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FT EPR Study of the Hydrated Electron Generated by Laser Excitation of Phenothiazine in Quinone-SDS Micellar Systems[||]

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Abstract: We have studied nanosecond kinetics of the hydrated electron (e^{-}_{aq}) generated by laser excitation of phenothiazine (PTH) in the presence of quinone in SDS solution using FT EPR. Using two different quinones, idebenone (IDB) and CoQ$_0$, we have observed the unique photochemical processes due to the micellar effect in the system. The analyses of FT EPR results suggested that IDB with the long alkyl alcohol chain at the 6-position became the corresponding anion radical by quenching of e^{-}_{aq}. On the other hand, CoQ$_0$, without the long chain, was reduced by two processes, quenching of e^{-}_{aq} and direct electron transfer from the triplet precursor. Moreover, the distinctive dispersive pattern, which implied the radical pair of [$PTH^{\bullet+}$...e^{-}_{aq}], was observed at 30 ns after the excitation of PTH in IDB/SDS micellar system but was not observed for CoQ$_0$.

Introduction

Formation and behavior of the hydrated electron (e^{-}_{aq}) in heterogeneous media are compelling subjects for study in photochemical processes. Knowledge of these processes has potential applications to biological systems as well as the storage of solar energy.[1−4] Investigation of the photoinduced electron transfer in micellar solutions could provide detailed information regarding the electron donor and acceptor in microenviroments.[5−7] Nanosecond photochemical events using quinone probes in a micellar solution can be studied by FT EPR (Fourier transform electron paramagnetic resonance). This spectroscopic technique has proven to be an ideal method for the investigation of photochemically generated transient paramagnetic species and photochemical events.[5]

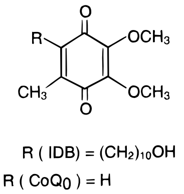

Figure 1. Structures of the quinones, idebenone (IDB) and CoQ$_0$, used.

Formation of e^{-}_{aq} produced by the laser photolysis of phenothiazine (PTH) in methanolic and aqueous sodium lauryl sulfate micellar solutions was initially investigated by Grätzel *et al.*[8] Production of the e^{-}_{aq} is a monophotonic process through singlet PTH and is much larger ($\phi \sim 0.5$) in the micellar as compared to methanolic ($\phi \sim 0.1$) solutions. This is an ideal case to study photoinduced electron transfer in heterogenous solution. However, no detailed e^{-}_{aq} quenching dynamics with relation to quinone acceptors have been demonstrated in SDS solution.

We have studied electron transfer from the excited PTH to quinones in SDS micellar solution using FT EPR. We have found that nanosecond photochemistry using two different quinones with the same quinone chromophore strongly depends on the quinone location in the micellar solution. The dynamics of the hydrated electron quenching associated with structure and location of the solute quinone radicals induced by laser excitation of the electron donor in the micellar solution are reported.

Materials and Methods

Samples. Idebenone (IDB), 6-(10-hydroxydecyl)-2,3-dimethoxy-5-methyl-1,4-benzoquinone, was kindly donated by Takeda Chemical Industries, Ltd. (Japan). 2,3-Dimethoxy-5-methyl-1,4-benzoquinone (CoQ$_0$, Tokyo Kasei, Japan), ion-pair chromatography grade sodium dodecyl sulfate (SDS, Tokyo Chemical Co., Japan), and phenothiazine (PTH, Nacalai Chemical, Japan) were used as received. Chemical structures of the quinone samples are presented in Figure 1. All other reagents were of the highest quality and used as received. The concentration of SDS was fixed at 0.15 M, and the solutes were kept at 2 mM unless otherwise noted. The solution was prepared in distilled water with ∼12 h sonication. Sample solutions were deoxygated with argon gas bubbling before and during the measurements and were pumped into a flow cell (3 mm O.D. at the resonator).

Spectrometers. FT EPR measurements were made on a home built X-band pulsed EPR spectrometer equipped with TE$_{102}$ cavity[9] and on a Bruker ESP 380E X-band pulsed EPR spectrometer equipped with a

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dielectric resonator.[10] The laser, a Quanta-Ray GCR-14S, was operated at 355 nm with ~8 ns pulse width and a repetition rate of 10 Hz. The laser energy was approximately 70 mJ. FT EPR spectra were obtained by the detection of free induction decay (FID) after the $\pi/2$ microwave pulse following laser excitation, using a four step phase cycling routine in order to suppress artifacts. Missing points due to the instrument dead time were handled with a linear prediction using the ESP 1600 Software.

