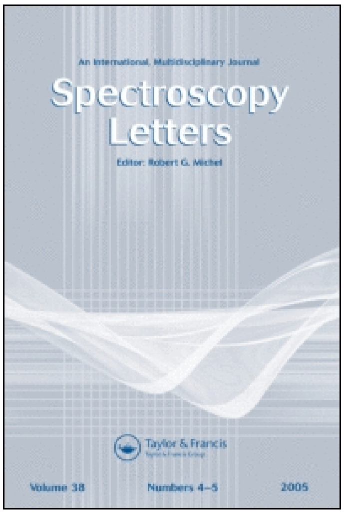

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A Time-Resolved Electron Spin Resonance Study of the Generation Mechanism of the Benzoquinone Anion Radical

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A Time-Resolved Electron Spin Resonance Study of the Generation Mechanism of the Benzoquinone Anion Radical

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Abstract: The chemically induced dynamic electron polarization (CIDEP) spectra for the photolysis of the *p*-benzoquinone (PBQ)/formamide (FM) system in acid, basic, and micellar environments were obtained with a homemade time-resolved electron spin resonance (TR-ESR) spectrometer. When the PBQ/formamide was photolyzed, the CIDEP spectrum consisted of strong CIDEP signals of the benzosemiquinone anion radical $PBQ^{\bullet -}$ and weak signals for the benzosemiquinone neutral radical $PBQH^{\bullet}$. When the PBQ/formamide was irradiated in basic or micellar solution, the CIDEP signal for $PBQ^{\bullet -}$ only was obtained. When the PBQ/formamide was irradiated in acid solution, only the CIDEP signal of $PBQH^{\bullet}$ existed. These experimental results

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indicate that the anion radical $PBQ^{\bullet -}$ was formed from the dissociation of the neutral radical $PBQH^{\bullet}$ accompanying polarization transfer.

Keywords: Chemically induced dynamic electron polarization (CIDEP), micelle, *p*-benzosemiquinone, time-resolved electron spin resonance (TR-ESR)

INTRODUCTION

Using a time-resolved electron spin resonance (TR-ESR) technique, many kinds of intermediates generated by photoexcitation have been studied in terms of chemically induced dynamic electron polarization (CIDEP).[1–4] Quinone compounds exist extensively in organisms and have important physiological functions. The study of quinone molecules has generated much interest in simulating photosynthesis research of purina-quinone system.[5–8] Yoshida, Kambara, and colleagues examed the ESR signal during the continous photolysis of a flowing solution of *p*-benzoquinone in ethanol and found that the benzosemiquinone anion radical was formed by a photoinduced one-electron transfer from solvent to *p*-benzoquinone.[9,10] There have been some other studies on CIDEP of photolyzed *p*-benzoquinone radical in ethylene glycol (EG) homogeneous solution with emphasis on the polarization generation mechanism and in micellar solutions with emphasis on the influence of the microenvironment upon the spin polarization.[11]

As we know, anion radical can be formed through the dissociation from the neutral radical or through electron transfer. In this paper, in order to explore the generation of $PBQ^{\bullet -}$, the CIDEP spectra of photolyzed *p*-benzoquinone in formamide solvent were recorded by a high TR-ESR spectrometer. The strong CIDEP signal of $PBQ^{\bullet -}$ and poor one of $PBQH^{\bullet}$ were obtained, and the generation mechanism of $PBQ^{\bullet -}$ is discussed.

MATERIALS AND METHODS

A homemade high TR-ESR spectrometer with a sub-microsecond resolution used to record CIDEP spectra is simply shown in Fig. 1.[12] An X-band K-129 klystron was used as microwave source. The microwave system adopts balance reflection bridge-type circuit and zero difference beat balance mixing frequency model without field modulation. The sample cavity is TE102 rectangle cavity with a high nonloading Q-value of about 2000. The output of the balance frequency mixer is transported to a broadband preamplifier with a response time of 50 ns and then to a digital oscilloscope (PM 3550) or to a boxcar integrator (SRS 252). A Lambda Physik LPX105 XeCl excimer laser operating at 308 nm with repetition rates of 20–40 Hz and pulse energy of 80 mJ was used as the photolysis source. The gate width of boxcar is 0.3 μs. The photolysis was carried out in a quartz flat sample cell. To avoid overheating, the sample was made to flow (see Fig. 2).

