrophobic solvent molecules interact with water molecules to lower extent than the more hydrogen-accepting molecules, and, therefore, might be easily aggregated to surround the hydrophobic moieties of the less charged radical pairs and ions, $EY^{-\cdot}$ and $MV^{+\cdot}$, to stabilize these species. In $EY^{-\cdot}$ the tricyclic moiety undergoing redox reactions is uncharged, and in $MV^{+\cdot}$ the positive charge is reduced to half compared with MV^{2+} and widely spread over the whole molecule. Accordingly, both $EY^{-}\cdot$ and $MV^{+}\cdot$ molecules will be more effectively solvated by more hydrophobic solvents. The stabilizing effect by the hydrophobic solvents increase the escape of the radical ion pairs from the solvent cage to enhance the yield of $MV^{+}\cdot$.

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