

One- and Two-Dimensional EPR Studies on the Radical Pair Generated by the Photoreduction of 9,10-Anthraquinone-1,5-disulfonate in Aerosol OT Reverse Micelles

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Spin-correlated radical pairs (SCRPs) formed by the photoreduction of 9,10-anthraquinone-1, 5-disulfonic acid (1,5-AQDS) disodium salt in aerosol OT (AOT) reverse micelles were studied using time-resolved and pulsed electron paramagnetic resonance (EPR) techniques. Photoirradiation of 1,5-AQDS in AOT micellar solution exhibited a strong polarized EPR spectrum in the presence of water-soluble hydroquinones (H_2Q). The polarization patterns varied from E^*/A of radicals to the antiphase structure (APS) of SCRPs in the early delay period after the laser pulse irradiation. By analysis of the spectra, the radicals were assigned to the corresponding benzoquinone anion radicals. On the basis of our results, the initial process of the 1,5-AQDS triplet quenching may be the electron transfer from H_2Q . The consecutive reaction mechanism was proposed for the generation of the SCRPs within the water pools. The slower evolution of the SCRPs polarization is a result of the sequential radical reactions followed by the spin selective reaction of the radical pair (RP). The peak-to-peak distance of the APS pattern and also the component line width were affected by the molar ratios between water and AOT ($[H_2O]/[AOT]$, w). A decreasing w value resulted in an increase in the magnitude of the exchange interaction, $|2J|$. From the peak-to-peak width of each APS spectral shape in the time-resolved EPR (TR-EPR) spectrum, at $w = 20$, the value of $|2J|$ was estimated of 0.04 mT. The value was extremely small compared with those of SCRPs reported previously and corresponded to 1.9 nm as the average separation of the radicals. Comparatively, the half-life of the APS polarization was longer than the T_1 values of the typical organic free radicals. The results suggest that the diffusion of the radicals was strongly restricted within the water pool of AOT micellar solution.

Introduction

Time-resolved (TR) and pulsed electron paramagnetic resonance (EPR) techniques have been successfully applied to the identification and characterization of reaction intermediates in photochemical reactions. The triplet quenching of quinones by electron and hydrogen donors has been extensively investigated using optical and TREPR methods. During the photoreductions of quinones and carbonyl compounds, polarization of the spin-correlated radical ion pair (SCRPs) was often observed both in alcoholic solutions and in the confined system.^{1–9} Of special interest, the photochemistry of 9,10-anthraquinonesulfonates (AQS) in aqueous solution has been investigated because of its relevance to important photosensitizing effects.^{10–12} Reverse micelles represent a model for water pockets in biomembranes and also create a unique environment for studying the behavior of solubilized species. Turro and Khudyakov have described the polarization of the SCRPs in reverse micellar solutions.⁹ The triplet state of the 9,10-anthraquinone-2,6-disulfonic acid disodium salt was quenched by an inorganic anion and exhibited a polarized EPR spectrum. To explain the unique behaviors of the SCRPs signals, the authors suggested the formation of associates such as an $AQ\bullet^-/Na^+/SO_3\bullet^-$ triad.

In this report, we present our investigations of the SCRPs produced by the photoreduction of 9,10-anthraquinone-1, 5-disulfonate (1,5-AQDS) in the presence of organic quenchers in aerosol OT (AOT) reverse micelles. The size of the water pool of this system has been well-defined.¹³ Size effects of the water

pool on the magnetic properties of SCRPs, which were composed by water-soluble organic radicals, were studied. Although the normal chemically induced dynamic electron spin polarization (CIDEP) signals were obtained in homogeneous water solution, strong SCRPs signals were observed in the presence of the quenchers in the confined system. Both the peak-to-peak width of the antiphase structure (APS) pattern and the component line width were affected by the water pool size indicating changes of the magnetic interactions between the paired radicals.

