

Spin–Orbit Coupling Induced Electron Spin Polarization: Influence of Heavy Atom Position

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Abstract: Echo-detected FT-EPR spectra have been observed for the quinone anion radical generated from the photoexcitation of duroquinone (DQ) in the presence of *N,N*-dimethylaniline (DMA) and its monohalogen substituents in 1-propanol. When DMA and 4-Cl DMA were used as the electron donor, the net-emissive polarization due to a triplet mechanism was observed. In contrast, the electron donors of 4-BrDMA and 4-IDMA gave unusual net-absorptive (A) CIDEP spectra of the DQ anion radical at the delay time of 200 ns between the laser and first microwave pulses. It was found that the enhancement factor of the net-A polarization remarkably depends on the heavy atom position in the donor. The net-A polarization observed is attributable to a spin–orbit coupling mechanism (SOCM). Simple explicit expressions have been given for the electron spin polarization generation due to SOCM.

Introduction

There has been considerable interest in the studies of electron spin polarization, since it provides valuable information on photochemistry and photophysics. CIDEP spectra are usually interpreted by two main mechanisms: a radical pair mechanism (RPM)¹ and triplet mechanism (TM).^{2,3} However, novel mechanisms recently have been proposed for the electron spin polarization production. Excited state molecules involved in the reaction systems sometimes create electron spin polarization. It has been shown that electron spin polarization is conserved during the triplet–triplet energy transfer in fluid solution, suggesting the importance of electron spin exchange interaction.⁴ The exchange effect plays an important role in the creation of the electron spin polarization in the electron spin transfer from the polarized triplet states to radicals.⁵ The transient EPR spectra generated from thermal populated triplet states also exhibit enhanced absorption.^{6–8} The radical triplet pair mechanism (RTPM) is the recent subject of much interest.^{9–11} In RTPM, electron spin polarization is created by the mixing of quartet and doublet spin states of triplet–double encounter complexes.

Recently, we proposed a new electron spin polarization mechanism, the spin–orbit coupling mechanism (SOCM) due to heavy atom effects.¹² When photosensitizers contain heavy atoms, net polarization can be created by SOC interaction. Unusual net absorptive CIDEP spectra were observed in xanthene dye sensitized photoinduced electron transfer reactions. The enhancement factor of the electron spin polarization increases with increasing atomic number of the halogen substitution in the photosensitizer. In contrast, the radical yield remarkable decreases with increasingly heavy atoms. The contact radical pair (RP) produced from the photoinduced electron transfer is the key intermediate for the generation of the electron spin polarization, because the direct SOC interaction due to heavy atoms is short-range interaction.

In this work, we present the effects of the heavy atom contained in the donor molecules which are not directly excited by photolysis. Echo detected FT-EPR spectra were measured for the radicals generated from the photoexcitation of duroquinone (DQ) in the presence of *N,N*-dimethylaniline (DMA) and its monohalogen substituents. Dependence of the electron spin polarization on the heavy atom position and the spin polarization production due to SOCM have been discussed.

Experimental Section

DQ was carefully purified by sublimation in the dark. 4-Chloro-*N,N*-dimethylaniline (4CIDMA) was synthesized from 4-amino-*N,N*-dimethylaniline by Sandmeyer reaction.¹³ 4-Iodo-*N,N*-dimethylaniline (4IDMA) was prepared by direct iodination of DMA.¹⁴ 4CIDMA and 4IDMA were purified by sublimation before use. 2-Bromo-*N,N*-dimethylaniline (4BrDMA) was prepared from 2-bromoaniline and methyl iodide, and 3-bromo-*N,N*-dimethylaniline (3BrDMA) was

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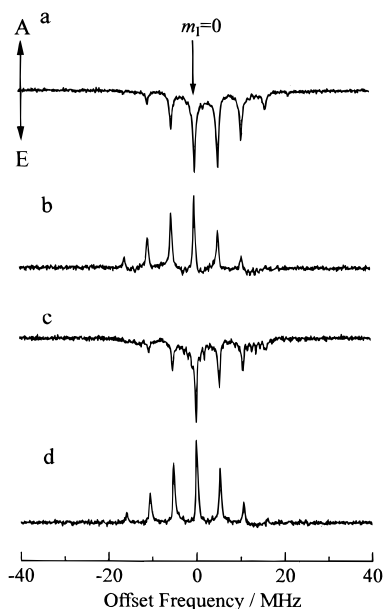


