

Spin dynamics and zero-field splitting constants of the triplet exciplex generated by photoinduced electron transfer reaction between erythrosin B and duroquinone

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Abstract

The spin dynamics of the duroquinone anion radical generated by photoinduced electron transfer reactions from triplet erythrosin B to duroquinone has been studied by using transient absorption and pulsed FT-EPR spectroscopy. Triplet exciplex formation as the reaction intermediate is verified by the observation of spin-orbit coupling induced electron spin polarization. The kinetic parameters for exciplex formation and the intrinsic enhancement factors of electron spin polarization are determined in various alcoholic solvents. The zero-field splitting constants of the triplet exciplex are determined by the analysis of the solvent viscosity dependence of the enhancement factors of the electron spin polarization. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The dynamics and reaction mechanisms of triplet exciplexes have received much attention in the field of photochemistry for a long time [1–9]. Significant progress has recently been made in understanding the character of triplet exciplexes. Magnetic field effects (MFEs) on the radical yield have provided fruitful information on the dynamics of the triplet exciplexes [1,10–16]. The MFE is attributed to the sublevel selective back electron

transfer (ET) reaction due to the SOC interaction from the triplet exciplex to the ground state. Recently, transient absorption bands observed in the infrared region were assigned to triplet exciplexes of quinones and aromatic molecules [7–9]. The rate constants of the exciplex formation and ET in the exciplexes were determined from the buildup and decay rates of the bands. We have found that the chemically induced dynamic electron polarization (CIDEP) technique is also a powerful tool to study triplet exciplexes [5,6,17–21]. Net-emissive (E) and unusual net-absorptive (A) CIDEP spectra have been observed in several photoinduced ET reaction systems containing heavy atoms. These CIDEP

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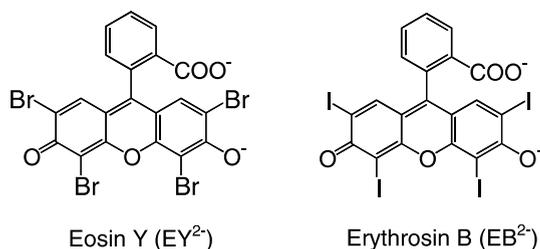


Fig. 1. Structures of eosin Y (EY^{2-}) and erythrosin B (EB^{2-}).

effects were interpreted in terms of the sublevel selective population type triplet mechanism (p-TM) or normal TM of the precursor triplet state and the sublevel selective depopulation type triplet mechanism (d-TM) of the triplet exciplex, respectively. The unusual net-A polarization is attributable to sublevel selective intersystem crossing (ISC) from the triplet exciplex or contact radical pair to the singlet ground state. Furthermore, in a recent Letter, we reported that the radical yield and intrinsic enhancement factor of the electron spin polarization for the eosin Y (EY^{2-})–duroquinone (DQ) system depend on the solvent viscosity (η) [22]. The ZFS parameters of the triplet exciplex intermediate were determined from the correlation between the enhancement factors of the electron spin polarization and η .

In the present work, we have studied the kinetics, radical yield and intrinsic enhancement factors of the electron spin polarization for the erythrosin B (EB^{2-} , Fig. 1)–DQ system to verify the heavy atom effect on the properties of the triplet exciplex intermediate using transient absorption and echo-detected Fourier transform-EPR (FT-EPR) spectroscopy. The triplet state of EB^{2-} (${}^3EB^{2-}$) is generated with a high yield (1.0) and has a long lifetime (~ 0.2 ms) [23]. We report significant heavy atom effects on the zero-field splitting (ZFS) parameters of the triplet exciplex determined from the solvent viscosity dependence of the intrinsic enhancement factors of the electron spin polarization.

2. Experimental

Erythrosin B (2', 4', 5', 7'-tetraiodofluorescein disodium salt, EB^{2-}) was purchased from Nacalai

Tesque. Eosin Y (2', 4', 5', 7'-tetrabromofluorescein disodium salt, EY^{2-}) was recrystallized from ethanol. DQ (Tokyo Kasei) was purified by vacuum sublimation in the dark. Fresh methanol (MeOH, reagent grade), ethanol (EtOH, spectrograde), 1-propanol (1-PrOH) and 1-butanol (1-BuOH) were used as the solvent without further purification.