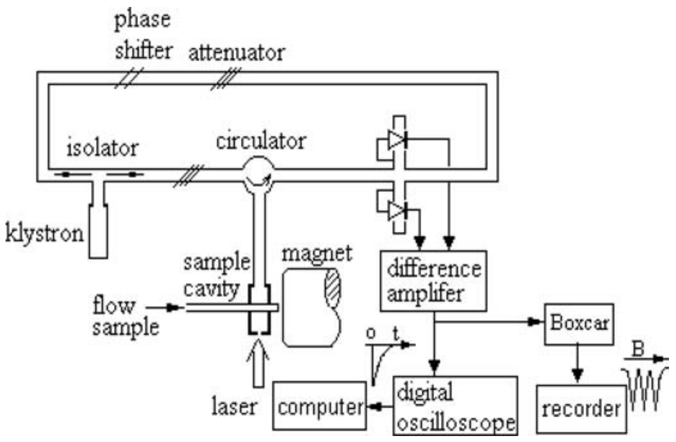

Figure 1. The schematic block of TR-ESR spectrometer system.

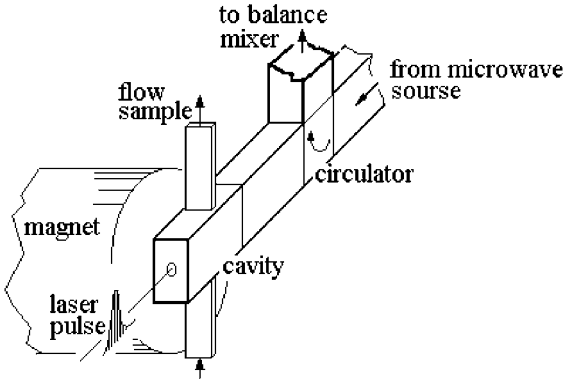

Figure 2. The schematic diagram of the laser irradiation and sample flow system.

All chemicals used were A.R. grade. PBQ was carefully recrystallized by sublimation in vacuum circumstance. Water was twice distilled, and formamide was used as purchased without further purification. The concentration of PBQ is 5×10^{-3} mol/L.

RESULTS

CIDEP Spectra of Photolysis of BQ/FM System

There was no CIDEP signal during the photolysis of formamide. When PBQ/formamide system was photolyzed, we obtained the CIDEP spectra shown in Fig. 3.

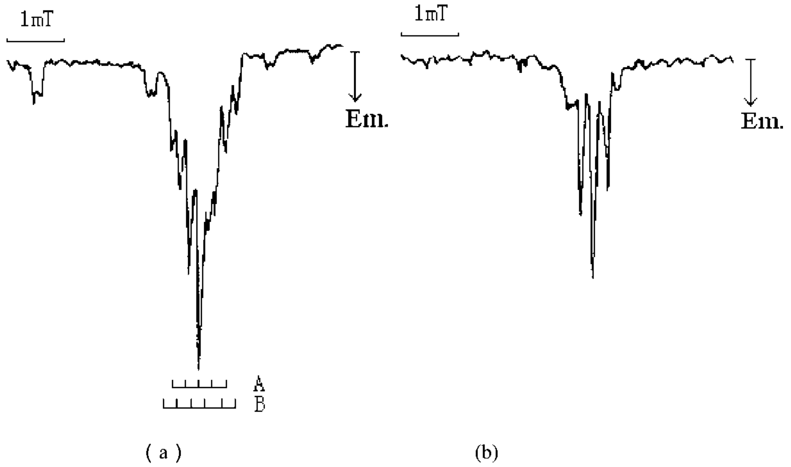

Figure 3. CIDEP spectra of PBQ/FM system. Delay: (a) 0.6 μs; (b) 1.4 μs.

It can be seen from Fig. 3a that the obtained spectrum consists of several strong peaks in the center and weak hyperfine coupling peaks in the low-field and high-field sides. Comparing Fig. 3a with Fig. 3b, it is obvious that the several lines in the center group have different decay rate, and the spectrum consists of only five hyperfine lines at the time delay of 1.4 μs. So the several lines in the center can be assigned to different radicals. The hyperfine coupling constant of the five hyperfine peaks of group A in Fig. 3a is 0.22 mT, and they can be assigned to the benzosemiquinone anion radical $PBQ^{\bullet -}$. The hyperfine coupling constant of the six hyperfine coupling peaks of group B in Fig. 3b is 0.48 mT and 0.17 mT, and they can be assigned to benzosemiquinone neutral radical $PBQH^{\bullet}$.