Figure 1. Echo FT-EPR spectra of $DQ^{+\bullet}$ generated from the excitation of DQ in the presence of DMA (a), 4BrDMA (b), 3BrDMA (c), and 2BrDMA (d) in 1-propanol at room temperature. The spectra were obtained at the delay time of 200 ns between the Nd:YAG laser (355 nm) and the first microwave pulses. The weak and complicated signals observed in part c are due to the neutral semiquinone radical (DQH^{\bullet}) produced from a hydrogen abstraction reaction.

synthesized by the literature method.¹⁵ DMA, 2BrDMA, and 3BrDMA were purified by distillation. 4-Bromo-*N,N*-dimethylaniline (4BrDMA) was purchased from Tokyo Kasei and was purified by recrystallization from the ethanol/ H_2O (1:1) solution. Fresh 1-propanol (reagent grade, Nacalai Co.), ethanol (Spectrophotometric grade, Wako Chem.), and methanol (HPLC grade, Nacalai Co.) were used as the solvent without further purification.

FT-EPR measurements were carried out using an X-band pulsed EPR spectrometer (Bruker ESP 380E) equipped with a dielectric resonator ($Q \sim 100$). The measurements of electron spin-echo signals and phase correction method were described in previous papers.¹² A Nd:YAG laser (Spectra-physics GCR-150, 355 nm, 30 Hz) was used as the light pulse source. All measurements were performed with the concentration of 3×10^{-3} mol dm^{-3} for donor and acceptor, respectively, at room temperature. The sample solution was deoxygenated by argon gas bubbling before and during the measurements, and was flowed into a quartz cell within the EPR cavity. The cation radical of 4BrDMA was measured to determine the g -value using an *in situ* electrochemical oxidation cell equipped with a platinum electrode in methylene chloride. Tetra-*n*-butylammonium perchlorate was used as the supporting electrolyte.

Results

Heavy Atom Effects. As shown in Figure 1a, the net-emissive (E) FT-EPR spectrum due to duroquinone anion radical ($DQ^{\bullet-}$) was observed from the photoexcitation of DQ in the presence of DMA as the electron donor. The spectrum was obtained at the delay time (t_d) of 200 ns between the laser and first microwave pulses. The net-E polarization is attributed to the triplet mechanism.¹⁶ We could not detect the signal of the counteraction radical, suggesting a short relaxation time. When 4CIDMA was used as the donor, a similar CIDEP spectrum was observed. On the other hand, photolysis of the DQ-4BrDMA system showed net-absorptive (A) CIDEP at t_d of 200 ns (Figure 1b). Laser photolysis of the DQ-4IDMA system also gave the net-A CIDEP spectrum. The net-A polarization

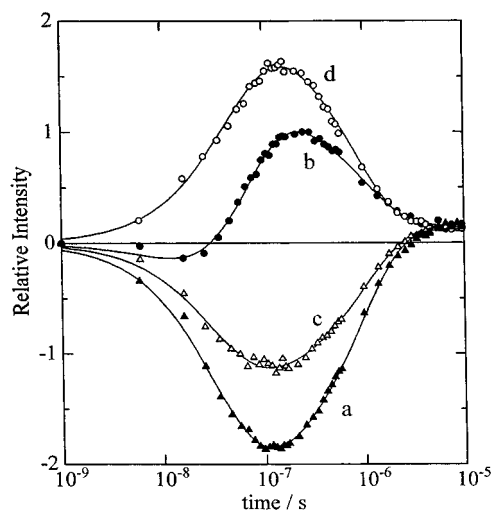


Figure 2. Time profiles of echo FT-EPR signals of the central hyperfine line ($m_1 = 0$) for $DQ^{+\bullet}$ observed from the photoexcitation of DQ in the presence of DMA (a), 4BrDMA (b), 3BrDMA (c), and 2BrDMA (d) in 1-propanol at room temperature. Solid lines were obtained from the curve fitting based on the nonlinear least-squares method using the sum of three exponential functions.

observed for $DQ^{\bullet-}$ would be caused by SOC interaction due to the heavy atoms in the donor as discussed later.

Effects of Bromine Atom Position in the Donor. Dependence of the electron spin polarization on the bromine atom position has been examined. Figures 1c and 1d depict the echo FT-EPR spectra generated from the excitation of DQ in the presence of 3BrDMA and 2BrDMA as the electron donor. The net-E-CIDEP spectrum due to $DQ^{\bullet-}$ was observed in the DQ-3BrDMA system, while net-A polarization was obtained from the DQ-2BrDMA system. The results indicate that the electron spin polarization of the acceptor anion radical significantly depends on the substituted position of the heavy atom in the donor.

