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Spin−Orbit Coupling-Induced Electron Spin Polarization Observed in Photosensitized Electron Transfer Reactions between Xanthene Dyes and *p*-Quinones

Akio Katsuki, Kimio Akiyama, Yusaku Ikegami, and
Shozo Tero-Kubota*

Institute for Chemical Reaction Science
Tohoku University, Katahira 2-1-1
Aobaku, Sendai 980, Japan

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During the past 2 decades, a number of studies have been concerned with the role of spin−orbit coupling (SOC) interaction in chemical reactions, such as the recombination of diradicals[1−4] and photoinduced electron and hydrogen transfer reactions.[5−9] Direct SOC interaction due to heavy atoms decreases sharply as the distance of pair radicals increases and works effectively in exciplexes or contact radical pairs (RPs). Since the SOC interaction causes sublevel selective reactions from the triplet exciplex or contact RP to a singlet state product, the electron spin polarization should be observed in the transient radicals which escaped from the nonequilibrated intermediates.

In this communication, we present evidence for SOC-induced electron spin polarization in the photoinduced electron transfer reactions between xanthene dyes and *p*-quinones. Remarkable heavy atom effects on the radical yield and enhancement factor of the CIDEP signals were observed.

Quinones used were carefully purified by double sublimation in the dark. Xanthene dyes were purified by recrystallization from ethanol. Fresh 1-propanol (reagent grade, Nacalai Co.) was used as the solvent without further purification. The time-resolved continuous wave (CW) EPR spectroscopy was described in a previous paper.[10] FT-EPR measurements were carried out using an X-band pulsed EPR spectrometer (Bruker ESP 380E) equipped with the dielectric resonator ($Q \sim 100$).[11] All spectra were measured at room temperature.[12]

The time-resolved CW-EPR spectra were measured for quinone anion radicals generated from the photosensitized reduction of 2,5-dichloro-*p*-benzoquinone (Cl_2BQ), *p*-benzoquinone (BQ), and duroquinone (DQ) with eosin Y ($FlBr_4^{2-}$). Net enhanced absorptive CIDEP spectra were observed in these systems. The unusual absorptive CIDEP spectrum is not ascribed to the triplet mechanism (TM), since the emissive TM is observed at the fast initial step of buildup of the signals by FT-EPR measurements presented later. It should be noted that the observed spectra are all absorptive, despite the different *g*-values for these quinone anion radicals ($Cl_2BQ^{\bullet-}$; 2.0055, $BQ^{\bullet-}$; 2.0048, and $DQ^{\bullet-}$; 2.0041). If the normal radical pair mechanism (RPM) is operative for the creation of the spin polarization, then the all-absorptive CIDEP spectral pattern should be affected by *g*-values of the radical pairs.[13,14] The polarization intensities ($7-\ 10P_{eq}$) observed are larger than expected from the reaction of the spin-equilibrated triplet state ($1.3P_{eq}$), where P_{eq} is the signal intensity at the Boltzmann population in the Zeeman splitting of a radical. It is known that the radical−triplet mechanism (RTPM) induces the hyperfine-independent polarization.[15−17] However, this mechanism is unlikely to be significant in the present system, because net emissive CIDEP should be detected from the triplet precursor.

In order to examine heavy atom effects on the electron spin polarization, we measured the CIDEP spectra for $DQ^{\bullet-}$ generated by the use of several sensitizers. Net absorptive CIDEP spectra were also observed in the photoreaction using dibromofluorescein ($FlBr_2^{2-}$) and erythrosin B (FlI_4^{2-}) as sensitizers. On the other hand, when fluorescein (Fl^{2-}) was used as the sensitizer, no CIDEP signal was obtained, while the intensity of the conventional EPR spectrum detected by 100 kHz field modulation was very strong. In Figure 1 are shown the time profiles of the transient CW-EPR signals of the central line ($m_I = 0$) of $DQ^{\bullet-}$ generated by photosensitization with xanthene dyes. The maximum intensities of the CIDEP signals significantly depend on the sensitizer. We estimated the enhancement factor of the electron spin polarization, $(I_{max} - I_0)/I_0$, where I_{max} and I_0 are the maximum and thermally equilibrated intensities obtained from the time-resolved CW-EPR spectra, respectively. As shown in Table 1, a striking heavy atom effect on the enhancement factor was observed. This factor increases with increasing atomic number of the halogen substituents in xanthene dye.