To make certain the above assignment, the time-dependent intensity curves of the hyperfine lines of group A and group B were recorded (Fig. 4). It was found that the five hyperfine lines of group A have the same polarization rising and decay rate, and so do the six hyperfine coupling peaks of group B. It takes 0.35 μs to increase in intensity from zero to the maximum for the hyperfine lines of group A but 0.8 μs for the hyperfine lines of group B. In addition, the polarization relaxation time of the hyperfine lines of group A and group B are 1.4 μs and 2.2 μs, respectively. Here, the difference of the polarization rising and decay rate between the hyperfine lines of group A and those of group B confirms the above assignment.

As for the poor hyperfine lines in the low-field and high-field sides in Fig. 3a, they can be attributed to formamide radical $HCON^{\bullet}H$. The hyperfine coupling constants for $HCON^{\bullet}H$ are 3.16 mT, 2.13 mT, and 0.15 mT.

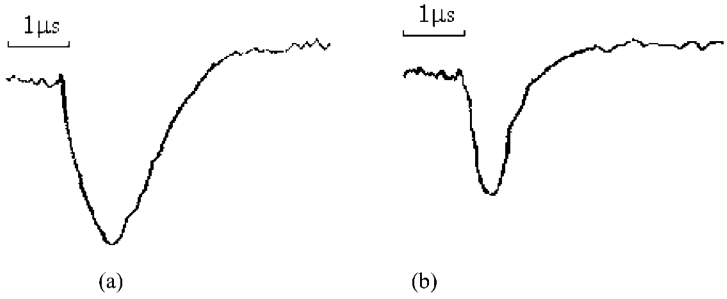

Figure 4. Time-dependent curves of the most intensive hyperfine line of group A (a) and group B (b).

CIDEP Spectra of Photolysis of PBQ/FM/NaOH (H_2SO_4) System

The CIDEP spectrum of PBQ/FM/NaOH (pH 8) system after laser irradiation is shown in Fig. 5a. It can be seen that the spectrum is composed of five peaks in the center belonging to $PBQ^{\bullet -}$ and the poor hyperfine coupling lines belonging to $HCON^{\bullet}H$. The signal of $PBQH^{\bullet}$ was almost not existent.

When a little H_2SO_4 was added into PBQ/FM solution (pH 6), we obtained the CIDEP spectrum of this system, shown in Fig. 5b. Here, only six hyperfine coupling lines in the center of $PBQH^{\bullet}$ were existent and the signal of $PBQ^{\bullet -}$ has disappeared. Furthermore, it can be seen that the addition of H_2SO_4 increases the signal of $PBQH^{\bullet}$ (Fig. 5b).

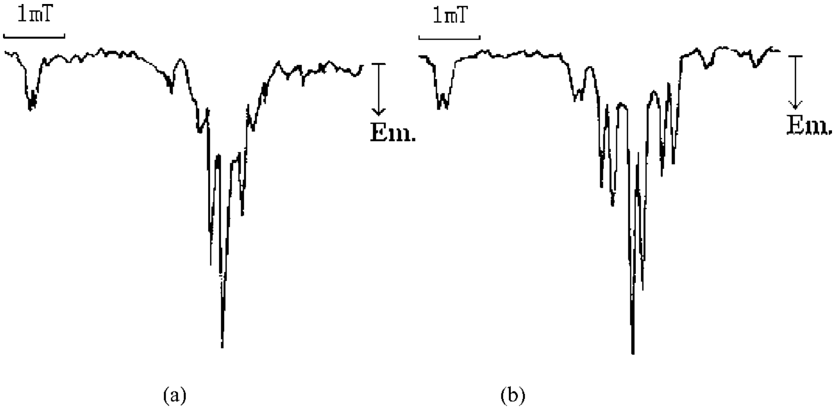

Figure 5. CIDEP spectra of photolyzed PBQ/FM system. Delay: 0.6 μs. (a) pH 8; (b) pH 6.

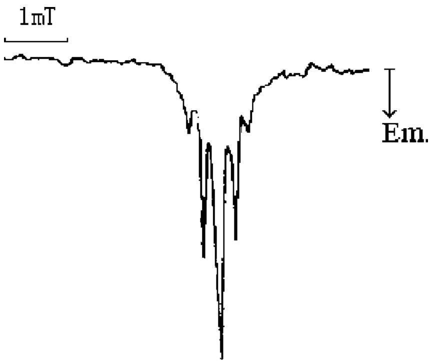

Figure 6. CIDEP spectra of photolyzed PBQ/FM/H_2O/TX-100 micelles system. [TX-100] = 0.125 mol/L. Delay: 0.6 μs.