Figure 2 shows the time profiles of the echo FT-EPR signals of the central ($m_1 = 0$) line of $DQ^{+\bullet}$ generated from the present systems. The signal intensities were normalized at those of the thermal population. We can describe these time developments using the sum of the exponential functions, since the electron spin relaxation times of the excited triplet state of DQ and $DQ^{\bullet-}$, as well as the time constant of the buildup of the A polarization, are significantly different from each other. The growth and decay curves of the polarized signals were analyzed by nonlinear least-squares curve fitting using the sum of the exponential functions:

$$S(t) = A_1 \{ \exp(-t/\tau_{\text{rise}}^E) - \exp(-k_d t) \} + A_2 \{ \exp(-t/\tau_{\text{rise}}^A) - \exp(-k_d t) \} + A_3 \{ 1 - \exp(-k_d t) \} \quad (1)$$

Where τ_{rise}^E and τ_{rise}^A are the buildup time constants of the net-E and A polarization's, respectively, and k_d is the decay rate of the transient EPR signals.

In the case of the DQ-4BrDMA system, the net-E CIDEP signal due to the TM was observed in the early time ($t_d < 100$ ns) and then the polarization changed to A. The buildup rate of the A polarization was 60 ns. Assuming a pseudo-first-order reaction, $k = 1/\tau_{\text{rise}}^A = k_{\text{et}}[Q]$, the rate constant for the electron transfer reaction (k_{et}) was obtained as 6.6×10^9 mol⁻¹ dm³ s⁻¹. This value is nearly identical to the diffusion-controlled rate in 1-propanol solution. The reduction of the donor concentration results in the decrease of the contribution of the TM and the increase of the buildup time constant of the net-A polarization.

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Only enhanced A polarization was observed at the donor concentrations less than $5 \times 10^{-4} \text{ mol dm}^{-3}$. The results suggest that the net-A CIDEP is generated by a bimolecular process.

The electron donors of 3BrDMA and DMA gave the net-E polarization of $\text{DQ}^{\bullet-}$, which shows the fast buildup ($\tau \sim 30 \text{ ns}$). The buildup rate constant corresponds to the electron spin relaxation time of the excited triplet state of DQ. It should be noteworthy that the absolute value of the apparent enhancement factor (f) due to the TM is smaller in the DQ-3BrDMA system ($f = -8.8$) than in the DQ-DMA one ($f = -13$). The factor is defined by $f = (S_{\text{max}} - S_0)/S_0$, where S_{max} and S_0 are the maximum and thermal populated EPR intensities, respectively. This is probably ascribed to the partial cancellation by the net-A polarization induced by the SOC interaction with bromine atom at the 3-position.

In contrast, only net-A polarization was observed in the DQ-2BrDMA system. The apparent enhancement factor of 10 was obtained. The buildup time constant of $\tau_{\text{rise}}^A = 60 \text{ ns}$ is the same as that of the DMA-4BrDMA system.

The curve fitting shown in Figure 2 gave the time constants of the decay (k_d^{-1}) of 0.7–1.2 μs . These values are much smaller than that of the electron spin relaxation time (T_1^R) of $\text{DQ}^{\bullet-}$ [reported $T_1^R = 6.7 \mu\text{s}$ in 2-propanol ($\eta = 2.39 \text{ cP}$ at 20°C)].¹⁶ The viscosity of 1-propanol ($\eta = 2.20 \text{ cP}$ at 20°C) is very similar to that of 2-propanol. No heavy atom effect on the decay rate of the transient EPR signals was observed. We examined the influence of the DQ concentration on the CIDEP time profile for the DQ-4BrDMA system. The variation of the growth and decay rates was negligible at concentrations less than $5 \times 10^{-3} \text{ mol dm}^{-3}$. Thus, the electron transfer reaction between $\text{DQ}^{\bullet-}$ and DQ is unimportant at the concentrations we used. It seems that the T_1^R of $\text{DQ}^{\bullet-}$ is reduced by long-range interaction between the acceptor and donor radicals in the present system.