In order to confirm a spin correlated radical pair (SCRP), two-dimensional (2D)-FT EPR nutation experiments were carried out. It has been theoretically and experimentally shown that the Coulomb-coupled radical pair having small exchange interaction is distinguishable from the free radical by the dependence of FT EPR signal intensity upon the turning angle of the microwave pulse.[11,12] The FID signal (time axis t_2) was observed using 2D-FT EPR nutation experiments while increasing the duration (t_1) of microwave pulse.[13] The FID signal ($S(t_1, t_2)$) obtained was converted into 2D frequency domain spectrum ($S(F_1, F_2)$) by 2D complex Fourier transformation.

In addition to the FT EPR, continuous wave time-resolved EPR (CW TREPR) was also performed to examine the phase of the paramagnetic species.[14] The g-values were obtained using a stable free radical (N-methylphenazinum tetracyanoquinodimethane radical, $g = 2.0031$) as a reference. The microwave frequency was read by HP Model 5342A frequency counter. All measurements were carried out at ambient temperature.

Results and Discussion

Idebenone. FT EPR spectra obtained by laser excitation of PTH in the presence of IDB in SDS solution are presented in Figure 2. There are two paramagnetic species within a 1 μs laser delay. The single peak appearing at lower offset frequency shows E/A (emissive/absorptive) polarization at the delay time $\tau_d = 30$ ns between the laser and the microwave pulses, and the polarization changes to E at $\tau_d > 40$ ns. The E polarization is consistent with that obtained for CW TREPR in the same solution system. The line width at the half height is ~2.5 MHz and does not change at the different delay times ($\tau_d > 40$ ns). The signal has a g-value of 2.0001. We have determined that the peak is hydrated electron (e^-_{aq}) based on the previously reported values[8,15] as well as the FT EPR experimental values.[16]

Hyperfine structure of the other species consists of nine lines which are symmetrical about the center. The hyperfine coupling constants of $a^5{}_{CH_3} = 0.19$ mT and $a^6{}_{CH_2} = 0.097$ mT as well as the g-value, 2.0043, are in good agreement with idebenone anion radical ($IDB^{\bullet-}$) obtained by CW EPR experiments.[17] It should be noted that we can ignore the possibility of electron transfer from excited IDB in the system since no FT EPR signal has been observed by laser excitation of IDB without PTH in SDS micellar solution. That is, the hydrated electron is produced from the photoexcitation of PTH.

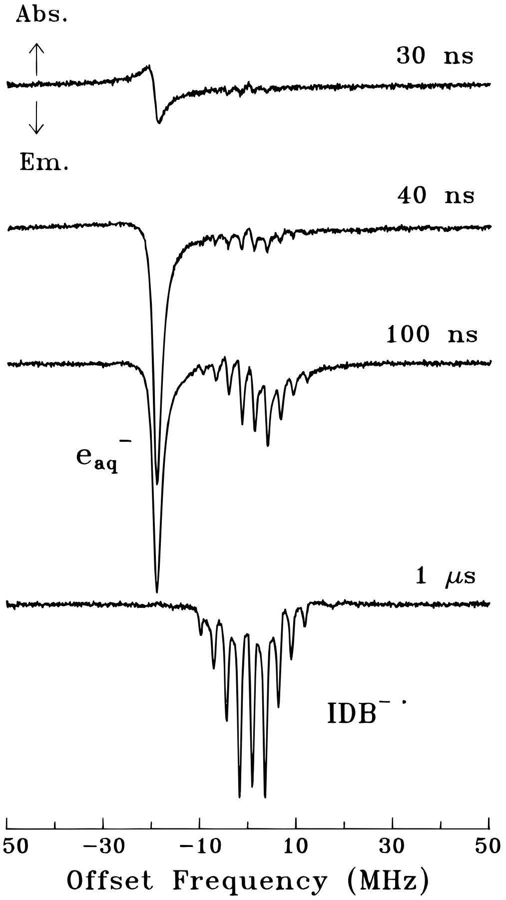

Figure 2. FT EPR spectra obtained at different delay times after Nd: YAG laser (355 nm) excitation of PTH (2 mM) in the presence of idebenone (2 mM) in SDS (0.15 M) solution. e^-_{aq} and $IDB^{\bullet-}$ indicate hydrated electron ($g = 2.0001$) and idebenone anion radical ($g = 20043$), respectively. The delay times after laser excitation are indicated. Applied magnetic field was set near the center of the idebenone anion radical. Laser power was kept at ~70 mJ. Each FID was accumulated 32 times with the four-step phase cycling routine.