CIDEP Spectrum of Photolysis of PBQ/FM in Micelle

With Triton X-100(TX-100) added to PBQ/FM/H_2O (10:1) system, the CIDEP spectrum of this micelles system after laser irradiation is shown in Fig. 6.

Compared with Fig. 3, the spectrum of this system has two obvious features. First, there were only five strong peaks of $PBQ^{\bullet -}$ in center. Second, the hyperfine lines at the low-field and high-field sides of $HCON^{\bullet}H$ almost disappeared.

DISCUSSION

Based on the fact that the strong emissive polarization signals of $PBQ^{\bullet -}$ were obtained accompanied by weaker signals of $PBQH^{\bullet}$ and $HCON^{\bullet}H$ in the laser photolysis of PBQ/FM system, the possible photochemical process may be as follows:

$$PBQ \xrightarrow{h\nu} {}^1PBQ^{\bullet} \xrightarrow{ISC} {}^3PBQ^{\bullet} \quad (1)$$

$$^3PBQ^{\bullet} + HCONH_2 \longrightarrow PBQH^{\bullet} + HCON^{\bullet}H \quad (2)$$

$$PBQH^{\bullet} \rightleftharpoons PBQ^{\bullet -} + H^+ \quad (3)$$

Reaction (1) shows that a PBQ molecule reaches its excited singlet state $^1PBQ^{\bullet}$ after having absorbed a photon, then gets to its excited triplet state $^3PBQ^{\bullet}$ through inter-system crossing (ISC). Reaction (2) indicates that $^3PBQ^{\bullet}$ captures a hydrogen from formamide, and spin-polarized $PBQH^{\bullet}$ and $HCON^{\bullet}H$ were formed. Here, formamide was hydrogen donor. We think that the polarization formation mechanism is triplet mechanism (TM), because the polarization of all radicals are mostly in emissive pattern. Reaction (3) shows the dissociation process of neutral $PBQH^{\bullet}$ to $PBQ^{\bullet -}$ with polarization transfer.

The following facts make us think the reaction (3) is existent. First, when a little NaOH was added into PBQ/FM system, the basic environment accelerated the dissociation of $PBQH^{\bullet}$ and only the CIDEP signal of $PBQ^{\bullet -}$ was obtained. If $PBQ^{\bullet -}$ was generated not by the dissociation from $PBQH^{\bullet}$ but by the electron transfer from solvent, the addition of NaOH would not affect the existence of $PBQH^{\bullet}$. Second, when a little H_2SO_4 was added to PBQ/FM system, the acidic environment restrained the dissociation of $PBQH^{\bullet}$ and only the CIDEP signal of $PBQH^{\bullet}$ existed. Moreover, the CIDEP signal of $PBQH^{\bullet}$ increased in intensity because of the combination of $PBQ^{\bullet -}$ and H^{+}. This is different from the results during the photolysis of *p*-benzoquinone with ethanol as solvent, where the formation of $PBQ^{\bullet -}$ was quenched by the addition of acetic acid without transformation to $PBQH^{\bullet}$.[10,11] Third, as viewed from the time-evolution curves, the rising rate of the signal of $PBQ^{\bullet -}$ is less than that of $PBQH^{\bullet}$ and the decay rate of $PBQH^{\cdot}$ is larger than that of $PBQ^{\bullet -}$. So we can believe that the polarization has been transferred effectively from $PBQH^{\bullet}$ to $PBQ^{\bullet -}$ with conservation in the dissociation before the polarization of $PBQH^{\bullet}$ relaxed completely. Just for this point, the polarization pattern of $PBQ^{\bullet -}$ was the same as that of $PBQH^{\bullet}$. Furthermore, we can believe that the dissociation rate from $PBQH^{\bullet}$ to $PBQ^{\bullet -}$ and H^{+} is larger than the polarization relaxation rate of $PBQH^{\bullet}$.

In micelle circumstance, the PBQ was solubilized in the polyethylene glycol shell,[11,12] so we have reason to think that the TX-100 molecules were the hydrogen donor instead of formamide. Just for this point, the CIDEP signals of $HCON^{\bullet}H$ were not existent. When $^{3}PBQ^{\bullet}$ captured a hydrogen from TX-100, the polarized $PBQH^{\bullet}$ was generated. However, the disappearance of the CIDEP signal of TX-100 radical may be the result of its fast relaxation. In the TX-100 micelles polyethylene glycol shell, the high pH caused by the bound water made the $PBQH^{\bullet}$ dissociate to $PBQ^{\bullet -}$ easily. This is the reason why only the CIDEP signal of $PBQ^{\bullet -}$ was obtained.

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