Effects of Solvent Polarity. The FT-EPR spectra have been measured to clarify the polarity effects of solvents for the DQ-4BrDMA system in ethanol and methanol. The CIDEP spectra are governed by the TM in the early time ($t_d < 20 \text{ ns}$) and then gradually replaced by the spectra as shown in Figure 3a and 3b ($t_d = 200 \text{ ns}$), respectively. The CIDEP spectrum observed in methanol is quite different from that in 1-propanol, while the spectrum in ethanol is similar. In methanol solution, $\text{DQ}^{\bullet-}$ shows very weak A polarization of the hyperfine line of $m_I = -1$ component and emission for the $m_I = -2$ line. Figure 4c depicts the simulated spectrum with pure RPM using the EPR parameters of $g = 2.0041$ and $a^H = 0.19 \text{ mT}$ for $\text{DQ}^{\bullet-}$, and $g = 2.0055$ for $4\text{BrDMA}^{\bullet+}$. The g -value of $4\text{BrDMA}^{\bullet+}$ was determined by the analysis of the CW-EPR spectrum obtained from the electrochemical oxidation. The FT-EPR spectrum of $\text{DQ}^{\bullet-}$ observed in methanol is well reproduced by pure RPM. The result clearly indicates that the CIDEP spectrum in methanol is due to the hyperfine interaction and so-called Δg effect in the ST_0 mixing, suggesting the generation of solvent-separated RP. It can be deduced that the lifetime of contact RP is too short to create SOC induced polarization in methanol solution because of the fast solvation.

Discussion

Spin–Orbit Coupling Mechanism. The CIDEP spectra of $\text{DQ}^{\bullet-}$ observed in the present systems were significantly affected by the position of the bromine atom as well as the atomic number of halogen substituents in the donor, implying the participation of SOC interaction for the unusual net-A polarization. The buildup rate suggests that the net-A polarization is generated during the bimolecular process. The SOC interaction

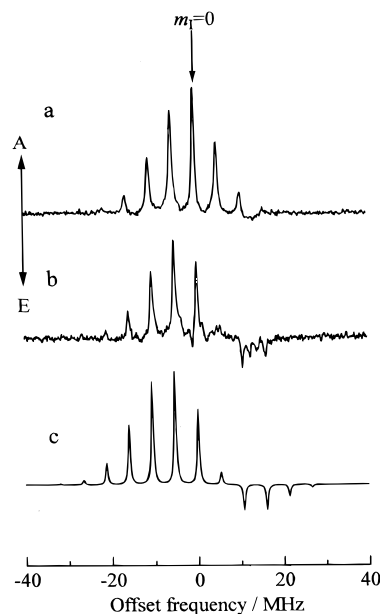


Figure 3. Echo FT-EPR spectra generated from the excitation of DQ in the presence of 4BrDMA in ethanol (a) and methanol (b). The spectra were measured at the delay time of 200 ns between the laser and first microwave pulses. The weak and complicated signals observed in part b are due to DQH^{\bullet} . The simulated CIDEP spectrum (c) with pure RPM using the EPR parameters of $g = 2.0041$ and $a^H = 0.19 \text{ mT}$ for $\text{DQ}^{\bullet-}$, and $g = 2.0055$ for $4\text{BrDMA}^{\bullet+}$.

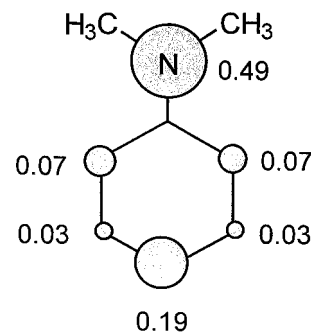


Figure 4. Electron spin densities of $\text{DMA}^{\bullet+}$ in the planar structure.

works effectively in the intermediate of exciplexes or contact RP's because of the short-range interaction. Since alcoholic solvents were used in the present work, the intermediate produced from the photoinduced electron transfer would be nearly a pure charge transfer complex or contact RP, ${}^3(\text{A}^-\text{D}^+)$. We assume that a sandwich-type contact RP has a sufficient lifetime to induce the back electron transfer by SOC interaction.^{12,17} We also postulate that the sublevel selective back electron transfer rate, k_b^{μ} ($\mu = x, y, z$), is proportional to the amount of singlet character, because the rate from the spin-allowed singlet state would be 2 or 3 orders of magnitude faster than that from pure triplet states.

