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Xanthene Dye-Sensitized Electron Transfer to Methylviologen in Aqueous Organic Solution. Effects of Organic Solvents and Heavy Atoms in the Dyes

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Electron transfer from the triplet state of xanthene dyes (FlI_n^{2-} and FlBr_n^{2-}, n=2, 3, and 4) to methylviologen (MV^{2+}) was investigated with a laser flash photolysis technique. Efficiency for the charge separation in aqueous organic solution to give free radical ions, $\mathrm{FlI}_n^{-\cdot}$ or $\mathrm{FlBr}_n^{-\cdot}$ and $\mathrm{MV}^{+\cdot}$, increased almost linearly with increasing mole fraction of added organic solvents such as acetonitrile, acetone, dioxane, ethanol, methanol, and DMSO in the decreasing order of efficiency. The effect of organic solvents on dissociation of radical ion pairs tends to increase with decrease of their hydrogen-accepting property expressed by Taft's β value. Halogen-atom substitution in FlI_n^{2-} and FlBr_n^{2-} reduced the $\mathrm{MV}^{+\cdot}$ yield, and this heavy-atom effect is associated with increase in the rate of recombination of triplet radical ion pairs accompanying spin inversion.

Recently, extensive work has been carried out for photo-induced electron transfer reactions in the presence of sensitizers.[1] Electron transfer from excited metal complexes to viologens has well been investigated,[2] and much attention has been also paid to organic dyes,[3–6] among which xanthene dyes seem to be promising candidates as sensitizer.

The triplet states of xanthene dyes carrying chlorine, bromine, or iodine atoms, in general, are generated with a nearly unit efficiency and their lifetimes are as long as 0.2 ms.[7,8] The long lifetime serves as an important criterion for effective electron transfer since it enables the use of a very low acceptor concentration for complete quenching of the triplet state, thereby favoring the product formation.[9] With erythrosine (FlI_4^{2-} or ER^{2-}) as an example, the triplet redox potentials are estimated to be about 0.8 V [$E(^3\mathrm{ER}^{2-*}/\mathrm{ER}^{3-\cdot})$] and −1.0 V [$E(\mathrm{ER}^{-\cdot}/^3\mathrm{ER}^{2-*})$] vs. SCE from its ground-state redox potentials[10] and lowest triplet energy level.[11] Use of MV^{2+} [$E(\mathrm{MV}^{2+}/\mathrm{MV}^{+\cdot})$=−0.62 V vs. SCE][12] as an electron acceptor and of triethanolamine [TEOA; $E(\mathrm{TEOA}^{+\cdot}/\mathrm{TEOA})$=0.82 V][13] as a sacrificial electron donor makes the system useful for photoconversion.

We have reported in a preliminary report that xanthene dyes such as eosin Y (FlBr_4^{2-} or EY^{2-}) and ER^{2-} work as sensitizers in reduction of MV^{2+} in aqueous solution, and that the yield of $\mathrm{MV}^{+\cdot}$ is markedly increased by adding alcohols like methanol, ethanol, and 2-propanol.[14] In the present study, the efficiencies for charge separation in the systems of xanthene dyes (FlI_n^{2-} and FlBr_n^{2-}, n=2, 3, and 4) MV^{2+} have been measured by means of laser flash photolysis with a view of quantitative understanding of solvent effects and heavy-atom effects, particularly of the enhancement in $\mathrm{MV}^{+\cdot}$ yield on addition of organic solvents.

Experimental

Erythrosine (FlI_4^{2-}) and eosin Y (FlBr_4^{2-}, Schmid) were crystallized from an ethanol–water mixture and dried at 100 °C under vacuum for 5 h. Other xanthene dyes (FlI_n^{2-} and FlBr_n^{2-}, n=2 and 3, Aldrich) were purified by gel filtration.[15] Sephadex G-25 (Pharmacia, Superfine grade, 50 g) was placed in a column after being washed three times and swelled with distilled water. A halogenated xanthene dye (100 mg) was put on the gel and separated by eluting with 0.05 M (M=mol dm^{-3}) aqueous ammonia. The dyes with different numbers of halogen atoms were eluted at different retention times and distinguished by reference to the reported absorption spectra.[15] Lithium perchlorate (Nacalai Tesque) and methylviologen (MV^{2+}, Sigma) were used as received.

A xanthene dye (1.25×10^{-5} M) and MV^{2+} (0—7×10^{-5} M) were dissolved in mixed solvents of varying ratios of water and an organic solvent [methanol, ethanol, acetonitrile, acetone, dioxane, and dimethyl sulfoxide (DMSO)]. Lithium perchlorate (0.02 M) was added to keep ionic strength of the solution constant.[16] The sample solutions were deaerated by bubbling with argon.

Phosphorescence measurements were carried out in ethanol on a Hitachi F-4000 spectrofluorimeter at liquid-nitrogen temperature (77 K).

