

Effects of TX-100 Micelles on the CIDEP Mechanism for Creating P-benzosemiquinone Radicals

Li Ganzuo Su Hongmei Li Fang
(Institute of Colloid and Interface Chemistry,
Shandong University, Jinan, 250100)

Lu Tongxing Zhang Wenmin
(Department of Physics, Anhui Normal University, Wu hu, 241000)

Abstract

A comparative study of the chemically induced dynamic electron polarization (CIDEP) spectra has been made experimentally with the time resolved ESR spectrometer for the photolyzed p-benzosemiquinone radicals (PBQH[•]) in ethylene glycol and Triton X-100 (TX-100) micelle solutions. The polarization of PBQH[•] is mainly the triplet mechanism (TM) of origin and at times also involves some radical pair mechanism (RPM) in TX-100 micelle solution, the effect of RPM increases, but there is not the same effect in homogeneous ethylene glycol (EG) solution; thus the influence of micelle microenvironment on transient behavior of radicals is shown. The polarization transference mechanism is discussed to explain these experimental results.

Keywords: CIDEP, p-benzosemiquinone radical, TritonX-100, micelle.

1. Introduction

The phenomenon of transient populations of electron spin states differing from the Boltzmann distribution has been known chemically as induced dynamic electron polarization (CIDEP)^[1]. CIDEP is a useful phenomenon for the study of photochemical and photophysical processes. There are mainly two mechanisms generating CIDEP on transient radicals: one is the triplet mechanism (TM) and the other is the radical pair mechanism (RPM).

If the TM operates, the radicals are created with single-phase spin polarization. However, they are often produced as a pair and so RPM effects are also expected. The relation time of spin polarization in general is within 10^{-10} μ s of radical creation in organic systems and they affect the ESR spectrum that was first observed by using the fast transient methods; therefore most spectra show their combined effects^[2].

Trifuna^[3] carried out some research on the CIDEP spectra of photolyzed *p*-benzosemiquinon radicals (PBQH[•]) taken at a different time after excitation by laser flash and concluded qualitatively that the spectra are affected by both TM and RPM mechanisms. Recently we obtained theoretically the result by calculation according to the time dependent intensity curve for polarized PBQH[•] radicals and rationalized the CIDEP process in terms of TM and RPM origins^[4]. Both TM and RPM of PBQH[•] radicals were studied only in homogeneous solutions. With increasing interest in the study of the behavior of transient radicals in microenvironments, such as micelle solution, through observation of the unusual CIDEP spectra of spin-correlated radical pairs, it has been discovered that micelles often prolong the spin-correlated time of radical pairs^[5,6].

In this paper the CIDEP spectra of PBOH[•] radicals in TX-100 micelle solution were studied with the time resolved ESR (TRESR) spectrometer. It is found that the effect of RPM increased in micelle solution, Based on the analysis of the operating proportion of the two polarization producing mechanisms (TM and RPM) respectively, the discussion is made about the effect of micelle microenvironment on the CIDEP process of transient radicals.

2 Experiment

All spectra were recorded on a time-resolved ESR spectrometer which have been illustrated in detail elsewhere^[7]. The instrument mainly consists of a conventional X-band ESR spectrometer, a SRS 252 boxcar integrator (Starford Comp.), a PM 2556 digital oscilloscope (Phillips Comp.) and a nomad broad-band preamplifier with response time of 50 ns. An excimer laser was used for photolysis of the samples, The laser, LPX 105 excimer laser (Xe/HCl gas mixture, Lambda physik), operating at 308 nm with a pulse energy of 60 mJ/pulse, at repetition rate of 20 HZ. The experiments were done with a flowing system consisting of a flat (light range 0.3 mm) cell.

TritonX-100(a nonionic surfactant) was obtained from Rohm and Haas product, which was used without further purification. PBQ, EG, (A.R) were purchased

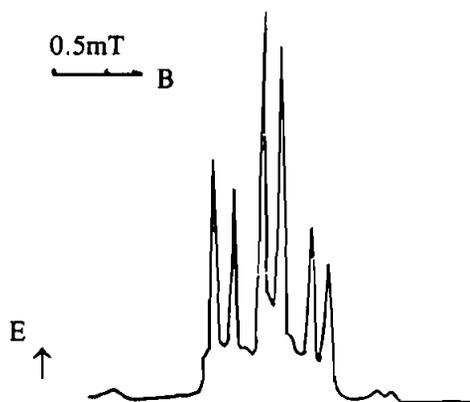
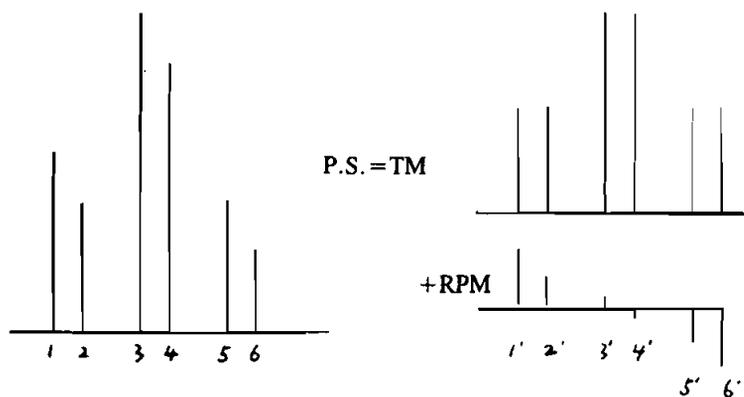


Fig.1. TRESR spectrum taken $1.2 \mu\text{s}$ after excitation of PBQ in EG solution ($0.01 \text{ mol} \cdot \text{L}^{-1}$).