Nanosecond transient absorption spectra were measured by using a multichannel analyzer (Diode array: Princeton Instruments, IRY-700) controlled with a personal computer as described previously [22]. A Holographic Notch-plusTM filter (Kaiser Optical System, HNPF-532) was used to protect the detector from the strong laser light. The transient signals were recorded with a digitizer (Tektronix, TDS 520D).

Echo-detected FT-EPR measurements were performed by using an X-band pulsed EPR spectrometer (Bruker ESP 380E) equipped with a dielectric resonator ($Q \sim 100$). The methods for the electron spin-echo detection and phase correction are described elsewhere [18]. A microwave pulse width of 16 ns was used for a $\pi/2$ pulse.

All sample solutions were deoxygenated by argon gas bubbling and allowed to flow into a quartz cell within a laser photolysis spectrometer or an EPR resonator. In the present study, xanthene dyes (Xn^{2-}) were selectively excited by a Nd:YAG laser (Spectra-Physics GCR-155, INDI-40-20, 532 nm).

3. Results

3.1. Transient absorption measurements

The transient absorption spectra were measured for the EB^{2-} –DQ system in several alcoholic solutions. Fig. 2 shows the transient absorption spectra obtained by laser photolysis of EB^{2-} (5×10^{-5} mol dm^{-3}) with 532 nm light in the presence of DQ ($[DQ] = 1 \times 10^{-3}$ mol dm^{-3}) in EtOH. The transient absorption band at 560–700 nm appeared immediately after the laser pulse is attributable to ${}^3EB^{2-}$ [23]. The decay of the T–T absorption was accompanied by the concomitant growth of the absorption with a peak maximum at

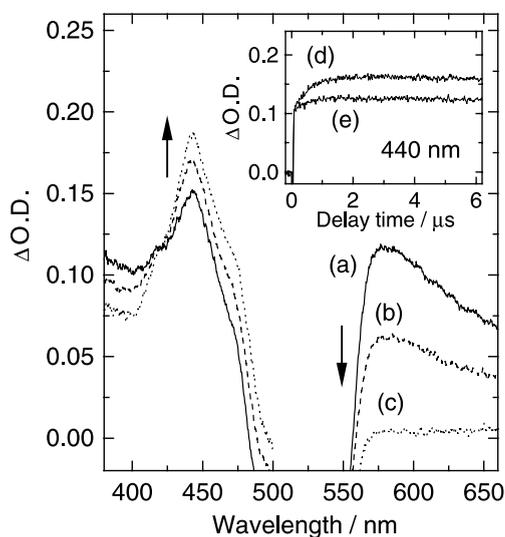


Fig. 2. Transient absorption spectra obtained by laser photolysis of EB^{2-} ($5 \times 10^{-5} \text{ mol dm}^{-3}$) with 532 nm light in the presence of DQ ($1 \times 10^{-3} \text{ mol dm}^{-3}$) in EtOH. The measurements were performed at 0.2–0.3 μs (a), 0.4–0.5 μs (b), and 2.0–2.1 μs (c) after the laser pulse. Inset: time profile obtained at 440 nm under the magnetic fields of zero (d) and 340 mT (e).

445 nm. The change in the transient absorption spectra in Fig. 2 clearly suggests that the ET occurs from the triplet state of EB^{2-} to DQ. Whether a triplet exciplex or contact RP is formed during the ET reaction cannot be decided from the present transient absorption experiments.