The relative radical yields were estimated from the conventional EPR intensities, which were calibrated with the triplet yields and molecular extinction coefficients of the sensitizers and the laser light intensities. In contrast to the enhancement factor, the radical yield observed remarkably decreases with increasingly heavy atoms. Heavy atom effects on the radical yield in the photoinduced electron transfer can be interpreted in terms of SOC interaction between the triplet exciplex or contact RP and the singlet ground state.[5,6] SOC interaction is effective only in the case of a direct contact between the radicals inducing the changes of spin and orbital simultaneously. The observation of the heavy atom effect on the radical yield clearly indicates the formation of the triplet exciplex or contact RP as the reaction intermediate in the present system. It is noteworthy

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[10] Katsuki, A.; Tero-Kubota, S.; Ikegami, Y. *Chem. Phys. Lett.* **1993**, *209*, 258. For time-resolved CW-EPR measurements, a dye laser (Lumonics HD-300) pumped by excimer laser (Lumonics HE-400, XeCl 308 nm) was used as the light pulse source.

[11] Electron spin echo (ESE) detection technique was used to eliminate the dead-time problem in the FID measurements. The echo signal was extracted from the transient signals generated from a two-pulse ($\pi/2-\tau-\pi$, τ = 88 ns) sequence. The unwanted FID signals were suppressed by 4-step phase cycling (Keijzers, C. P.; Reijerse, E. J.; Schmidt, J., Eds. *Pulsed EPR: a new field of applications*; North Holland: Amsterdam, 1989). The FT-EPR spectroscopy was equipped with a Nd:YAG laser (Quanta-Ray GCR-14S, 532 nm) as the light source.

[12] The sample solution was deoxygenated by argon gas bubbling and flowed into a quartz cell within EPR cavity. Measurements were performed on the 1-propanol solution with concentrations: 1×10^{-4} mol dm^{-3} for xanthene dyes and 1×10^{-3} mol dm^{-3} for quinones. In the present experimental conditions, the electron transfer mainly occurs from the excited triplet states of sensitizer to the acceptor quinone (Koizumi, M.; Kato, S.; Mataga, N.; Matsuura, T.; Usui, Y. *Photosensitized reaction*; Kagaku-dojin: Tokyo, 1978).

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[14] The g-value of the counterradical, $FlBr_4^{\bullet-}$, is uncertain. If the g-value of $FlBr_4^-$ is larger than 2.01, it is possible to create the net absorptive spin polarization observed. However, this value seems to be unreasonable, since it is known that the reduced form of eosin Y, $FlBr_4H_2^{\bullet-}$ has the g-value of 2.0025.

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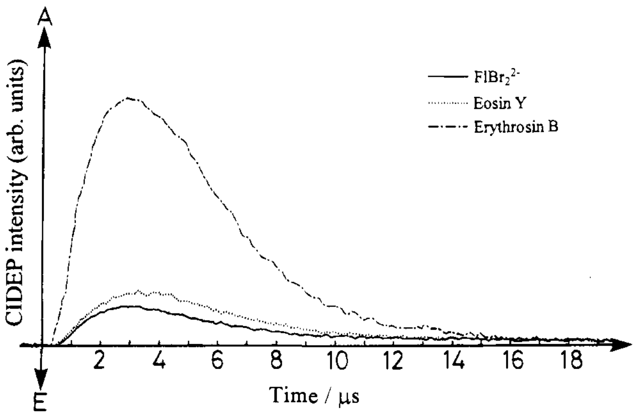


Figure 1. Time profiles of CW-EPR signals of the central hyperfine line ($m_I = 0$) for duroquinone anion radicals observed from the photosensitized reactions with dibromofluorescein, eosin Y, and erythrosin B in 1-propanol at room temperature. In the case of fluorescein, the transient EPR signal is too weak to be observed by direct detection method with our spectrometer.

Table 1. Molar Extinction Coefficient (ϵ) and S_1-T_1 Intersystem Crossing Yield (ϕ_{isc}) of Xanthene Dyes and Relative Radical Yields and Enhancement Factors for the Various Xanthene Dyes−Duroquinone Reaction Systems

	ϵ^a	$\phi_{isc}{}^b$	relative radical yield	enhancement factor f^c
fluorescein (Fl^{2-})	7.2×10^4	0.03	~5	0
dibromofluorescein ($FlBr_2{}^{2-}$)	8.7×10^4	0.29	1.0	6.2
eosin Y ($FlBr_4{}^{2-}$)	1.1×10^5	0.32	1	6.8
erythrosin B ($FlI_4{}^{2-}$)	1.1×10^5	0.69	0.25	58