Experimental Section

Continuous wave (CW) TR-EPR system was described in a previous paper.¹⁴ A Nd:YAG laser (Spectra Physics GCR 150; 3rd harmonics, 355 nm) was used as the light pulse source. Pulsed EPR measurements were carried out using a commercial pulsed EPR spectrometer (Bruker ESP 380) equipped with a dielectric resonator. For detection of the free induction decay (FID), the width of $\pi/2$ pulse set to 16 ns and the CYCLOPS routine was applied to remove the image signals. Backward linear prediction and singular value decomposition (LPSVD) procedures were used to reconstruct the missing signal during the dead time of the spectrometer, which was about 100 ns. Two-dimensional nutation experiments were carried out using the procedures as previously reported.¹⁵ For the nutation pulse, the width was started from 8 ns with increments of 8 ns. Data sets of [512, 128] were subjected to two-dimensional Fourier transformation (FT). Prior to FT zero-filling in the axis of nutation frequency and Gaussian window functions were applied to both axes.

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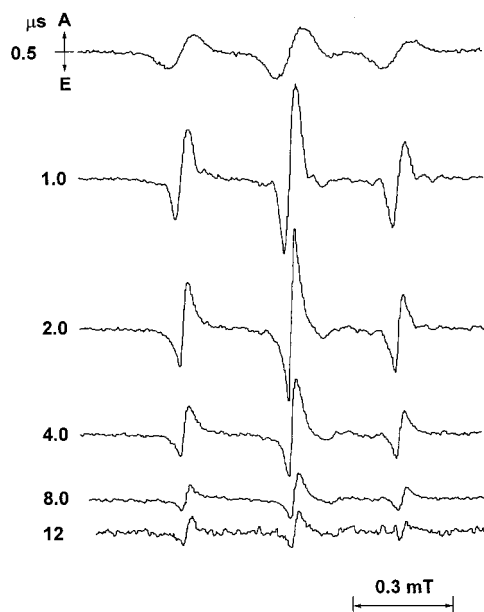


Figure 1. CWTR-EPR spectra observed by the laser pulse irradiation (355 nm) to 15-AQDS (5×10^{-4} M) in AOT reverse micellar solution ($w = 30$) in the presence of H₂QDS (1×10^{-3} M). The spectra were taken at different times after the laser pulse.

Solutions containing the reverse micelles were prepared by dissolving AOT (0.3 M) in isooctane, dissolving the water-soluble components in water, and then mixing both solutions using quantities that would result in the desired molar ratios between water and AOT ($[H_2O]/[AOT]$, w). The micellar solutions were sonicated for at least 30 min prior to the TR-EPR and pulsed EPR experiments and deaerated by bubbling argon gas before and during the measurements. AOT (Nacalai tesque) was purified according to procedures as previously reported.¹⁶ The disodium salt of 1,5-AQDS (Tokyo Kasei) was recrystallized twice from water–ethanol before use. Hydroquinone (H₂Q, Nakali Tesque), hydroquinone sulfonic acid potassium salt (H₂QS, Tokyo Kasei), hydroquinone-2,5-disulfonic acid dipotassium salt (H₂QDS, Aldrich), and the solvent isooctane (Nakali Tesque, spectrophotometric grade) were used without further purification.

Results

The TREPR spectra exhibited by the excitation of 1,5-AQDS (5×10^{-3} M) in the presence of H₂QDS (1×10^{-2} M) irradiated with the Nd:YAG laser (355 nm) in an AOT reverse micellar solution ($w = 20$) are shown in Figure 1. The spectra were taken at the indicated times after the laser pulse irradiation. Well-separated three-line spectra were easily assigned to the benzoquinone-2, 5-disulfonate (QDS) anion radical ($a^H(2H) = 0.315$ mT, $g = 2.0045$). However, in the absence of 1,5-AQDS, the TR-EPR spectrum was not observed using the excitation with light (355 nm). The APS spectral pattern that was observed in each hyperfine (hf) line indicated SCRP formation in reversed micellar solutions. The polarization of SCRP decayed with a rather slow rate and remained at 12 μs after the laser pulse (Figure 1). The EPR pattern and line widths did not depend significantly upon time except in the time range of up to 1 μs after the laser pulse irradiation. A linear relation, with the slope of unity, was observed between the signal intensity and the incident laser power. The results indicated that a one-photon excitation process is dominant within the range of the laser power examined. As shown in Figure 2, SCRP polarizations