The assignment of $\text{EB}^{\cdot-}$ and $\text{DQ}^{\cdot-}$ is confirmed by the quenching reaction of $\text{EB}^{\cdot-}$ by triethanolamine (TEOA) [22,24]. The escape radical yield (ϕ_{esc}) was determined by using the ratio of the $\Delta\text{O.D.}$ values of ${}^3\text{EB}^{2-}$ ($\epsilon(580 \text{ nm}) = 11000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and $\text{EB}^{\cdot-}$ ($\epsilon(458 \text{ nm}) = 18000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) [23]. The ϵ value of $\text{EB}^{\cdot-}$ was estimated from the ϵ value of the 1,4-naphthoquinone anion radical ($\epsilon(390 \text{ nm}) = 12500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) obtained by the photoinduced ET between EB^{2-} and 1,4-naphthoquinone in EtOH [25]. The ϕ_{esc} value of 0.40 determined in the present system is smaller than the value (0.54) in the EY^{2-} –DQ system [22]. A similar spectral change was also observed in MeOH, 1-PrOH and 1-BuOH but significant solvent effects on ϕ_{esc} were obtained. The ϕ_{esc} values were 0.46, 0.28 and 0.22 in MeOH, 1-PrOH and 1-BuOH, respectively.

In order to analyze the dynamics of the CIDEP spectra as described later, we have measured the external magnetic field (\mathbf{B}) dependence of the radical yield. The ϕ_{esc} value steeply increased as the \mathbf{B} increased and then it monotonically decreased. The positive MFE observed at low field is interpreted in terms of the hyperfine coupling mechanism. The negative MFE observed at high field is attributable to the SOC induced d-type TM and the Δg mechanism [1]. The inset in Fig. 2 shows the time profiles of the transient absorption signals at 440 nm observed by the laser photolysis of the EB^{2-} ($5 \times 10^{-5} \text{ mol dm}^{-3}$) – DQ ($1 \times 10^{-3} \text{ mol dm}^{-3}$) system without magnetic field (d) and at $\mathbf{B} = 340 \text{ mT}$ (e) in EtOH. The ϕ_{esc} values of 0.40 and 0.35 were obtained without magnetic field and at $\mathbf{B} = 340 \text{ mT}$, respectively. As summarized in Table 1, significant MFEs on ϕ_{esc} were observed in the present alcoholic solutions. For $\phi_{\text{esc}}(\mathbf{B} = 340) / \phi_{\text{esc}}(\mathbf{B} = 0)$, values of 0.91, 0.88, 0.79 and 0.77 were obtained in MeOH, EtOH, 1-PrOH and 1-BuOH, respectively. The quenching rate constants of triplet EB^{2-} (k_{q}) were determined from the buildup rate by assuming a pseudo-first-order reaction ($k_{1\text{st obs}}$). The k_{q} values of $(5.6 \sim 1.5) \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ obtained in the present alcoholic solvents are slightly smaller than the diffusion-controlled rate constants.

We also measured the temperature (T) dependence of k_{q} in the EB^{2-} –DQ system in 1-PrOH (Fig. 3). Table 2 summarizes the kinetic parameters and ϕ_{esc} determined for the EB^{2-} –DQ system by transient absorption measurements in 1-PrOH. The $k_{\text{q}}(1/T)$ relationship observed in the EY^{2-} –DQ system is also shown in Fig. 3. Almost identical k_{q} values were obtained in the EB^{2-} –DQ and EY^{2-} –DQ systems, indicating that these systems have very similar activation energies (E_{a}) and energy gap values for the charge separation (G_{CS}).

We examined the acceptor concentration dependence of the $k_{1\text{st obs}}$ values because a nonlinear relationship is the diagnostic of a pre-equilibrium intermediate between the donor and acceptor [7–9,27]. For concentrations up to 0.05 mol dm^{-3} in 1-PrOH at room temperature, the kinetics plots revealed the linear dependence of the $k_{1\text{st obs}}$ on the DQ concentration. Although similar experiments were also carried out at lower temperatures, the

Table 1
Kinetic parameters and intrinsic enhancement factors of DQ^- generated by photoinduced electron transfer from EB^{2-} in several alcohols at room temperature as determined from transient absorption and FT-EPR spectroscopy

Solvent ($\eta/\text{m Pa s}$, ϵ)	ϕ_{esc} (0 mT)	ϕ_{esc} (340 mT)	$k_{\text{q}}/10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	T_1^{T}/ns	$T_1^{\text{R}}/\mu\text{s}$	V_{pd}	V_{d}
MeOH (0.545, 32.6)	0.46	0.42	(5.6) ^a , 5.8 ^b	8	0.7	-30(\pm 4)	25(\pm 3)
EtOH (1.10, 24.4)	0.40	0.35	(3.2) 3.4	8	0.8	-34(\pm 4)	40(\pm 4)
1-PrOH (1.97, 20.3)	0.28	0.22	(2.5) 2.4	9	0.9	-30(\pm 4)	50(\pm 4)
1-BuOH (2.61, 17.5)	0.22	0.17	(1.5) 1.4	10	0.9	-30(\pm 4)	56(\pm 4)

^a Determined from the transient absorption experiments.