Laser flash photolyses were performed at ambient temperature by using an excimer laser (Lambda Physik EMG 101, XeCl, 308 nm)-pumped dye laser (Lambda Physik FL-3002). Coumarin 307 was used as a laser dye to obtain visible laser pulses at wavelengths of 505, 510, 520, and 526 nm for exciting the xanthene dyes. A pulsed 150-W xenon arc (Wacom KXL-151) was used as a monitoring light source. The monitoring light passing through the sample solution in a 1-cm quartz cuvette at the right angle to the exciting laser beam was dispersed by a monochromator (JASCO CT25) equipped with a photomultiplier (Hamamatsu R928). Changes in monitoring light intensity with delay time were measured on a storage oscilloscope (Iwatsu TS-8123) as a function of monitoring wavelength. Transient absorption spectra at particular delay times ranging from nanoseconds to microseconds were obtained with the aid of a microcomputer (NEC PC-9801VX21).

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Reaction Scheme

The reaction scheme after the formation of dye triplets, $^3(D^{2-})^*$, is reasonably described as shown in Scheme 1. The D^{2-} triplets are quenched by MV^{2+} to give triplet radical ion pairs of D^- and $MV^{+\cdot}$ in a solvent cage. The pair components subsequently undergo either diffusion from the solvent cage to give free radical ion, D^- and $MV^{+\cdot}$, or recombination accompanying spin inversion to afford the ground-state species, D^{2-} and MV^{2+}. According to this scheme, the quantum yield of free $MV^{+\cdot}$, $\Phi_{MV^{+\cdot}}$, is given by Eq. 2;

$$\begin{array}{l} ^3(D^{2-})^* + MV^{2+} \xrightarrow{k_q} {}^3(D^-\cdots MV^{+\cdot}) \xrightarrow{k_{ce}} D^- + MV^{+\cdot} \\ \qquad\qquad\qquad\qquad\qquad \downarrow k_{TS} \\ \qquad\qquad\qquad\qquad\quad D^{2-} + MV^{2+} \end{array} \qquad (1)$$

Scheme 1.

$$\Phi_{MV^{+\cdot}} = \Phi_{isc} \cdot \Phi_q \cdot \Phi_{ce}, \qquad (2)$$

where Φ_{isc} is the quantum yield for intersystem crossing of D^{2-}, Φ_q the quenching efficiency of $^3(D^{2-})^*$ by MV^{2+}, and Φ_{ce} the cage escape efficiency of the triplet radical ion pair;

$$\Phi_q = \frac{k_q[MV^{2+}]}{k_q[MV^{2+}] + \tau_T^{-1}}, \qquad (3)$$

$$\Phi_{ce} = \frac{k_{ce}}{k_{ce} + k_{TS}}, \qquad (4)$$

where τ_T is the lifetime of $^3(D^{2-})^*$.

Results

Transient Absorption of Xanthene Dyes. Figures 1a—c show the transient absorption spectra of EY^{2-} observed on 520-nm laser excitation of deaerated solutions of EY^{2-} (1.25×10^{-5} M) in water–ethanol mixed solvents containing 0, 50, and 75 vol% ethanol, respectively. Measurements in the 480—560-nm region were not achieved because of a strong bleaching of the ground-state absorption. The spectra can be ascribed to (i) EY^{2-} triplets [$^3(EY^{2-})^*$] at 560—700 nm and radical ions produced by self-quenching of $^3(EY^{2-})^*$, i.e., (ii) one-electron oxidized dye, $EY^{-\cdot}$, around 456 nm[17] and (iii) one-electron reduced dye, $EY^{3-\cdot}$, around 408 nm.[17] The triplet lifetime of EY^{2-} increased and the yield of radical ions by the self-quenching reaction was reduced on addition of ethanol. Other xanthene dyes employed showed similar spectral behavior in the mixed solvents. Table 1 summarizes the triplet lifetimes of xanthene dyes in water. The lifetime decreases with increasing the number of halogen atoms for FlI_n^{2-} and $FlBr_n^{2-}$. In Table 1 are also listed their phosphorescence maxima and lifetimes measured in ethanol at 77 K as well as their ground-state absorption maxima in water.

Transient Absorption of Xanthene Dye/Methylviologen Systems. Figure 2 shows the transient absorption sepctra measured on laser excitation of EY^{2-} in the presence of MV^{2+} in the three kinds of water–ethanol mixtures. Three transient absorption bands are observed, which are due to $^3(EY^{2-})^*$, $EY^{-\cdot}$ around 456 nm, and $MV^{+\cdot}$ around 396 nm, indicating that quenching of $^3(EY^{2-})^*$ by MV^{2+} leads to the formation of $MV^{+\cdot}$ and $EY^{-\cdot}$.