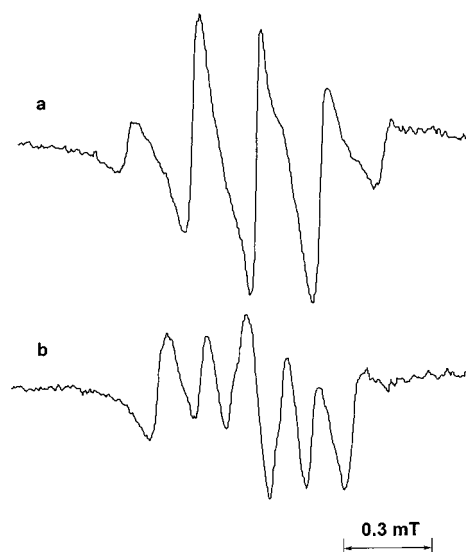


Figure 2. CW TR-EPR spectra observed by the laser pulse irradiation (355 nm) to 15-AQDS (5×10^{-4} M) at 1 μs after the laser pulse in AOT reverse micellar solution ($w = 20$) in the presence of (a) H₂Q (1×10^{-2} M) and (b) H₂QS (1×10^{-2} M).

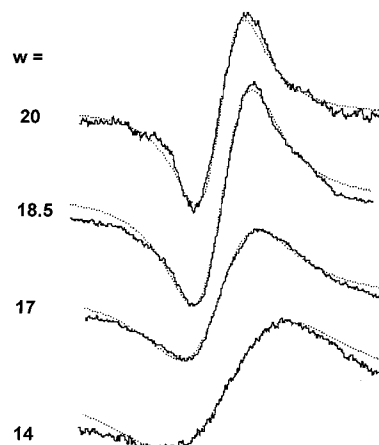


Figure 3. Effects of water pool size on the antiphase line width in AOT reverse micellar solution. The CW TR-EPR signals correspond to the central peaks of the QDS anion radical and are observed at 2 μs after the laser pulse irradiation.

TABLE 1: Hyperfine Splitting Parameters and g Values of Water-Soluble Benzoquinone Anion Radicals

radical	hfs coupling (mT)	g value
benzoquinone	$a(4H) = 0.235$	2.0043
benzoquinone-2-sulfonic acid	$a(1H, 3) = 0.265$	2.0045
	$a(1H, 5) = 0.155$	
	$a(1H, 6) = 0.305$	
benzoquinone-2,5-disulfonic acid	$a(2H, 3,6) = 0.315$	2.0046

were also observed by the irradiation of 1,5-AQDS in the presence of H₂Q and H₂QS in AOT reverse micelles. The hfs constants for each anion radical were assigned and summarized in Table 1 with their g values.

As shown in Figure 3, both peak-to-peak splitting and line width of the APS spectral shape were affected by the water contents in the AOT reverse micellar solution. Figure 3 shows the TREPR signals that correspond to the central peak of the QDS anion radical, which was observed at 2 μs after the laser pulse irradiation. Decreases in the w value resulted in significant increases in the line width and diminishing intensity of SCRP signals below $w = 14$, at concentrations of 5×10^{-3} M for

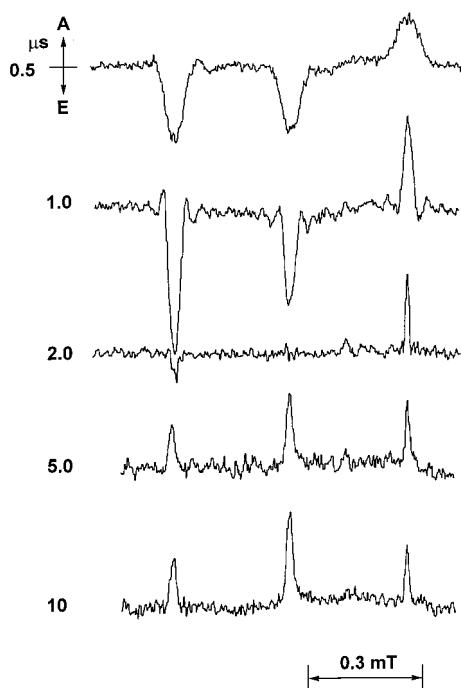


Figure 4. CW TR-EPR spectra observed by the laser pulse irradiation (355 nm) to 15-AQDS (5×10^{-3} M) in an aqueous solution and in the presence of H₂QDS (1×10^{-2} M). The spectra were taken at different times after the laser pulse.