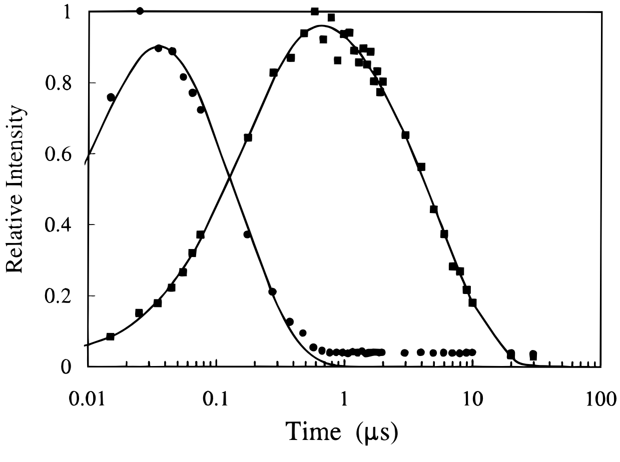

Figure 3. Total signal areas versus laser delay time for the hydrated electron (●) and idebenone anion radical (■). The experimental conditions are the same as in Figure 2.

The observed FT EPR spectra show a gradual increase of $IDB^{\bullet-}$ signal as a function of the laser delay (Figure 2). The decay of e^-_{aq} and the rise of $IDB^{\bullet-}$ seem to correlate with each other. In order to obtain detailed kinetic information for both e^-_{aq} and $IDB^{\bullet-}$, we have taken total signal intensities for both species, as presented in Figure 3. The curve fitting in Figure 3 is based on a nonlinear least-squares method. Detailed kinetic

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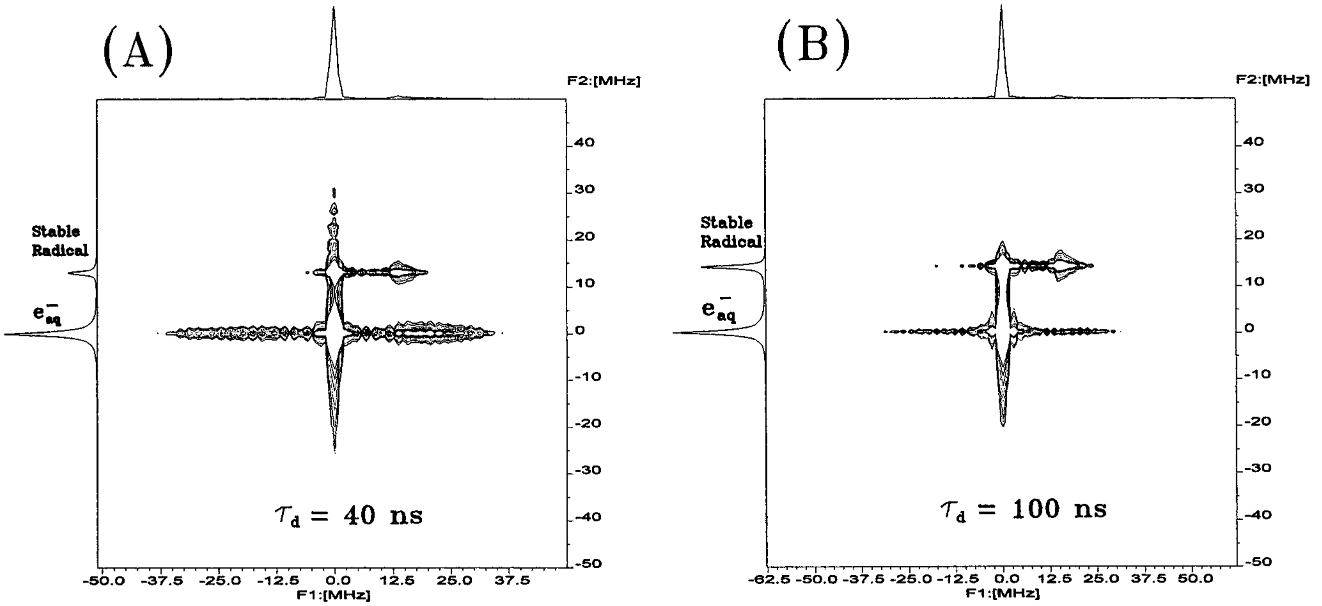