In the presence of MV^{2+} the $^3(EY^{2-})^*$ lifetime was virtually reduced. Determination of the lifetimes with varying concentrations of MV^{2+} afforded the rate constant (k_q) for quenching of $^3(EY^{2-})^*$ by MV^{2+}. The k_q values for xanthene dyes were determined in various water–ethanol mixtures as listed in Table 2. Table 2 indicates that the k_q valules are independent of the kind

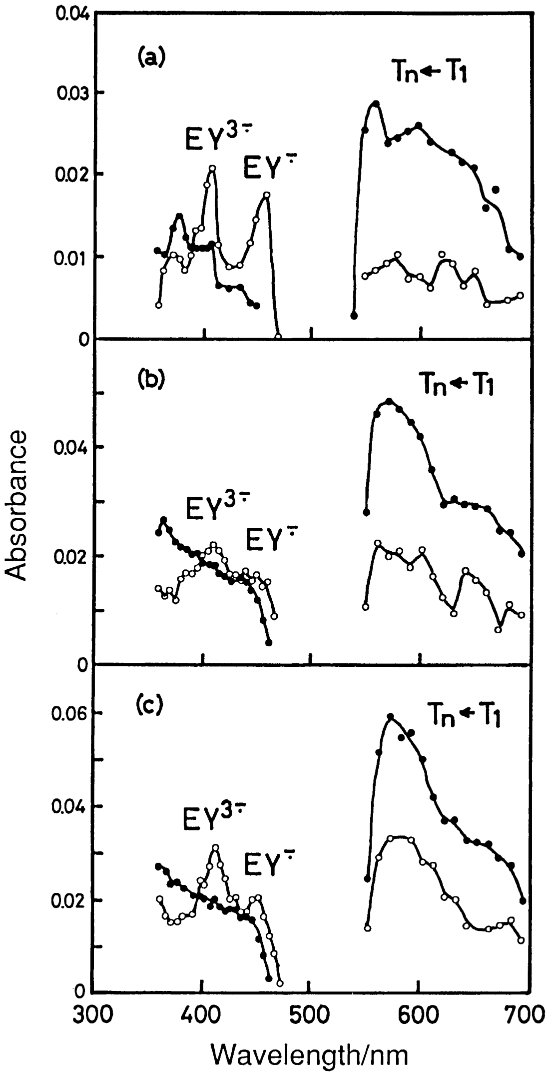

Fig. 1. Transient absorption spectra observed at delay times of 3.1 (●) and 89.3 μs (○) after 520-nm laser excitation of deaerated solutions of EY^{2-} (1.25×10^{-4} M) in water–ethanol mixtures. Water/ethanol ratios (v/v) in the mixtures are 100/0 (a), 50/50 (b), and 25/75 (c).

Table 1. Characteristics of Ground-State and Triplet–Triplet Absorption Spectra of Xanthene Dyes

Xanthene dye	Absorption maximum[a)]	Phosphorescence maximum[b)]	Triplet lifetime	
	nm	nm	At 77 K/ms[b)]	At R.T./μs[a)]
$FlBr_2^{2-}$	504			80.3
$FlBr_3^{2-}$	512			68.0
$FlBr_4^{2-}(EY^{2-})$	516	659	1.4	54.8
FlI_2^{2-}	508	643	1.1	80.4
FlI_3^{2-}	518	653	0.3	62.6
$FlI_4^{2-}(ER^{2-})$	527	658	0.2	42.0

a) In water (at room temperature). b) In ethanol (at 77 K).