Using a first-order perturbation treatment, the back-electron-transfer rate is written as,

$$k_b \propto |\langle {}^3(\text{A}^-\text{D}^+) | H_{\text{SO}} | {}^1(\text{A}^-\text{D}^+) \rangle|^2 / \Delta E \quad (2)$$

$$H_{\text{SO}} = \sum \sum \sum \xi_{kj} \mathbf{l}_{\mu j} \cdot \mathbf{s}_{\mu j}$$

where ΔE is the energy difference between the ${}^3(\text{A}^-\text{D}^+)$ and ${}^1(\text{A}^-\text{D}^+)$ states, and ξ_{kj} is the effective SOC interaction for j th electron in atom k ($\xi_{kj} = \alpha^2 Z / 2r_{kj}^3$, α is the fine structure

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constant).¹⁸ The intermolecular axis of the sandwich-type contact RP is taken as the z axis. We consider only one-centered SOC interaction at the heavy atom because of the short-range interaction. Thus, the important non-zero matrix elements in eq 2 are given by the mixing of the singlet charge transfer states, $^1(p_{\nu,h} \rightarrow a)$, where $p_{\nu,h}$ denotes the non-bonding p_x and p_y orbitals of halogen in the donor, and a is the LUMO of the acceptor. The two-electron wave functions responsible for the matrix elements are

$$\text{LUMO of the acceptor; } |a\rangle = \sum C_k \chi_k \quad (3)$$

$$\text{HOMO of the donor; } |d\rangle = \sum C_l \chi_l \quad (4)$$

$$\text{in plane p-orbitals of halogen; } |p_{\nu,h}\rangle, \quad \nu = x, y \quad (5)$$

Therefore, non-zero matrix elements are given by

$$\begin{aligned} \langle {}^3(A^-D^+) | H_{SO} | {}^1(A^-D^+) \rangle = \\ \langle {}^3(ad) | \sum \sum \sum \xi_{hj} I_{ij} \cdot \mathbf{s}_{mj} | {}^1(ap_{\nu,h}) \rangle = \\ \langle d | \xi_h \mathbf{I}_x | p_{y,h} \rangle + \langle d | \xi_h \mathbf{I}_y | p_{x,h} \rangle = \\ \langle C_h \chi_h | \xi_h \mathbf{I}_x | p_{y,h} \rangle + \langle C_h \chi_h | \xi_h \mathbf{I}_y | p_{x,h} \rangle \quad (6) \end{aligned}$$

where ξ_h is the effective SOC constant for the halogen atom and C_h is the atomic coefficient at halogen of the HOMO of the donor. We obtain the sublevel dependent back-electron-transfer rates

$$k_b^x \propto |\langle C_h \chi_h | \xi_h \mathbf{I}_x | p_{y,h} \rangle|^2 = C_h^2 \zeta_h^2 \quad (7)$$

$$k_b^y \propto |\langle C_h \chi_h | \xi_h \mathbf{I}_y | p_{x,h} \rangle|^2 = C_h^2 \zeta_h^2 \quad (8)$$

$$k_b^z \sim 0 \quad (9)$$

Where, $\zeta_h = \langle p_{z,h} | \xi_h | p_{z,h} \rangle$. Equations 7–9 indicate that the back-electron-transfer rates are dependent on the sublevel in the triplet contact RP and proportional to the square of the SOC interaction (ζ) as well as to the spin density on the heavy atom halogen ($\rho_h = C_h^2$).

The sublevel selectivity of the back-electron-transfer reaction in the triplet contact RP was discussed in the molecular coordinate, because the molecular selection rules govern the selectivity. We have to carry out the transformation from the molecular coordinates to the laboratory frame and treat the rotation of the triplet contact RP in the fluid solution. The procedure is quite similar to that of the normal TM.^{2,3} When a pair of radicals escapes with the rate of k_{esc} from the rotating contact RP (the electron spin relaxation time, T_1^T ; the rotational correlation time, τ_R), in high magnetic field, the enhancement factor (f) of the spin polarization is described as follows,

$$f = \frac{\langle S_z^* \rangle - \langle S_z^0 \rangle}{\langle S_z^0 \rangle} \frac{k_{\text{esc}} T_1^T}{1 + k_{\text{esc}} T_1^T} \quad (10)$$

where

$$\langle S_z^* \rangle = \frac{4}{15} \omega_0 DK \left\{ \frac{4}{4\omega_0^2 + (k_{\text{esc}} + \tau_R^{-1})^2} + \frac{1}{\omega_0^2 + (k_{\text{esc}} + \tau_R^{-1})^2} \right\} \quad (11)$$