^b Determined from the FT-EPR experiments.

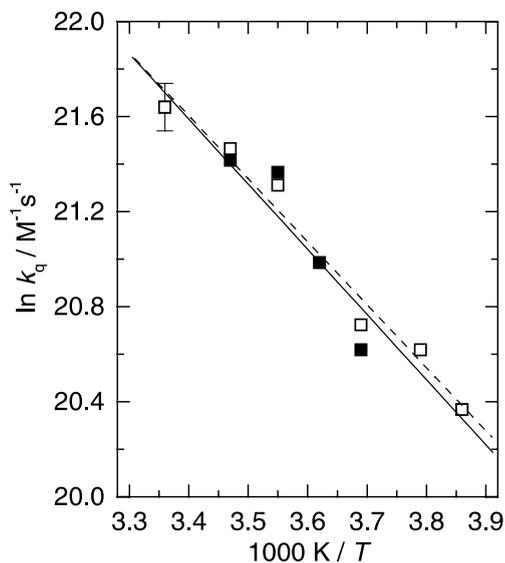


Fig. 3. Plots of the quenching rates of triplet EB^{2-} (\square) and EY^{2-} (\blacksquare) by DQ in 1-PrOH against the inverse of temperature ($1/T$).

low solubility of DQ gave no indication of the discrepancy from the linear relationship between the $k_{1\text{st obs}}$ and $[\text{DQ}]$.

3.2. FT-EPR measurements

Laser photolysis of EB^{2-} in the presence of DQ gave strong absorptive (A) CIDEP spectra due to the DQ anion radical ($\text{DQ}^{\cdot-}$, $a^{\text{H}} = 0.19 \text{ mT}$ and $g = 2.0041$) in the present alcoholic solvents. Fig. 4 depicts the evolution and decay of the FT-EPR signals due to $\text{DQ}^{\cdot-}$ generated by laser photolysis of the EB^{2-} -DQ system in 1-PrOH. The measurements were performed for an EB^{2-} concentration of $1 \times 10^{-4} \text{ mol dm}^{-3}$ and DQ concentrations of $1 \times 10^{-2} \text{ mol dm}^{-3}$ (a), $1 \times 10^{-3} \text{ mol dm}^{-3}$ (b) and $1 \times 10^{-4} \text{ mol dm}^{-3}$ (c). When the DQ concentration was higher than $1 \times 10^{-2} \text{ mol dm}^{-3}$, very weak net-E CIDEP spectra due to TM were observed during the early time ($t \leq 20 \text{ ns}$). Subsequently, the net-A CIDEP signals appeared. The net A-CIDEP is attributable to the SOC induced polarization due to heavy atoms [18]. The quenching rates can be determined from the buildup rates of the net A-CIDEP. The solid lines are obtained from the nonlinear least squares fits based on the modified

Table 2
Temperature dependence of the kinetic parameters and intrinsic enhancement factors of DQ^- generated by the photoinduced electron transfer from EB^{2-} in 1-PrOH as determined from transient absorption and FT-EPR spectroscopy

T / K	$\eta/\text{m Pa s}^a$	$\phi_{\text{esc}} (0 \text{ mT})$	$\phi_{\text{esc}} (340 \text{ mT})$	$k_{\text{q}}/10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	T_1^T/ns	T_1^R/s	V_{pd}	V_d
298	1.97	0.28	0.22	(2.5) ^b 2.6 ^c	9	0.9	-30(±4)	50(±4)
288	2.54	0.22	0.17	(2.1) 2.5	9	1.0	-30(±4)	58(±4)
282	2.96	0.20	0.15	(1.8) 1.8	9	1.0	-34(±4)	56(±4)
271	3.98	0.17	0.12	(1.0) 1.3	10	1.0	-34(±4)	56(±4)
264	4.88	0.13	0.10	(0.9) 1.2	10	1.1	-30(±4)	58(±4)
259	5.68	0.12	0.08	(0.7) 0.9	10	1.1	-32(±4)	60(±4)

^a Ref. [26].