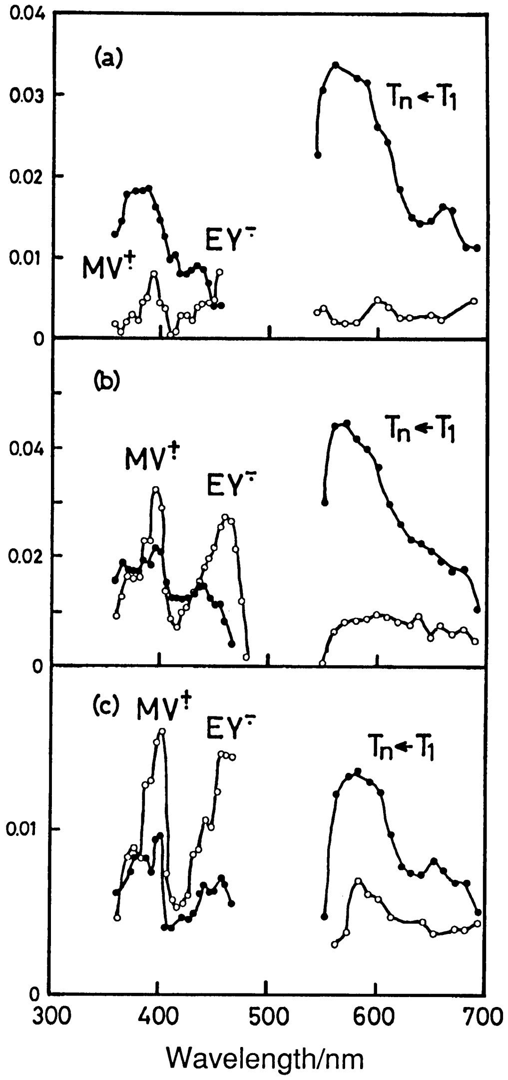

Fig. 2. Transient absorption spectra observed at delay times of 78 ns (●) and 1.8 μs (○) (in a), and 120 ns (●) and 3.1 μs (○) (in b and c) after 520-nm laser excitation of deaerated solution of EY^{2-} (1.25×10^{-4} M) and MV^{2+} (6.0×10^{-5} M) in water–ethanol mixtures. The water/ethanol ratios (v/v) in the mixtures are 100/0 (a), 50/50 (b), and 25/75 (c).

and number of the halogen atoms in dye molecules, but decrease with increasing content of ethanol in solvent.

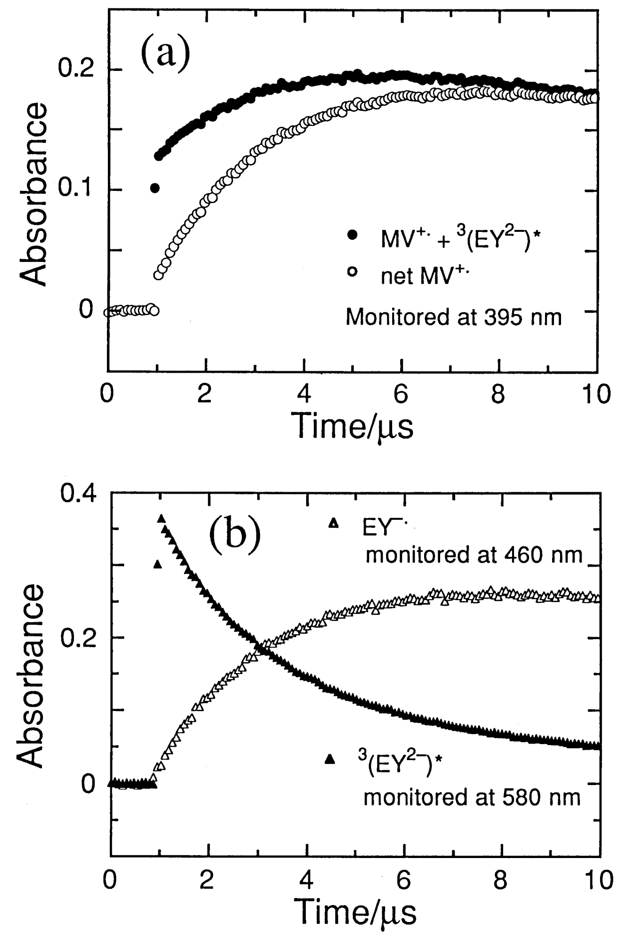

Fig. 3. Time profiles of the transient absorption at 395 nm and net build-up of $MV^{+\cdot}$ (a) and those of the transient absorptions of ${}^3(EY^{2-})^*$ and $EY^{-\cdot}$ (b) on 520-nm laser excitation of deaerated solutions of EY^{2-} (1.25×10^{-4} M) and MV^{2+} (6.0×10^{-5} M) in water–ethanol mixtures (50/50).

Figure 3a (closed circles) illustrates a time profile of the transient absorption measured in a water–ethanol (50 : 50) mixture at 395 nm until 10 μs after laser excitation of EY^{2-}. At this wavelength the observed absorption is not only due to the resulting $MV^{+\cdot}$ but also due to the dye triplet. Therefore, to see a net time profile of $MV^{+\cdot}$, a first-order decay curve of ${}^3(EY^{2-})^*$ (Fig. 3b) was subtracted from the observed 395-nm decay curve on a computer. The resulting profile showing the net build-up of $MV^{+\cdot}$ is displayed in Fig. 3a (open circles). This profile indicates that $MV^{+\cdot}$ is gradually increased to get to a plateau at nearly 10 μs after laser excitation. The resulting $MV^{+\cdot}$ disappears within 200 μs as observed by transient spectroscopy at a longer time scale.