1,5-AQDS and 1×10^{-2} M for H₂QDS. The distances between the maximum and minimum of each hf APS component in the TR-EPR spectra was also dependent on the w values. Detailed analysis of the APS spectral shape will be discussed in the latter section in terms of the SCRP mechanism of electron spin polarization.

In contrast to the results of AOT reverse micelles, CIDEP spectra, which were composed of E(TM) and E/A(RPM), were observed in water as shown in Figure 4. The well-separated three-line spectrum was easily assigned to the QDS anion radical. The phase of polarization was E*/A at initial period and was change to A/A* at 5 μs after the laser pulse. The initial E*/A polarization was ascribed by the superposition of TM and RPM. On the other hand, A/A* was denoted by E/A (RPM) and A, where A is attributable to the contribution from the thermal equilibrated species.

The initial step of the photoreaction may be the photoinduced electron transfer from H₂QDS to ³(15-AQDS)* as will be discussed in a later section. However, in the CW experiments, in AOT reverse micelles or in water, neither the 1,5-AQDS anion radical nor the neutral semiquinone (15-AQDSH) radical was detected. The 1,5-AQDSH radical was expected to be produced by protonation to the corresponding anion radical. To obtain the information on the reaction pathway and on the SCRP formation in AOT reverse micelles, we carried out pulsed EPR measurements, which have better time resolutions as compared to that of our TR-EPR system. Figure 5 shows the FT-EPR spectra observed by laser pulse irradiation of 1,5-AQDS, in the presence of H₂QDS and in AOT reverse micelles. The spectrum observed at 1.5 μs after the laser pulse agreed well with that of the CW TREPR experiments. On the other hand, the polarization patterns observed at the initial period (30–200 ns) were substantially different than those observed at later times. The main contributions to the spectra were the E/A+E polarization patterns. The rise time of E-polarization was within the range

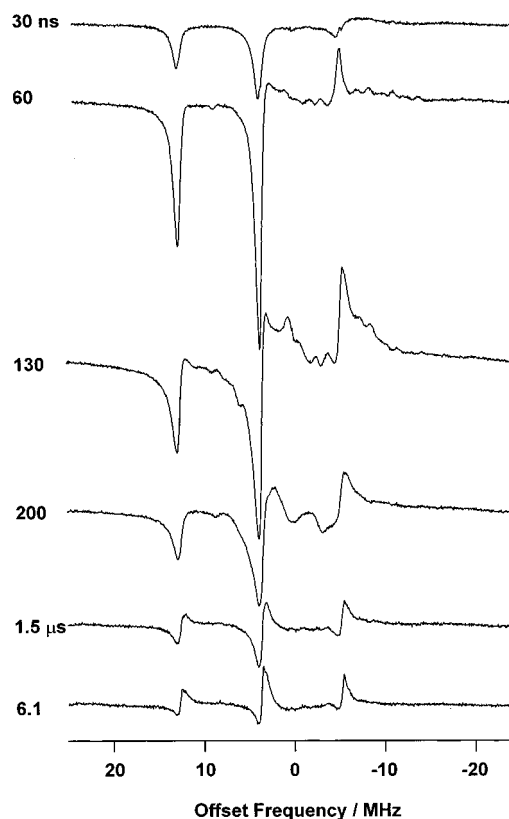


Figure 5. FT-EPR spectra observed by the laser pulse irradiation (355 nm) to 15-AQDS (5×10^{-3} M) in AOT reverse micellar solution ($w = 20$) in the presence of H₂QDS (1×10^{-2} M). The spectra were taken at different times after the laser pulse.

of the response time of our pulsed EPR system. The temporal behavior of E-polarization was equivalent to the TM polarization observed for the homogeneous solution. The APS contribution was negligible small within this period of time, indicating that the formation of SCRP is rather slow. From the spectra exhibited at 60 and 130 ns after the laser pulse irradiation, weak signals were observed, which indicate rather complicated hf structures and has different g value than the AQDS anion radical. The weak components were reproducible using hfs constants of 0.039 mT (1H), 0.059 mT (1H), 0.099 mT (2H), 0.182 mT (1H), 0.198 mT (1H), and 0.340 (1H). The g value was evaluated to be 2.0033. The values were in good agreement with those of neutral semiquinone radical, 15-AQDSH, obtained from the analysis of the spectrum in acidic water (pH = 4).