^b Determined from the transient absorption experiments.

^c Determined from the FT-EPR experiments.

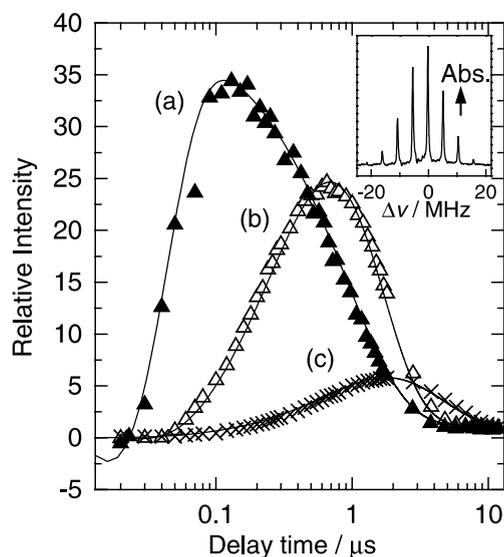


Fig. 4. Acceptor concentration dependence of the time profiles of the echo FT-EPR signals ($M_I = 0$) due to DQ^- generated from the laser photoexcitation of EB^{2-} in the presence of DQ in 1-PrOH. The measurements were carried out with the concentrations of $[\text{EB}^{2-}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{DQ}] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ (a), $1 \times 10^{-3} \text{ mol dm}^{-3}$ (b) and $1 \times 10^{-4} \text{ mol dm}^{-3}$ (c). Inset: echo FT-EPR spectra observed in the EB^{2-} - DQ ($1 \times 10^{-3} \text{ mol dm}^{-3}$) system at the delay time of 250 ns. The solid lines represent nonlinear least squares curve fits based on the data shown in Table 1.

Bloch equation (discussed later). The observation of the unusual net-A polarization suggests the production of the triplet exciplex as the reaction intermediate, because the SOC interaction due to heavy atoms is a short-range interaction [1–9]. The intermediate would be a nearly pure charge transfer complex or contact RP in the polar solvent.

4. Discussion

4.1. Triplet exciplex formation process

The free energy of the charge separation from triplet EB^{2-} - DQ (ΔG_{CS}) in polar solvents is estimated from Eq. (1).

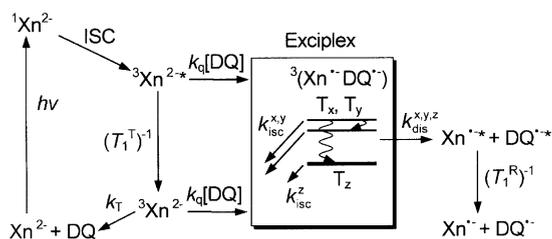
$$\Delta G_{\text{CS}} = E^{\text{T}} - (E_{\text{ox}}^{\circ} - E_{\text{red}}^{\circ}), \quad (1)$$

where E^{T} is the triplet energy level of the dyes, and E_{ox}° and E_{red}° are oxidation and reduction potentials

Table 3

Free energy of charge separation and activation energy of triplet exciplex formation

Xn^{2-}	E^T/eV^a	$E_{\text{ox}}^0/\text{V}^b$	$E_{\text{red}}^0/\text{V}^c$	$\Delta G_{\text{CS}}/\text{eV}$	E_a/eV
EY^{2-}	1.83	0.89	DQ -0.73	-0.21	0.24
EB^{2-}	1.82	0.86	DQ -0.73	-0.23	0.23

^a Ref. [28].^b Ref. [29].^c Ref. [30].