Inspection of the time profiles of absorptions shows that the $MV^{+\cdot}$ and EY^{-} absorptions (Figs. 3a and b, respectively) grow up with nearly the same time constants (5.7×10^5 and 5.3×10^5 s^{-1}, respectively) as that of the EY^{2-} triplet decay (3.8×10^5 s^{-1}, Fig. 3b). This value might be underestimated because of the absorption tailing due to $MV^{+\cdot}$ around 580 nm; however, the difference from the rise rate constants is within the experimental error of our instruments. The time constant for recovery of the absorption of ground-state EY^{2-} analyzed at 530 nm according to first-order kinetics was almost identical with that for the decay of $^3(EY^{2-})^*$ monitored at 580 nm. On the basis of these results, the concentration of the generated EY^{2-} triplet was estimated from the decrease in absorbance at 530 nm, though $^3(EY^{2-})^*$ as well as $MV^{+\cdot}$ contributes to the absorbance to some extent at this wavelength.[18)]

The transient absorption spectra measured on laser excitation of ER^{2-} in the presence of MV^{2+} in the water–ethanol mixtures exhibited very similar behavior except for a slightly lower efficieny of $MV^{+\cdot}$ formation. Figure 4a shows an example.

Estimation of the Cage Escape Yield (Φ_{ce}). In the presence of a sufficient concentration of MV^{2+} the dye triplets can be almost completely quenched by MV^{2+} ($\Phi_q\approx1$), and thus $\Phi_{MV^{+\cdot}}$ is governed by Φ_{isc} and Φ_{ce}. Φ_{isc} depends upon the composition of solvents; Φ_{isc} of EY^{2-} is 0.7 in water and 0.5 in ethanol.[19)] Under these conditions Φ_{ce} is estimated by Eq. 5;

$$\Phi_{ce}=[MV^{+\cdot}]_0/[^3(D^{2-})^*]_0, \quad (5)$$

where $[MV^{+\cdot}]_0$ and $[^3(D^{2-})^*]_0$ are the concentrations of $MV^{+\cdot}$ and $^3(D^{2-})^*$ generated on laser excitation of D^{2-}, respectively. The $[^3(D^{2-})^*]_0$ value was determined from the depletion of the ground-state D^{2-} absorption (515—530 nm), and the $[MV^{+\cdot}]_0$ value was estimated from the absorbance at the absorption peak (395—396 nm) of $MV^{+\cdot}$ by using the reported molar extinction coefficient (ε=42000).[20)] The Φ_{ce} values were determined under conditions of $[D^{2-}]=1.25\times10^{-5}$ M and $[MV^{2+}]=5—7\times10^{-5}$ M in varying water–ethanol mixtures. The determined Φ_{ce} values are included in Table 2. To see the effects of organic solvents Φ_{ce}'s were determined for EY^{2-} and ER^{2-} in various water–organic solvent mixtures. Figures 5a and 5b show plots of Φ_{ce} against the mole fraction (x_{os}) of organic solvents; lines for a few solvents are omitted to avoid crowding.

Figure 5 indicates that Φ_{ce} linearly increases with increasing mole fraction of organic solvents and that the slope, which corresponds to an enhancing efficiency of

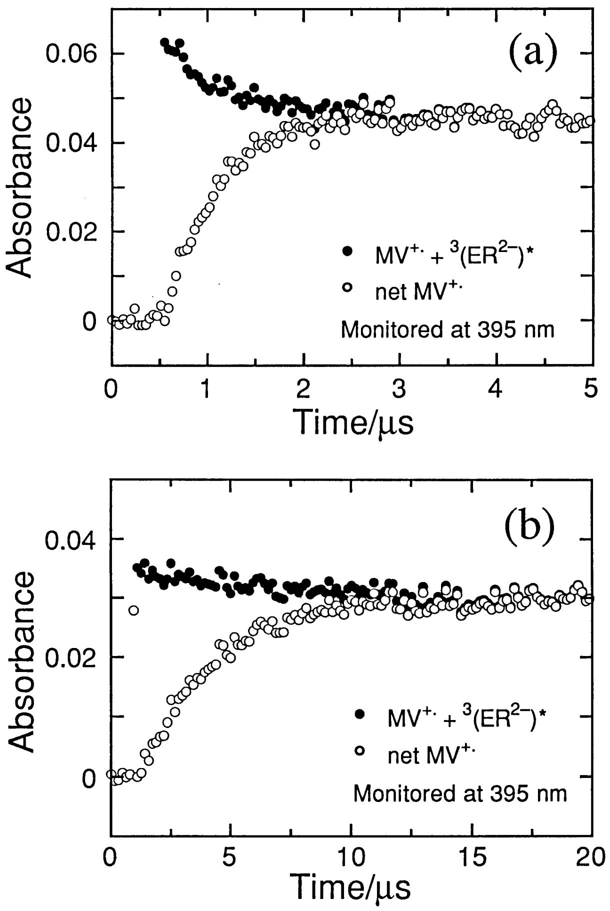

Fig. 4. Time profiles of the transient absorption at 395 nm and net build-up of $MV^{+\cdot}$ on 520-nm laser excitation of deaerated solutions of ER^{2-} (1.25×10^{-4} M) and MV^{2+} (4.0×10^{-4} M) (a), and of ER^{2-} (1.25×10^{-5} M), MV^{2+} (6.0×10^{-5} M), and TEOA (1.0×10^{-2} M) (b), in water–ethanol mixtures (25/75).