with

$$K = \left\{ \frac{1}{2}(k_b^x + k_b^y) - k_b^z \right\} / k$$

$$k = \frac{1}{3}(k_b^x + k_b^y + k_b^z)$$

Here, $\langle S_z^0 \rangle$ corresponds to the magnetization due to the Boltzmann population and ω_0 is the microwave angular frequency. In the present treatment, one of the ZFS parameters of E is assumed to be zero. Using the Debye equation ($\tau_R^{-1} = kT/8\pi a^3 \eta$), we estimated the τ_R value of 8×10^{-10} s in 1-propanol at room temperature, where the molecular radius of $a = 0.4$ nm was assumed for the contact RP. This means that the present condition satisfies the slow rotational limit ($\omega_0 \tau_R \gg 1$). The escape rate would be approximated as $k_{\text{esc}} \sim 10^9$ s⁻¹. Thus, eq 11 is reduced to

$$\langle S_z^* \rangle = 8DK/15\omega_0$$

Assuming ideal selectivity of the back-electron transfer, $D \sim 0.02$ cm⁻¹ and $T_1^T \sim 2 \times 10^{-8}$ s for the contact RP, we obtained the maximum enhancement factor due to SOCM of 45. The intrinsic enhancement factor is expected to be larger than the apparent factor (6–10) observed, because the A polarization due to SOCM is partially cancelled by the E-TM. The observation of the net-A polarization in the DQ-4BrDMA and DQ-2BrDMA systems suggests that SOC enhances the back-electron transfer from the upper sublevels in the triplet contact RP's.

Effects of the Halogen Position. We can assume that ρ_h is proportional to the π -electron spin density at the halogen-substituted carbon of the donor cation radical. Spin densities of DMA^{•+} estimated from the EPR spectrum¹⁹ are shown in Figure 4. Since the spin densities are very small at the 3 and 5 positions, the SOC interaction due to the bromine atom is too weak to create sufficient A polarization over the E-TM in the DQ-3BrDMA system. In the DQ-2BrDMA system, no E-TM was observed and the apparent enhancement factor ($f = 10$) for the A polarization was larger than that of the DQ-4BrDMA system ($f = 6.1$). The result indicates the largest effect of bromine at the ortho position of the cation radical. This is probably due to the structural change in 2BrDMA^{•+} induced by the steric interaction between the bromine atom and methyl group.

In order to obtain the optimized structures for 4BrDMA and 2BrDMA, we carried out the semiempirical restricted Hartree–Fock calculations with the AM1 approximation.²⁰ The results indicate that the dihedral angles between the nitrogen p-orbital of the dimethylamino group and aromatic ring–C–Br plane are $\sim 90^\circ$ and $\sim 35^\circ$ in the ground states of 4BrDMA and 2BrDMA, respectively. It can be deduced that the direct overlap between the unpaired p-orbital of the nitrogen atom and *o*-bromine atom leads to the enhancement of the SOC interaction in 2BrDMA^{•+}.

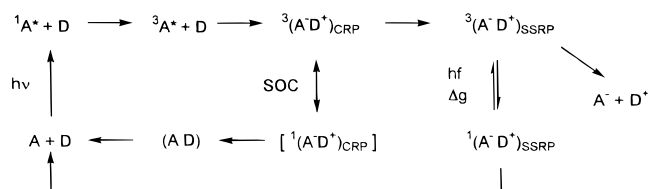
Contact RP and Solvent-Separated RP. The present results show that the unusual CIDEP spectra obtained from the excitation of DQ in the presence of the DMA derivatives with heavy atoms in ethanol and 1-propanol can be interpreted by the SOCM. It can be considered that the contact RP is generated

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Scheme 1



as the reaction intermediate in these solvents. On the other hand, in methanol the normal RPM (ST_0 mixing) governs the CIDEP spectrum of the same donor-acceptor system, indicating the generation of the solvent-separated RP as the reaction intermediate. Thus, we can depict the reaction process for the present photoinduced electron transfer system as shown in Scheme 1. In methanol, the lifetime of the contact RP would be too short to create the net-A polarization due to the SOCM. Heavy atom effects on the CIDEP spectra are interpreted in terms of sublevel selective back-electron-transfer reaction which is induced by the singlet character, $^1(A-D^+)_{CRP}$ in the triplet contact RP.

Conclusion

The present results show that the atomic number of halogen substituents as well as the position of the heavy atom in the donor significantly affect the CIDEP spectra of the quinone anion radical generated from the photoexcitation of DQ in the presence of monohalogen substituted DMA's. The unusual net-A polarization observed is explained in terms of SOC interaction which induces sublevel selective back-electron transfer in the triplet exciplexes or contact RP's. It is also obtained that the electron spin polarization due to SOCM is very sensitive to the solvent polarity. Simple explicit expressions have been given for the electron spin polarization generation due to SOCM.

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