Scheme 1.

of donor and acceptor in polar solvents, respectively. From the values of the E^T and redox potentials (Table 3) [28–30], the ΔG_{CS} value of -0.23 eV for the EB^{2-} –DQ system was estimated. As listed in Table 3, the ΔG_{CS} values are very similar to each other in the EB^{2-} –DQ and EY^{2-} –DQ systems. It can be, therefore, predicted that the reorganization energy values (λ) for both systems are also comparable and the effects of the heavy atom substitutions on the forward ET rates are negligible.

The activation energies (E_a) of 0.23 and 0.24 eV obtained from the Arrhenius plots for the EB^{2-} –DQ and EY^{2-} –DQ systems (Fig. 3) correspond to that of the triplet exciplex formation in 1-PrOH. The present results suggest that the kinetic parameters for the forward ET process from the triplet states of EB^{2-} and EY^{2-} to DQ are very similar to each other.

4.2. Spin dynamics

Scheme 1 shows the net electron spin polarization mechanism from the spin-polarized and spin-equilibrated triplet precursor via the triplet exciplex in the present photosensitized reaction. The photoinduced ET occurs dominantly from the p-TM polarized triplet states of xanthene dyes ($^3Xn^{2-}$) because of the fast ISC. This is supported by

the observation of net-E TM during the initial stage. The relaxation process of the spin polarized triplet state (triplet relaxation time; T_1^T) competes with the quenching reaction, $k_q[\text{DQ}]$. The net-A CIDEP signals are attributable to the sublevel selective ISC, which produces directly the ground singlet state. According to Scheme 1, we obtain the magnetization based on the Bloch equation as follows,

$$\begin{aligned} \frac{dM_z}{dt} = & k_q[\text{DQ}]\phi_{\text{esc}}P_dC_T + k_q \\ & \times [\text{DQ}]\phi_{\text{esc}}P_{\text{dp}}C_{T^*} \\ & - \frac{M_z - \phi_{\text{esc}}(t)P_{\text{eq}}}{T_1^T}, \end{aligned} \quad (2)$$

where, the first term corresponds to the net-A polarization due to the d-TM with the enhancement factor of P_d , the second term is the contribution from the d-TM and p-TM with the enhancement factor of P_{dp} , and the last term represents the dynamics of the thermally populated radical with polarization of P_{eq} , respectively. The concentrations of the spin-equilibrated (C_T) and spin-polarized (C_{T^*}) triplet precursor and the time evolution of the escape radical yield are described as a function of the kinetic parameters and the acceptor concentration (see Appendix A).

A significant solvent viscosity dependence of the escape radical yield and enhancement factors was observed in the EB^{2-} –DQ systems. As summarized in Table 2, the ϕ_{esc} values decrease with increasing viscosity in 1-PrOH, indicating that the dissociation rate of the exciplex decreases with increasing the viscosity. Heavy atom substituents induce a sublevel selective ISC from the triplet exciplex into the ground state, but the dissociation of the exciplex is not sublevel selective. Since $k_T \ll k_q[\text{DQ}]$ in the present experimental condition, the escape yield of the free radicals from the solvent cage is described as follows.

$$\phi_{\text{esc}} = \left(1 + \frac{\sum k_{\text{isc}}^i}{\sum k_{\text{dis}}^i} \right)^{-1}, \quad (3)$$

where k_{isc}^i and k_{dis}^i ($i = x, y, z$) denote the rate constants of the ISC and dissociation of the triplet exciplex, respectively. We assumed an idealized sublevel depopulation in the present work: $k_{\text{isc}} = k_{\text{isc}}^x = k_{\text{isc}}^y$ and $k_{\text{isc}}^z = 0$. The dissociation rate of the triplet exciplex is not sublevel selective: $k_{\text{dis}} = k_{\text{dis}}^i$ ($i = x, y, z$).