Table 2. Quenching Rate Constants (k_q) of Dye Triplets with Methylviologen and Quantum Yields (Φ_{ce}) for Charge Separation in Water–Ethanol Mixtures

Xanthene dye	$k_q/10^9$ M^{-1} s^{-1}				Φ_{ce}			
	EtOH vol%				EtOH vol%			
	0	30	50	75	0	30	50	75
$FlBr_2^{2-}$	7.7	3.5	2.8	2.4	0.066	0.14	0.29	0.32
$FlBr_3^{2-}$	7.4	3.6	3.1	2.4	0.030	0.072	0.12	0.15
$FlBr_4^{2-}(EY^{2-})$	7.7	3.8	3.1	3.1	0.027	0.047	0.11	0.15
FlI_2^{2-}	7.9	3.7	3.1	2.4	0.036	0.065	0.11	0.16
FlI_3^{2-}	8.2	4.2	3.1	2.9	0.021	0.037	0.064	0.090
$FlI_4^{2-}(ER^{2-})$	8.0	3.7	3.5	2.8	0.020	0.030	0.047	0.069

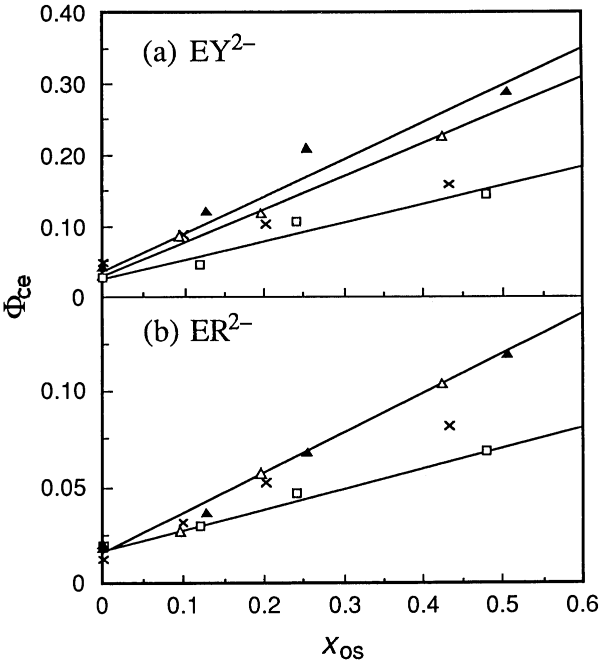

Fig. 5. Plots of cage escape yields (Φ_{ce}) on sensitization with EY^{2-} (a) and ER^{2-} (b) in water-organic solvent mixtures as a function of mole fraction (x_{os}) of the organic solvent; ethanol (□), acetone (△), DMSO (×), and acetonitrile (▲).

charge separation for each organic solvent, decreases in the order of acetonitrile, acetone, dioxane, ethanol, methanol, and DMSO.

The Φ_{ce} value also depends on sensitizers as indicated in Table 2; Φ_{ce} decreases with increasing the number of halogen atoms for both series of $FlBr_n^{2-}$ and FlI_n^{2-}, and for FlX_n^{2-} with the same number of halogen atoms Φ_{ce} is higher for X=Br than for X=I.

Transient Absorption of Xanthene Dye/Methylviologen/Triethanolamine Systems. Triethanolamine (TEOA) is a well-known scavenger of radical cations. Addition of TEOA to deaerated solutions of EY^{2-} and MV^{2+} remarkably increased the absorbance of the resulting MV$^{+\cdot}$ absorption on laser excitation (Fig. 4b). This is attributed to scavenging of the produced EY$^{-\cdot}$ by TEOA to inhibit recombination of MV$^{+\cdot}$ with EY$^{-\cdot}$. The maximum yield of MV$^{+\cdot}$ was observed under conditions where [EY^{2-}]=1.25×10^{-5} M, [MV^{2+}]=6.0×10^{-5} M, and [TEOA]=1.0×10^{-2} M. The decay rate of EY^{2-} triplets was little affected by addition of TEOA, and the rate constant of MV$^{+\cdot}$ formation was almost the same as that of triplet decay, indicating that the dye triplet is quenched predominantly by MV^{2+} but little influenced by TEOA.[5)] The quenching rate constant of EY^{2-} triplets by TEOA was estimated to be 10^6 M^{-1} s^{-1}, which is in good agreement with the reported value.[5)]

Discussion

Effects of Organic Solvent on Charge Separation. The charge separation is reasonably assumed to proceed according to Scheme 1, since the spectral analysis based on Scheme 1 gave a good accordance between the rise and decay rate constants of the relevant transient species under our experimental conditions. The quantum yield of free MV$^{+\cdot}$ production, Φ_{ce}, is dependent upon the rates of the competing processes, as expressed by Eqs. 2—4.