Figure 4. 2D-FT EPR nutation contour plots of the PTH/IDB/SDS system obtained at (A) 40 n and (B) 100 ns laser delay. F_1 and F_2 are nutation and EPR frequencies, respectively. The stable radical is described in the text. The spin quantum of one for the e^-_{aq} signal suggests the radical pair [$PTH^{\bullet+}$...e^-_{aq}]: [$1/2$, $1/2$].

analyses have been done with the model function,

$$S(t) = A[-\exp(-k_r t) + \exp(-k_d t)] \qquad (1)$$

where k_r and k_d are rise and decay rates, respectively. The results show that the decay rate (6.6×10^6 s^{-1}) for e^-_{aq} is almost identical to the formation rate (5.4×10^6 s^{-1}) for $IDB^{\bullet-}$. These rates imply that IDB quenches the e^-_{aq} and becomes $IDB^{\bullet-}$ in the micellar solution. When experiments with 1 mM IDB and 2 mM PTH in the SDS solution were conducted, the slower rising rate obtained further supported that IDB quenches the e^-_{aq}. Since the E-CIDEP (emissive-chemically induced dynamic electron polarization) of $IDB^{\bullet-}$ shows the slow rise time of ~185 ns, it can not be attributed to TM (triplet mechanism), suggesting negligible electron transfer from the T_1 state PTH to IDB. Therefore, the E-polarization of $IDB^{\bullet-}$ is the result of electron spin polarization transfer from e^-_{aq}.

The spin polarization of e^-_{aq} observed at 30 ns is unusual. The dispersive pattern of the hydrated electron observed at early times after the excitation is indicative of SCRP[11−13,18] with $PTH^{\bullet+}$. To confirm the radical pair, we have performed 2D-FT EPR nutation experiments of PTH alone as well as PTH in the presence of IDB in SDS solution. Figure 4 shows the 2D-FT EPR nutation contour plots taken at two different times after the laser pulse. F_1 and F_2 in the Figure 4 are nutation and EPR frequencies, respectively. The nutation frequency of the stable radical (F_1 ~15 MHz) is independent on the delay times. The maximum nutation frequency observed for e^-_{aq} at $\tau_d = 40$ ns is approximately twice that for the stable radical, indicating the production of SCRP (Figure 4(A)). Moreover, the e^-_{aq} signal shows broadening for the EPR frequency axis taken at $\tau_d = 40$ ns, while the broadening is not observed at 100 ns (Figure 4(B)). The broadening can be attributed to the short relaxation time of e^-_{aq}. The results for both systems prove that e^-_{aq} forms the radical pair within 40 ns after the laser excitation and that no formation is taking place at $\tau_d > 50$ ns.

In addition, the E/A polarization at 30 ns suggests a positive value of electron spin exchange interaction (J) in the SCRP since the ejection of e^-_{aq} is a one photon process through singlet PTH.[19] We have also confirmed the process by investigating laser power dependence using FT EPR and CW TREPR in the same solution. Thus, the net E polarization of the e^-_{aq} observed at $\tau_d > 50$ ns is not attributed to TM. It can be due to a Δg-effect in the $S-T_0$ mixing of RPM (radical pair mechanism) due to the large difference of the g-values between e^-_{aq} ($g = 2.0001$) and $PTH^{\bullet+}$ ($g = 2.0052$).[20] Although the electron spin polarization of $PTH^{\bullet+}$ in the SDS solution is uncertain, A-CIDEP should be observed for $PTH^{\bullet+}$. In addition, we have examined the e^-_{aq} polarization using CW TREPR and FT EPR with the stable radical crystal (N-methylphenazinum tetracyanoquinodimethane radical, $g = 2.0031$) kept in a sealed capillary which was attached to the outside of the flow cell as a reference phase and have confirmed the E polarization at $\tau_d > 50$ ns in PTH/IDB as well as PTH alone in SDS solution.