The solid lines shown in Fig. 4 are obtained from the nonlinear least squares curve fits based on the modified Bloch equation. The analysis provides the intrinsic enhancement factors for the d-TM ($V_d = P_d/P_{\text{eq}}$) and the concomitant enhancement factor of d-TM and p-TM ($V_{\text{dp}} = P_{\text{dp}}/P_{\text{eq}}$). The obtained enhancement factors for d-TM (V_d) and for concomitant d-TM and p-TM (V_{dp}) were 50 and -30 for the EB^{2-} -DQ system in 1-PrOH, respectively. The time profiles observed in the different donor concentrations are well reproduced by using the same parameter set. This result strongly supports the fact that the fitting parameters obtained are reasonable. The kinetic parameters and enhancement factors are listed in Table 1. The value of the intrinsic enhancement factors ($V_d = 50$) for the EB^{2-} -DQ system in 1-PrOH is much larger than that for the EY^{2-} -DQ system ($V_d = 14$), suggesting that the SOC interaction governs the net polarization.

We measured the echo-FT-EPR spectra to clarify the solvent viscosity effects on the intrinsic enhancement factors of the polarization for the present system in several alcoholic solvents. The net-A CIDEP signals due to the SOC interaction in the triplet exciplex were also observed in MeOH, EtOH and 1-BuOH. The time-profiles observed in these alcohols were also well reproduced on the basis of the modified Bloch equation. The kinetic parameters and intrinsic enhancement factors obtained by FT-EPR spectroscopy are summarized in Table 1. The k_q values obtained from the analysis of the buildup of the FT-EPR signals well agree with those determined by the transient absorption experiments. We obtained the V_d values of 25, 40, and 56 in MeOH, EtOH, and 1-BuOH, respectively. Fig. 5 shows the plots of the V_d values listed in Tables 1 and 2 against solvent

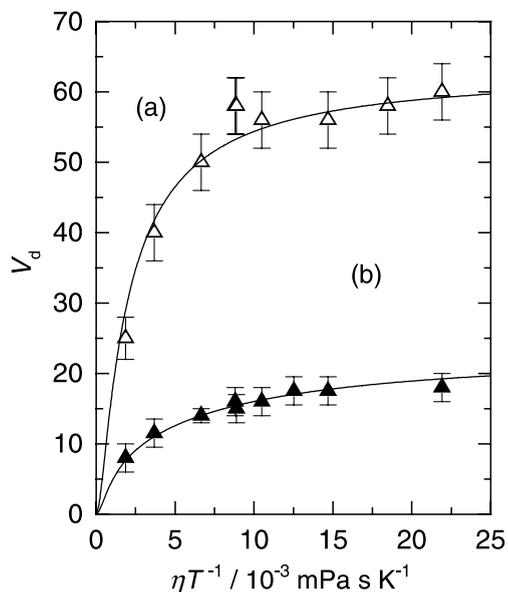


Fig. 5. Solvent viscosity dependence of the intrinsic enhancement factors (V_d) in alcoholic solvents listed in Tables 1 and 2 and [22]: EB^{2-} -DQ (a) and EY^{2-} -DQ (b) systems. The solid lines are the best fits obtained by the calculations based on Eq. (4).

viscosity (η). The data for the EY^{2-} -DQ system [22] are also shown for comparison.

4.3. Zero-field splitting constants of the triplet exciplex

The η dependence of the V_d value was analyzed by using the analytical expression derived by Serebrennikov and Minaev [31]. The effects of the anisotropic SOC on the electron spin polarization are described on the basis of the density matrix formalism. In the case of slow spin-lattice relaxation of the triplet exciplex, the expression for the P_d as the function of the external magnetic field (\mathbf{B}) and solvent viscosity is given as follows,

$$P_d(\mathbf{B}, \eta) = \frac{4\omega k_{\text{dis}}(D_{\text{EX}}D_- + 3E_{\text{EX}}E_-)}{45k_0^2k_1^2} \times \left(\frac{1}{1 + (\omega/k_1)^2} + \frac{4}{1 + 4(\omega/k_1)^2} \right), \quad (4)$$

where

$$k_1 = k_0 + 6D_r, \quad (5)$$

$$k_0 = k_{\text{dis}} + k_{\text{isc}}/3. \quad (6)$$

The rotational diffusion constant of the triplet exciplex for zero-field, D_r , is given by,

$$D_r = \frac{kT}{8\pi a^3 \eta}, \quad (7)$$

where a is the molecular radius. The ZFS parameters of the triplet exciplex are represented by D_{EX} and E_{EX} . The sublevel selective depopulation rates are described by $D_- = (k_{\text{isc}}^x + k_{\text{isc}}^y)/2 - k_{\text{isc}}^z$ and $E_- = (k_{\text{isc}}^x - k_{\text{isc}}^y)/2$.