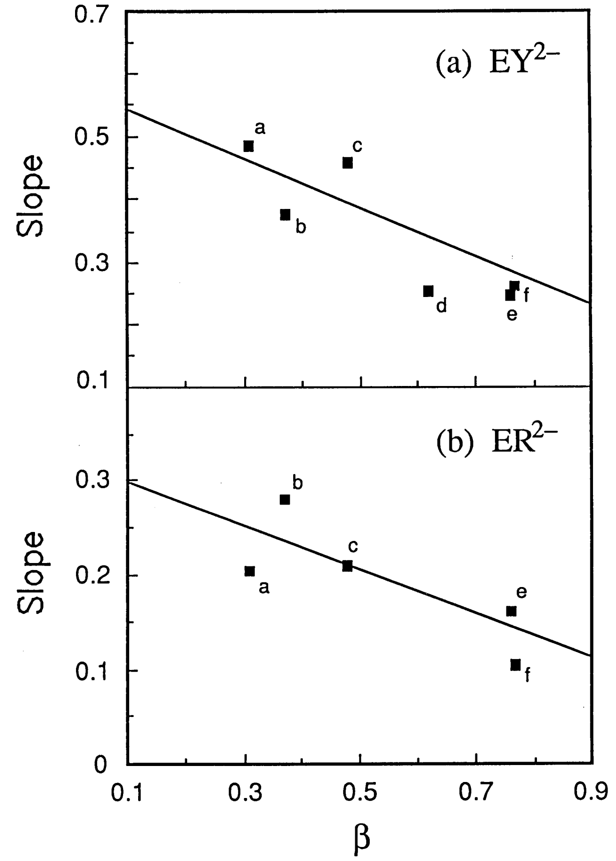

Fig. 6. Plots of the slopes of straight lines in Fig. 5 vs. Taft's β values of organic solvents; acetonitrile (a), dioxane (b), acetone (c), methanol (d), DMSO (e), and ethanol (f).

In the present system, Φ_{ce} increases almost linearly with increasing mole fraction, x_{os}, of the organic solvent in water–organic solvent mixtures, as shown for EY^{2-} and ER^{2-} in Fig. 5. As estimated from the slope in Fig. 5, the enhancing efficiency of organic solvent increases in the order of DMSO, methanol, ethanol, dioxane, acetone, and acetonitrile. Similar enhancing effects by added organic solvents were observed in all the xanthene dyes studied.

Also, the polarity of the mixtures is dependent on the added organic solvent. The dielectric constants of the employed organic solvents[21)] are 46.7, 37.5, 32.7, 24.6, 20.7, and 2.21 for DMSO, acetonitrile, methanol, ethanol, acetone, and dioxane, respectively. Such variation in the dielectric constant has no correlation with the magnitude of the above enhancing efficiencies.

The above solvent sequence is correlated with Taft's β value, a parameter of hydrogen-accepting property (hydrophilicity) of solvent.[22)] Figure 6 shows plots of the slopes of straight lines in Fig. 5 against Taft's β values. This figure indicates that the less favorable the added organic solvent to hydrogen bonding with protons of water molecules, the more efficient the charge separation.

The radical ions, D^{-} and $MV^{+\cdot}$, generated in a pair, carry large hydrophobic organic moieties with rather small hydrophilic charged moieties. In D^{-} 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. In a water–organic solvent mixture these radical ions as well as the dye molecules tend to be surrounded by organic solvent molecules at their hydrophobic moieties. The situation must be similar for diffused radical ions and also for solvent-separated radical ion pairs. As a result, the aqueous mixtures with a higher composition of organic solvents will stabilize the solvent-separated radical ion pairs as well as the diffused radical ions to enhance the charge separation rather than those with a lower composition of organic solvents.

Since less hydrogen-accepting, i.e., more hydrophobic organic solvent molecules (with lower β values) interact with water molecules to a lower extent than more hydrogen-accepting molecules (with higher β values), and therefore, might easily constitute their own cluster separated from clustered water, those molecules surround more favorably the hydrophobic moieties of the radical ion pairs and radical ions, D^{-} and $MV^{+\cdot}$, to stabilize these species. Accordingly, both D^{-} and $MV^{+\cdot}$ molecules will be more effectively solvated than D^{2-} and MV^{2+} by hydrophobic solvents. The stabilizing effect by the hydrophobic solvents increases the escape of the radical ion pairs from the solvent cage to enhance the yield of $MV^{+\cdot}$.

It is worth noting that the stabilization of organic solvent molecules by hydration, as determined by means of mass spectrometry of adiabatically expanded jets of an aqueous solution,[23] decreases in the order of ethanol, acetone, and acetonitrile, which is just in the same order as above.