To confirm the slow rise of the SCRP, we measured the two-dimensional nutation spectra at different times after the laser pulse irradiation. This method will be able to distinguish the spin multiplicity of the paramagnetic species on the 2D counter map.^{15,17,18} As shown in Figure 6, the two-dimensional nutation spectra, in which the nutation pulses were applied at 50 ns (a) and at 500 ns after the laser pulse irradiation (b), clearly indicated differences between the two counter maps. The species that provided the nutation frequency of 22–23 MHz correspond to the doublet species. The frequency was confirmed by comparison to the results using the stable nitroxide radical (TEMPO), and performed under identical instrumental conditions. The presence of the $S = 1$ species in the system should result in additional peaks to appear around twice in the nutation frequency axis. At 50 ns, the contribution from $S = 1$ component was significantly smaller as compared to that of the doublet. However, at 500 ns, the peaks around 47 MHz were large. These

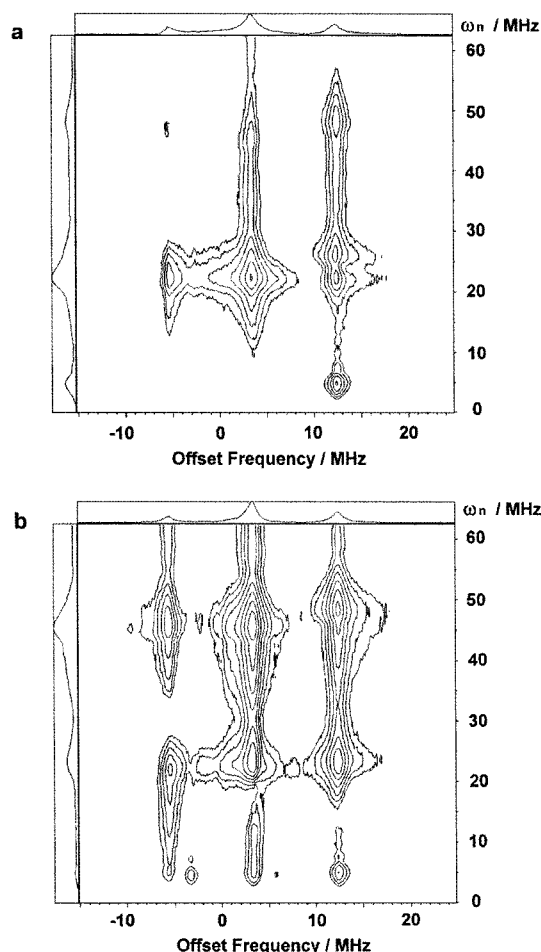


Figure 6. Two-dimensional FT-EPR nutation spectra observed at (a) 50 ns and (b) 500 ns after the laser pulse irradiation to 15-AQDS (5×10^{-3} M) in the presence of H_2QDS (1×10^{-2} M) in AOT reverse micellar solution.

results indicate that the radical pair formation occurred during these periods after the laser pulse irradiation.