The solid lines shown in Fig. 5 are obtained by the nonlinear curve fits based on Eq. (4). Assuming the ideal sublevel selective ISC ($k_{\text{isc}}^z = 0$) and the molecular radius of $a = 0.44$ nm for the triplet exciplex, the ZFS values of $D_{\text{EX}} = 0.073$ cm⁻¹ and $D_{\text{EX}} = 0.025$ cm⁻¹ were obtained for the EB²⁻-DQ and EY²⁻-DQ systems, respectively. The D_{EX} value in the former system is increased by a factor of about 3 compared with the latter system. The result suggests that the sublevels of the triplet exciplex are significantly perturbed by SOC interaction. The D_{EX} value results from the sum of the electron spin dipolar interaction (D_{SS}) and SOC interaction (D_{SO}) terms, $D_{\text{EX}} = D_{\text{SS}} + D_{\text{SO}}$. It has been reported that the D values of triplet states of the parent xanthene dyes depend on the atomic number of the halogen substituents. The D value of ³EB²⁻ is 1.8 times as large as that of ³EY²⁻ [32]. The present work clarified that the D values of the triplet exciplexes are much more sensitive to the heavy atom substituents compared with the T_1 states of the parent xanthene dyes. The SOC interaction due to iodine makes the dominant contribution to the D value of the triplet exciplex of EB²⁻ and DQ⁻.

5. Conclusions

Triplet exciplex formation as the reaction intermediate was verified in the photoinduced ET reaction from triplet EB²⁻ to DQ in alcohols by the observation of net A-polarized CIDEP due to

heavy atom induced SOC interactions. The temperature dependences of the quenching rates of triplet EB²⁻ and EY²⁻ by DQ are very similar to each other, suggesting similar activation energies of triplet exciplex formation in both systems. In contrast, significantly increased heavy atom effects on the radical yield and intrinsic enhancement factors of the net-spin polarization were obtained. The ZFS parameters of the triplet exciplex were determined on the basis of the viscosity dependence of the intrinsic enhancement factors of the electron spin polarization. The present results clarified that the heavy atoms significantly affect the D value of the triplet exciplex as well as the sublevel selective ISC rates.

Appendix A

The concentrations of the spin-equilibrated (C_T) and spin-polarized (C_{T^*}) triplet precursor and the time evolution of the escape radical yield depend on a function of the kinetic parameters and the acceptor concentration as follows:

$$C_T = \left(1 - e^{-t/T_1^T}\right) \cdot e^{-k_q[\text{DQ}]t}, \quad (\text{A.1})$$

$$C_{T^*} = e^{-t/T_1^T} \cdot e^{-k_q[\text{DQ}]t}, \quad (\text{A.2})$$

$$\phi_{\text{esc}}(t) = \phi_{\text{esc}}(1 - e^{-k_q[\text{DQ}]t}). \quad (\text{A.3})$$

In these equations, it has been assumed that $k_q[\text{DQ}] \gg k_T$. The evolution and decay of the FT-EPR signals were normalized by the thermally equilibrium intensity described as follows,

$$M_z(t)/M_{\text{eq}} = 1 + Ae^{-t/T_1^R} + Be^{-k_q[\text{DQ}]t} - \left(\frac{1}{T_1^R + k_q[\text{DQ}]}\right)t, \quad (\text{A.4})$$

$$B = \frac{1}{k_q[\text{DQ}] - \frac{1}{T_1^R}} \left(\frac{1}{T_1^R} - k_q[\text{DQ}]V_d \right), \quad (\text{A.5})$$

$$C = \frac{k_q[\text{DQ}]}{\frac{1}{T_1^R} - \frac{1}{T_1^T} - k_q[\text{DQ}]} (V_{\text{dp}} - V_d), \quad (\text{A.6})$$

$$A = -1 - B - C. \quad (\text{A.7})$$

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