Heavy-Atom Effect on the Cage Escape Efficiency. In Table 2 the Φ_{ce} values are relatively higher for $FlBr_n^{2-}$ than for FlI_n^{2-}, and also significantly increase with decreasing the number of halogen atoms in respective series of $FlBr_n^{2-}$ and FlI_n^{2-}. These results indicate that the spin-orbit coupling effected by the halogen atoms accelerates spin recombination of the triplet radical ion pairs, $D^{-}+MV^{+\cdot}$, to reduce Φ_{ce}.

The triplet radical ion pairs will undergo recombination with a rate constant, k°_{TS}, even when a dye molecule carries no halogen atom. The presence of halogen atoms in the dye molecules accelerates the spin recombination and its rate can be assumed to be proportional to the number of heavy (halogen) atoms (n) involved in the dyes and the square of their spin-orbit coupling constant (ζ).[24] Then, the rate constant for the spin recombination (k_{TS}) is expressed by Eq. 6, where α is a proportionality constant;

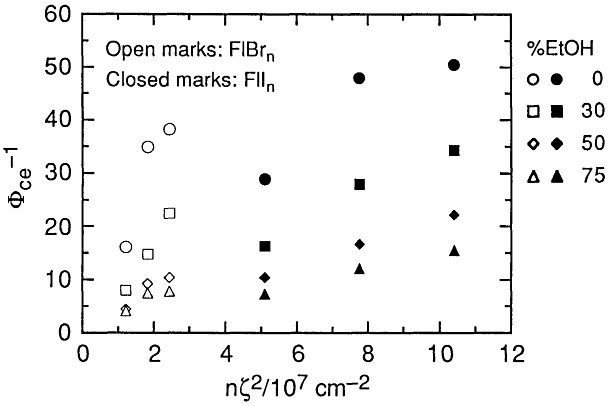

Fig. 7. Heavy-atom effects on the cage escape yield (Φ_{ce}) for xanthene dyes with varying numbers of halogen atoms in water–ethanol mixtures. The Φ_{ce}^{-1} values are plotted against the products of the square of spin-orbit coupling parameter (ζ) and the number (n) of substituted halogen atoms (n=2—4).

$$k_{TS} = k^{\circ}_{TS} + \alpha n\zeta^2. \tag{6}$$

Under the present experimental conditions, the quantum yield for the spin recombination can be taken as $1-\Phi_{ce}$. Then, the following equation can be derived;

$$\frac{\Phi_{ce}}{1-\Phi_{ce}} = \frac{k_{ce}}{k_{TS}} = \frac{k_{ce}}{k^{\circ}_{TS} + \alpha n\zeta^2}. \tag{7}$$

Accordingly,

$$\Phi_{ce}^{-1} = 1 + \frac{k^{\circ}_{TS}}{k_{ce}} + \frac{\alpha n\zeta^2}{k_{ce}}. \tag{8}$$

Thus, Φ_{ce}^{-1} is expected to increase linearly with $n\zeta^2$.

Figure 7 shows plots of Φ_{ce}^{-1} against $n\zeta^2$ for various dyes examined in varying water–ethanol mixtures. In each solvent Φ_{ce} tends to increase almost linearly with $n\zeta^2$ for the series of $FlBr_n^{2-}$ and FlI_n^{2-}; however, a linear relationship does not hold for all dyes of both series. The slope is steeper for $FlBr_n^{2-}$ than for FlI_n^{2-}.

Several workers have already dealt with the heavy-atom effect on electron transfer via triplet radical ion pairs or triplet exciplexes in solvent cage.[3,6,25,26] The present results provide an example of this kind of effect on a different type of radical ion pairs.

It should be noted that the k_q values are almost constant irrespective of xanthene dyes on going from FlI_n^{2-} to $FlBr_n^{2-}$, as seen in Table 2. This means that there is no specific heavy-atom effect on the rate constant k_q in these series of xanthene dyes.

The singlet radical ion pairs dissociate with a rate constant of 5×10^8 s^{-1}, as seen, for example, in the pair of a pyrene anion radical and an amine cation radical in acetonitrile.[27] As for the present results, the magnitude of k_{TS} can be estimated to be ca. 10^9 s^{-1} for the triplet pair of EY^{-} and $MV^{+\cdot}$ in an aqueous solution of a high mole fraction of acetonitrile ($\Phi_{ce} = 0.3$) under an assumption that k_{ce} is 5×10^8 s^{-1}. The k_{TS} value of nearly 10^9 s^{-1} is reasonable,[28] since the process involves the free energy change estimated as -1.55 eV.

Summarizing the present study, we can deduce the following conclusions:

1) The cage escape process is influenced by stiffness of the solvent cage composed of hydrogen-bonded networks of solvent molecules. This can be described by using microscopic environmental parameters such as Taft's β value.

2) Perturbation by heavy atoms involved in dye sensitizer reduces the cage escape yield depending on the number of heavy atoms or the magnitude of spin-orbit coupling. It can be explained as due to enhancement of the spin recombination in conformity with Scheme 1.

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