Discussion

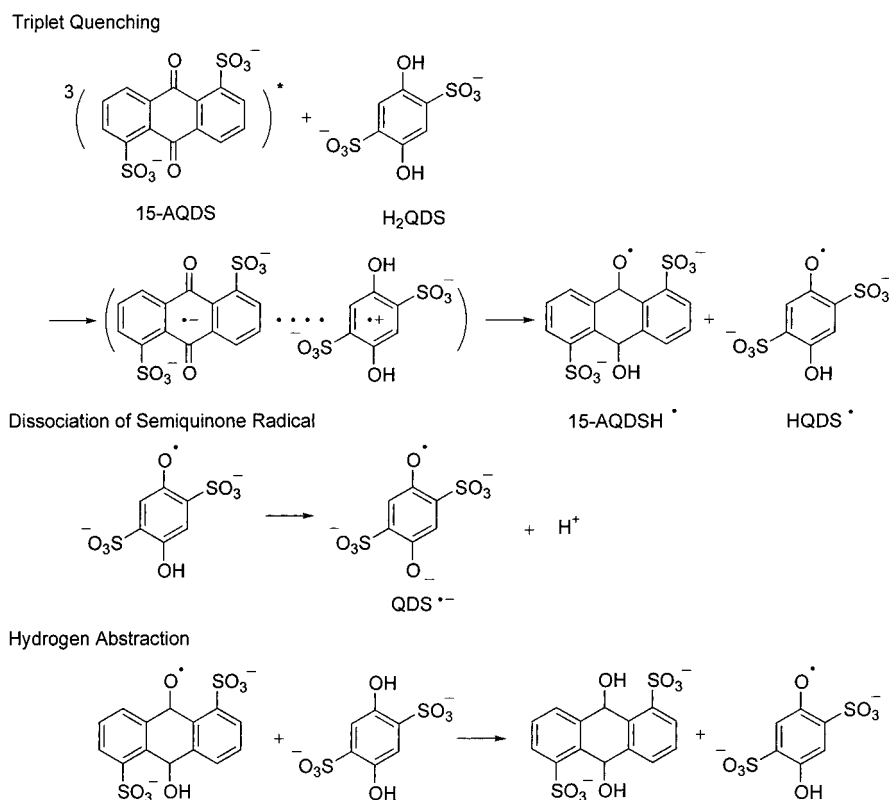
At neutral conditions all the hydroquinones exist predominantly in their hydroxy forms. Their $\text{p}K_1$ values have been reported for many of the hydroquinones, which are typically 9.5–11.¹⁹ Taking into account the $^3(1,5\text{-AQDS})^*$ energy level of 2.36 eV, and the standard electrode potential of -0.50 V for 1,5-AQDS and 1.12 V for HQ,^{20,21} the free energy change of the electron-transfer process from HQ to $^3(1,5\text{-AQDS})^*$ is a negative value. Thus, the initial step of the photoreaction was the photoinduced electron transfer from the H_2Q^* 's to the $^3(1,5\text{-AQDS})^*$. The resulting H_2Q cation radical, because of the small $\text{p}K_a$ values of -2 ,²² dissociated and produced the benzosemiquinone radical. Under neutral conditions, the benzosemiquinone radical further deprotonated and yielded the quinone anion radical, since a $\text{p}K_a$ value of 4 was reported for the HQ neutral radical.²³ In the pulsed EPR experiments we detected the neutral semiquinone (15-AQDSH) radical at early time delays but not the 1,5-AQDS anion radical. We also observed that the disappearance of the 1,5-AQDSH signals was accompanied by the appearance of the SCRP antiphase signals. Thus, the radical that was formed by the reaction of 1,5-AQDSH participated in the SCRP and showed the characteristic APS structure in the spectrum. Consecutive pathways were confirmed that there was

a linear relation with the signal intensity having a slope of unity, indicating the participation of the one-photon process in the reaction. This observation indicated that the radical pair responsible for the APS polarization was formed with significant delay following the excitation of 15-AQDS. Comparisons among two-dimensional nutation spectra exhibited at different delay times after the laser pulse irradiation provided direct information on the formation of the radical pair. At 50 ns after the laser pulses contributions from the $S = 1$ component in the two-dimensional nutation spectrum were insignificant. However, because of the contributions were major at 500 ns, it can be implied that the radical pair was produced within this time period after the excitation of 1,5-AQDS. Through these observations we tentatively proposed that the reaction sequence in the photoreduction of quinone triplet by hydroquinone as described by Scheme 1.

A decrease in the w value ($[\text{H}_2\text{O}]/[\text{AOT}]$) resulted in the decrease of the SCRP signal intensities, which completely disappeared at the content of 5% (v/v) water ($w = 9.6$). We can explain this from the statistical distribution of the quinone and the hydroquinone molecules in the water pool. In the solution containing 0.3 M AOT and 7% water ($w = 14$) the radius of water pool is 2.0 nm.¹³ In this case the molar water pool concentration is 3.7×10^{-4} M. Since the aqueous quinone solution has a concentration of 5×10^{-3} M, at 7% (v/v) water in isooctane, the total quinone concentration is 3.5×10^{-4} M, which then corresponds to the average occupancy of 1 quinone molecule/water pool. Since the concentrations of the hydroquinones were 1×10^{-2} M for each experiment, at least two molecules were involved in a water pool. By a decrease of the w values, the possibility of zero occupancy becomes significant and resulted in a sharp decrease of the SCRP signal intensities. At $w = 10$, the average occupancies became 0.5 for quinone and 1 for hydroquinone and under these SCRP signals were not observed, which indicated that the sequential reactions in the water pool were inhibited. When we used lower aqueous quinone and/or hydroquinone concentrations, the w value, at which the SCRP signals have diminishing intensities, became larger.