Therefore, the photochemical reaction scheme for PTH/IDB/SDS system is as follows (Figure 5, Scheme 1). The laser excited singlet state PTH produces the singlet radical pair ^{1}[$PTH^{\bullet+}$... e^-_{aq}] and ^{3*}PTH. The radical pair quickly goes to solvent separated radical pair (SSRP). In the presence of IDB, the e^-_{aq} is quenched to produce the corresponding radical anion since recombination with the parent cation is inhibited by the repulsive charge barrier of the micellar surface. In order to confirm no contribution of the triplet state in the formation of $IDB^{\bullet-}$, we have performed optical experiments. Measurements of the nanosecond transient absorption indicate that T−T absorption (420 nm) of the excited PTH decays over 10 μs in the presence of IDB in SDS solution. Therefore, the direct

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(19) After this work was completed, a paper on the photoionization of phenothiazine has appeared (Turro, et al. *J. Am. Chem. Soc.* **1995**, *117*, 12273). They have proposed that two photon process involving an upper triplet state slightly contributes to the formation of $PTH^{\bullet+}$ and e^-_{aq}, and the net E-CIDEP is due to TM. However, our data on the laser power dependence for the e^-_{aq} signal show one photon process as reported by Grätzel.[8] In addition, if TM is operative, strong E-CIDEP should be observed at the delay time 30 ns because of the rapid buildup rate of TM signals. Further studies on the initial process are underway using transient absorption method as well as FT EPR experiments.

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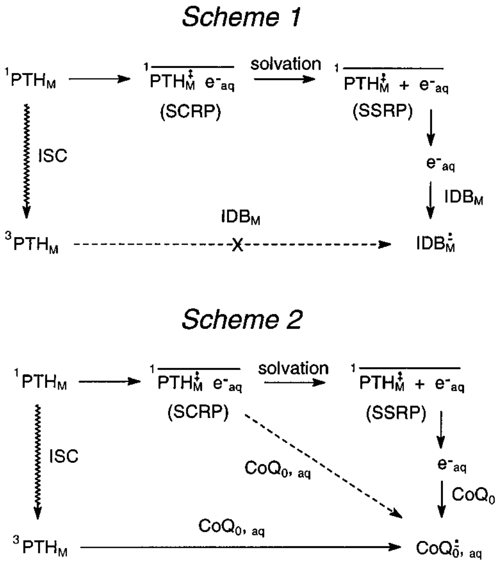

Figure 5. Empirical photochemical reaction schemes for the laser excitation of PTH in the presence of IDB (Scheme 1) and CoQ_0 (Scheme 2) in the SDS solutions. SCRP and SSRP mean spin correlated radical pair and solvent separated radical pair, respectively. Subscript M and aq indicate micelle and aqueous phases, respectively. ISC is intersystem crossing.

electron transfer from the ^{3*}PTH to IDB is negligible in this system. The effective trapping of e^-_{aq} by IDB suggests that the quinone chromophore can be located at the surface region of the micelle.

CoQ_0. When 2 mM CoQ_0 for the homologue of IDB is used, the anion radical with E polarization appears right after laser excitation of PTH in SDS solution (a reference spectrum is shown in Figure 6(a)). However, we did not observe the hydrated electron at any laser delay time studied. The total peak areas at each laser delay are plotted and presented in Figure 7(a). The kinetic analyses of the plot have been done using the eq 2.

$$S(t) = A_1[-\exp(-t/{}^3T_1)+\exp(-t/{}^2T_1)] + A_2[-\exp\{1 - \exp(-t/{}^2T_1)\}] \quad (2)$$

where $^3T_1$ and $^2T_1$ are electron spin relaxation times of triplet state and radical, respectively. The buildup rate ($6.9 \times 10^7\ s^{-1}$) for $CoQ_0^{\bullet -}$ is much faster than that for $IDB^{\bullet -}$ ($5.4 \times 10^{6}\ s^{-1}$) indicating the participation of TM in the photochemical reaction. The CoQ_0 anion radical decays with the rate of $5.2 \times 10^6\ s^{-1}$.

When 0.5 mM CoQ_0 is used, the e^-_{aq} is observed (Figure 6(b)). No e^-_{aq} signal with the dispersive pattern is observed at 30 ns. It may be due to a very short lifetime of the SCRP in the system. The signal areas are plotted as a function of the laser delay as shown in Figure 7(b). For the rise, two processes are considered, a fast one and slower one. The fast process is due to TM precursor, and the slow one is the hydrated electron quenching process. Thus, for 2 mM CoQ_0, we have not observed the e^-_{aq} since TM is the dominant reaction path. The empirical photochemical reaction scheme is presented in Figure 5 (Scheme 2). The dotted arrow indicates a possible e^-_{aq} quenching reaction path from the singlet precursor. These results imply that CoQ_0, which does not have the alkyl alcohol chain at the 6-position, goes through two paths to become the corresponding anion radical: quenching of e^-_{aq} and direct electron transfer from the triplet precursor. Both processes are very fast because, unlike IDB, CoQ_0 is mobile in SDS solution.