[a] λ_{max} = 485 (Fl^{2-}), 516 ($FlBr_2{}^{2-}$), 528 ($FlBr_4{}^{2-}$), and 535 nm ($FlI_4{}^{2-}$), respectively. [b] Reference 23. [c] $f = (I_{max} - I_0)/I_0$, where I_{max} and I_0 are the maximum and thermally populated EPR intensities observed, respectively.

that the present heavy atom effects are significantly sensitive to the solvent polarity and viscosity.[18]

FT-EPR measurements were carried out to clarify the dynamics of the spin polarization and to search for the contact RP or exciplex in the initial stage. Figure 2 shows the FT-EPR spectra of $DQ^{\bullet-}$ generated by the photoinduced electron transfer from $^3FlBr_4{}^{2-}$. The spectra observed at the delay time between the laser and first microwave pulses of $\tau_d < 60$ ns exhibit emission signals, while for $\tau_d > 100$ ns, enhanced absorption was measured. Based on the nonlinear least-squares curve fitting for the buildup rate of the absorptive CIDEP,[19] assuming the pseudo-first-order reaction, a rate constant of 2.8×10^9 M^{-1} s^{-1} for the electron transfer reaction was obtained. This value is nearly identical to the diffusion-controlled rate in 1-propanol solution. The emissive polarization in the initial stage would be generated from the polarized T_1 state of $FlBr_4{}^{2-}$. The polarization pattern observed is consistent with the anisotropic ISC in the T_1 state of $FlBr_4{}^{2-}$.[10] At $\tau_d \sim 80$ ns, a dispersive spectrum was clearly observed. This is attributed to the effect of spin-correlated RP as discussed in previous papers.[20-22] We could not detect the $FlBr_4{}^{\bullet-}$ signal by the pulsed EPR method, suggesting a short electron spin transverse relaxation time.

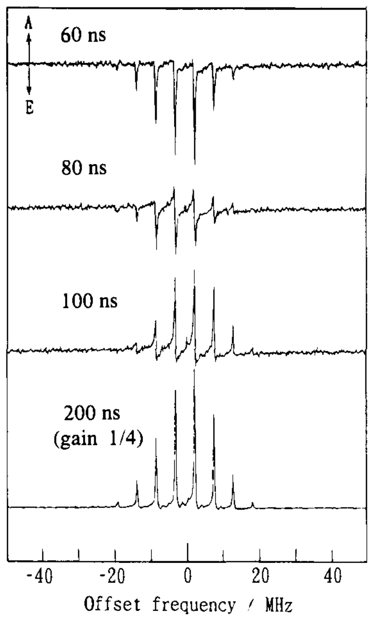
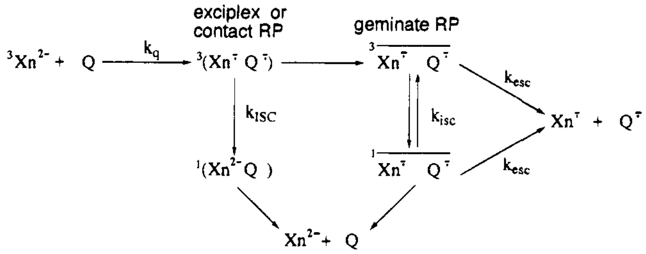


Figure 2. FT-EPR spectra of duroquinone anion radical generated by the photoinduced electron transfer from eosin Y in 1-propanol at room temperature. The delay times between the laser (Nd:YAG 532 nm) and first microwave pulses are shown.

Scheme 1



Thus, the reaction process is summarized as shown in Scheme 1, where k_q and k_{esc} are the rate constants for the quenching of $^3Xn^{2-}$ and the escape from the geminate RP, respectively. k_{ISC} and k_{isc} are the ISC rate constants for the triplet exciplex or contact RP and for the geminate RP, respectively.

The SOC interaction causes simultaneous changes of the orbital angular and spin operators, leading to the sublevel selective back electron transfer from the triplet exciplex or contact RP to the singlet ground state. Therefore, a nonequilibrium spin population may be induced in the intermediates. The observation of net absorptive CIDEP indicates that SOC enhances the ISC rate from the upper sublevel(s) of the triplet exciplex or contact RP to the singlet ground product. The mechanism for the present SOC-induced electron spin polarization is similar to the normal TM, but their spin dynamics and polarization are different.

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(18) We measured the enhancement factor for $FlBr_4{}^{2-}$−DQ system in several alcoholic solutions: the enhancement factors obtained were 4, 6, and 11 for methanol, absolute ethanol, and 1-butanol, respectively. The addition of water significantly diminished the enhancement factor.

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