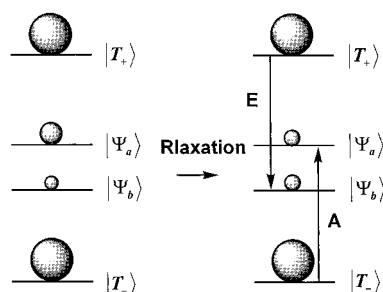
Almost of the SCRP observed using the EPR techniques originated from the geminate RP. The polarization pattern was well interpreted using the four level scheme. The initial populations in the states depend on the spin multiplicities of the precursor states, and the resulting population differences cause the antiphase SCRP polarization in the spectrum. In the present case, the pair was formed from the diffusion of the radicals that were generated by consecutive reaction steps. Although the initial step of the reaction was the electron transfer to $^3(1,5\text{-AQDS})$, each radical of the geminate RP converts to a different one. If the correlations between them were conserved during the sequential reaction steps, the resulting radical pair will have a triplet character, which will lead to the excess populations in the states, which were triplet in their character. On the other hand, if it is not the case for the present radical pair, there will be no population differences between each state. With initiation of this condition, if the pair possesses a substantially long lifetime and the reaction occurs from its singlet state as usual case, the relatively excess population should evolve in the states having a triplet character. It would be expected that the disproportionation reaction occurs between negatively charge radicals. The situation was the same with a triplet born SCRP, and the procedure to generate the polarization was similar to that of F-pair polarization in RPM of CIDEP. In both cases, as shown in Scheme 2, the resulting SCRP

SCHEME 1

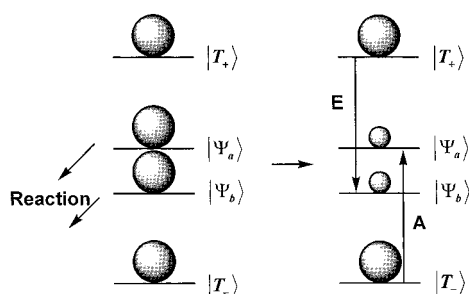


SCHEME 2

Case 1 Triplet Born SCRP



Case 2 Spin Selective Reaction in Free RP



polarization patterns were E/A for each hf lines. We cannot discriminate between them from the polarization pattern of SCRP.

The APS spectral shapes were affected by the amount of water in the AOT reversed micellar solution. A decrease in w values resulted in the increase of both the line widths and the peak-to-peak distances of the APS pattern. To analyze the spectral shape, we first studied the line widths of the polarized

TABLE 2: Effects of Water Contents on the Apparent Relaxation Time and the Exchange Interaction of SCRP in AOT Reverse Micellar Solution

w	water pool size/nm	T_2^*/ns	$ J /\text{mT}$	r/nm
14	3.0	210	1.1×10^{-2}	1.7
17	3.4	340	0.7×10^{-2}	1.8
18.5	3.7	550	0.3×10^{-2}	1.8
20	3.9	740	0.2×10^{-2}	1.9

signals, using the relationship between the homogeneous line width (Γ) and the transverse relaxation time (T_2) as follows:

$$\frac{1}{T_2} = \kappa \gamma_e \Gamma$$

Here κ is a constant dependent on the line shape and γ_e is the electronic magnetogyric ratio. Thus, the broadening of the signal is caused by shortening of T_2 . To estimate T_2 values, the FID signals were analyzed. The simple three-line spectrum is easily fit to the FID signal involved in the parameters of an apparent transverse relaxation time (T_2^*) and offset frequencies of each hf line. As depicted in Table 2, the T_2^* values were estimated from the nonlinear least-squares fitting of the FID signals with different w values, where the Lorentzian lines ($\kappa = 1$) and $T_2 = T_2^*$ were assumed for the fittings. The line widths were estimated using by the T_2^* values with different w values. The peak-to-peak distances of the APS pattern were treated as adjustable parameters for the fittings. When the population differences between the T_0 and the S states of RP were negligible ($P_{T0} = P_S$), the observed line shapes were well reproduced. The exchange interaction of J was evaluated for the RP with different water pool sizes from the line shapes fitting of the spectra as shown in Figure 3 and summarized in Table 2.