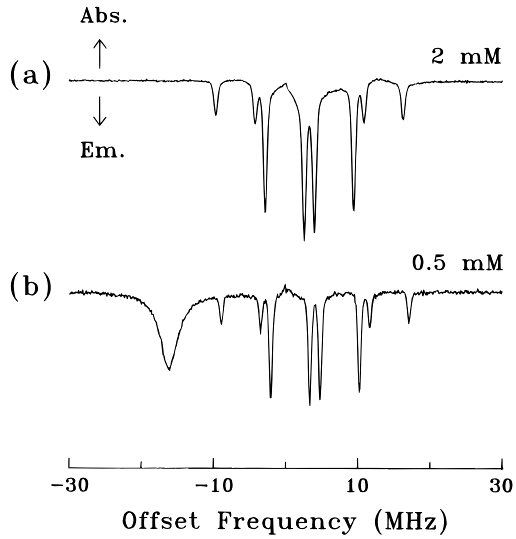

Figure 6. FT EPR spectra obtained at 50 ns after the laser excitation of PTH (2 mM) in the presence of different CoQ_0 concentrations in the SDS (0.15 M) micellar solution. (a) CoQ_0, 2 mM. The anion radical has $g = 2.0043$. (b) CoQ_0, 0.5 mM. The g-values for the anion radical and e^-_{aq} at the lower offset frequency are 2.0043 and 2.0001, respectively.

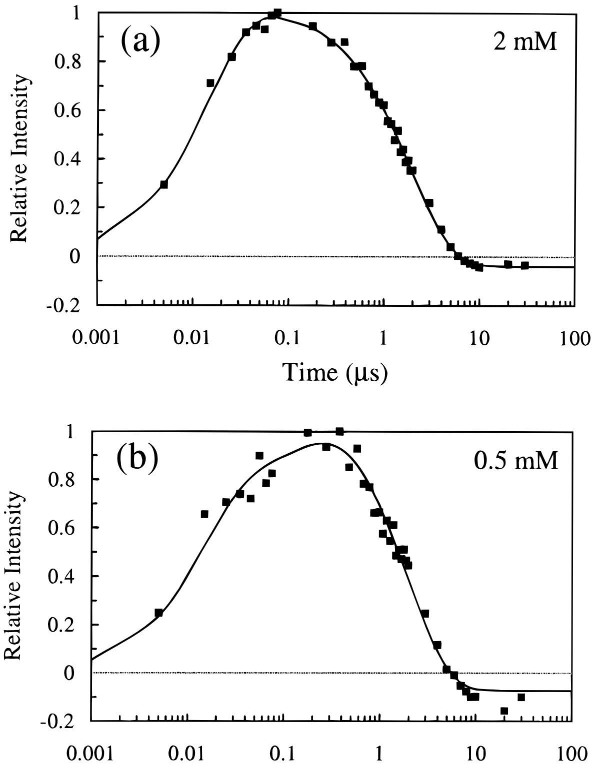

Figure 7. Total signal areas of CoQ_0 anion radical versus laser delay time for (a) CoQ_0, 2 mM and (b) CoQ_0, 0.5 mM corresponding to Figure 6. There are two rising processes, fast and slow, observed for (b). The signal areas of E-polarization were plotted as positive values. Negative intensity in the figure means that the signals turn into A-polarization which is a Boltzmann distribution of electron spins.

Conclusions

We have provided the nanosecond kinetics of the e^-_{aq} and the solute quinone radicals induced by electron transfer in micellar solution. We have observed the micellar effect on the photochemical events using two different quinones as the acceptors. IDB with the long alkyl alcohol chain at the

6-position quenches the hydrated electron and the net E-CIDEP of IDB anion radical is due to the polarization transfer from e^-_{aq}. The kinetic analyses of the photochemical reactions show that the quinone chromophore of IDB is located at the surface region of the micelle. On the other hand, the homologue CoQ_0 without the long chain, located in aqueous phase, is reduced by the trapping of e^-_{aq} and direct electron transfer from the triplet precursor ^{3*}PTH. In addition, the distinctive E/A pattern of e^-_{aq} is observed at early time after laser excitation in PTH/IDB/SDS system and the pattern is indicative of SCRP, $[PTH^{\bullet +}...e^-_{aq}]$. The 2D-FT EPR nutation experiments have supported the existence of SCRP in the system. However, there is no such evidence for the PTH/CoQ_0/SDS system.

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