The exchange interaction is described by an exponential dependence on the distance of the two radicals as given by²⁴

$$J = J_0 \exp \left[\frac{-(r - R)}{\lambda} \right]$$

where r is the average separation between the radicals, J_0 is the value of J at the contact distance (R) defined above (typically 0.6 nm), and λ is a parameter whose value usually assumed to be about 0.5 nm. J_0 is typically assumed to be about 1.3×10^{10} rad/s for carbon radical pairs.²⁵ Average separations between the radicals were estimated by using the J values and summarized in Table 2. Increase in the w values resulted in decreases of the average exchange interaction, $|J|$. This indicated that the average distance between the two benzoquinone anion radicals was strongly depended on the water pool size.

The present treatment is based upon the effective exchange interaction. Recently, the theory of TR-EPR of SCRPs was developed in considerable detail to interpret the APS spectral shapes.²⁶ Further detailed calculations are currently in progress.

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References and Notes

- (1) Closs, G. L.; Forbes, M. D. E.; Norris, J. R. *J. Phys. Chem.* **1987**, *91*, 3592.
- (2) Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307.
- (3) Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Chem. Phys.* **1990**, *92*, 5175.
- (4) Levstein, P. R.; van Willigen, H. *Chem. Phys. Lett.* **1991**, *187*, 1401.
- (5) Wu, C.-H.; Jenks, W. S.; Koptiyug, I. V.; Ghatlia, N. D.; Lipson, M.; Tarasov, V. F.; Turro, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 9583.
- (6) Ishiwata, N.; Murai, H.; Kuwata, K. *Res. Chem. Intermed.* **1993**, *19*, 59.
- (7) Khudyakov, I. V.; McGarry, P. F.; Turro, N. J. *J. Phys. Chem.* **1993**, *97*, 13234.
- (8) Ishiwata, N.; Murai, H.; Sakaguchi, Y.; Hayashi, H. *Z. Phys. Chem.* **1993**, *182*, 41.
- (9) Turro, N. J.; Khudyakov, I. V. *J. Phys. Chem.* **1995**, *99*, 7654.
- (10) Loeff, I.; Rabani, J.; Terenin, A.; Linschitz, H. *J. Am. Chem. Soc.* **1993**, *115*, 8933.
- (11) Loeff, I.; Goldstein, S.; Terenin, A.; Linschitz, H. *J. Phys. Chem.* **1991**, *95*, 4423.
- (12) Scharf, H. D.; Weitz, R. *Tetrahedron* **1979**, *35*, 2255.
- (13) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730.
- (14) Akiyama, K.; Tero-Kubota, S.; Ikoma, T.; Ikegami, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5324.
- (15) Hanaishi, R.; Ohba, Y.; Akiyama, K.; Yamauchi, S.; Iwaizumi, M. *J. Chem. Phys.* **1995**, *103*, 4819.
- (16) Wong, M.; Gratzel, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 2391.
- (17) Harashanori, K.; Levanon, H.; Tang, J.; Bowman, M. K.; Norris, J. R.; Gust, D.; Moore, T. A.; Moore, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6477.
- (18) Kroll, G.; Pluschau, M.; Dinse, K.-P.; van Willigen, H. *J. Chem. Phys.* **1990**, *93*, 8709.
- (19) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants*; Chapman and Hall: London, 1971.
- (20) Loeff, I.; Rabani, J.; Treinin, A.; Linschitz, H. *J. Am. Chem. Soc.* **1993**, *115*, 8933.
- (21) Huie, R. E.; Neta, P. *J. Phys. Chem.* **1985**, *89*, 3918.
- (22) Dixon, W. T.; Murphy, D. J. *Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1221.
- (23) (a) Adam, G. E.; Michael, B. D. *Trans. Faraday Soc.* **1967**, *63*, 1171. (b) Rao, P. S.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 2274.
- (24) Molin, Y.; Salikov, K.; Emaraev, K. *Spin Exchange*; Springer-Verlag: New York, 1980; Chapter 4.
- (25) Trasov, V. F.; Ghatlia, N. D.; Buchachenko, A. L.; Turro, N. J. *J. Am. Chem. Soc.* **1992**, *114*, 9517.
- (26) Tarasov, V. F.; Forbs, M. D. E. *Spectrochim. Acta, Part A* **2000**, *56*, 245 and references therein.