Note: In this and all subsequent figures, signals above the base line are in emission and those below are in absorption, and the gate aperture of the boxcar average is kept $0.3 \mu\text{s}$.



note: P.S. = Practical Spectrum

Fig.2 Elementary model explaining why the proportion of RPM in CIDEP spectra.

note: P.S. = practical spectrum

Beijing Chemicals, China. PBQ (p-benzoguinone) was further purified by sublimation. Samples were prepared by dissolving $0.01 \text{ mol} \cdot \text{L}^{-1}$ of PBQ. The following is the different concentration of TX-100: 0.013, 0.037, 0.065, $0.105 \text{ mol} \cdot \text{L}^{-1}$ in the ethylene glycol.

3. Results and Discussion

3.1 CIDEP of PBQH \cdot radicals in homogeneous PBQ/EG system

The TRESR spectrum obtained by direct detection of a laser flash photolyzed EG solution of PBQ is shown in Fig. 1, with polarization of PBQH \cdot originated from TM. All the six hyperfine lines of PBQH \cdot radicals are in emission. TM yields spectra with the relative intensities of hyperfine lines equal to static ESR spectra^[8]. However, the intensities of experimental lines are distorted, with the hyperfine lines in high field weaker than their symmetrical ones in low field. All this indicates that there are also some RPM involved in the CIDEP process, considering the RPM spectra are characteristic of lines in absorption being in high field and lines in emission being in low field.

The above emissive spectrum mixed with some E/A (emissive lines in low field and absorptive lines in high field) spectrum is due to the combining effects of both TM and RPM. The proportion of E/A spectrum on the whole spectrum is the proportion of RPM effect in the whole CIDEP mechanism. To analyze the proportion of RPM in the above CIDEP spectra the experimental spectra are taken as "bar" spectra without width at first; then the "bar" lines are decomposed into single TM lines and single RPM lines as shown in (Fig. 2).

With Y_i standing for the intensity of i line the experimental spectrum, the intensity of RPM line Y'_i is: $Y'_1 = (Y_1 - Y_6)/2 = Y'_6$, $Y'_2 = (Y_2 - Y_5)/2 = Y'_5$, $Y'_3 = (Y_3 - Y_4)/2 = Y'_4$. The proportion of RPM in CIDEP spectra is $2 Y'_1 / (Y_1 + Y_6) = 2 Y'_2 / (Y_2 + Y_5) = 2 Y'_3 / (Y_3 + Y_4)$ by using such a method to analyze Fig. 1. The RPM proportion in CIDEP of PBQH \cdot in EG solution is known to be 22.0%.

3.2 CIDEP of PBQH \cdot radicals in PBQ/TX-100/EG micelle system

With some surfactant TX-100 added to the PBQ/EG system, the deviation of intensities between lines in high field and their symmetrical ones in low field increased apparently as shown in Fig. 3, compared with Fig. 1. The result indicates that the proportion of RPM effect in PBQ/TX-100/EG system increases in comparison with PBQ/EG system.

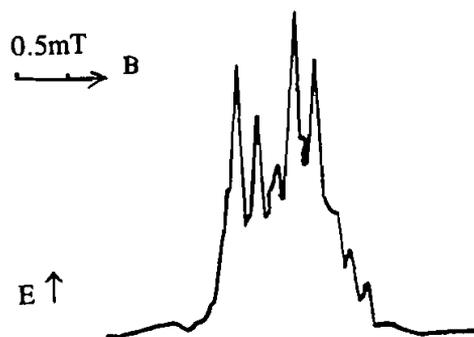


Fig.3 TRESR spectrum taken $1.2 \mu s$ after excitation of PBQ in EG solution of TX-100 with $[TX-100] = 0.105 \text{ mol.l}^{-1}$.

Table 1 Proportion of RPM effect on polarization of PBQH'

$[TX-100]/\text{mol.l}^{-1}$	0.000	0.037	0.065	0.105
$[RPM]\%$	22.0%	21.6%	39.3%	40.9%

Moreover, the spectra of PBQH' in PBQ/TX-100/EG systems with a series of TX-100 concentration were studied ($T_d = 1.2 \mu s$) and the corresponding proportion of RPM effect was analyzed, with the data shown in Table I. Among the TX-100 concentrations the 0.037 mol.l^{-1} was below the critical micelle concentration (cmc) of TX-100, 0.05 mol.l^{-1} [9].

Table 1 proportion of RPM effect on polarization of PBQH' in PBQ/TX-100/EG systems with different TX-100 concentration

Data in Table I shows that the proportion of RPM effect in PBQ/TX-100/EG system with the concentration of TX-100 below CMC (0.037 mol.l^{-1}) is equal to that in PBQ/EG system (0.000 mol.l^{-1}) within the experimental error. However, the effect of RPM increased when TX-100 micelles formed in the systems with TX-100 concentration above CMC (0.065 or 0.105 mol.l^{-1}). When surfactant concentration is above CMC, these increased values of the effect of RPM in the CIDEP of PBQH' are almost equal.

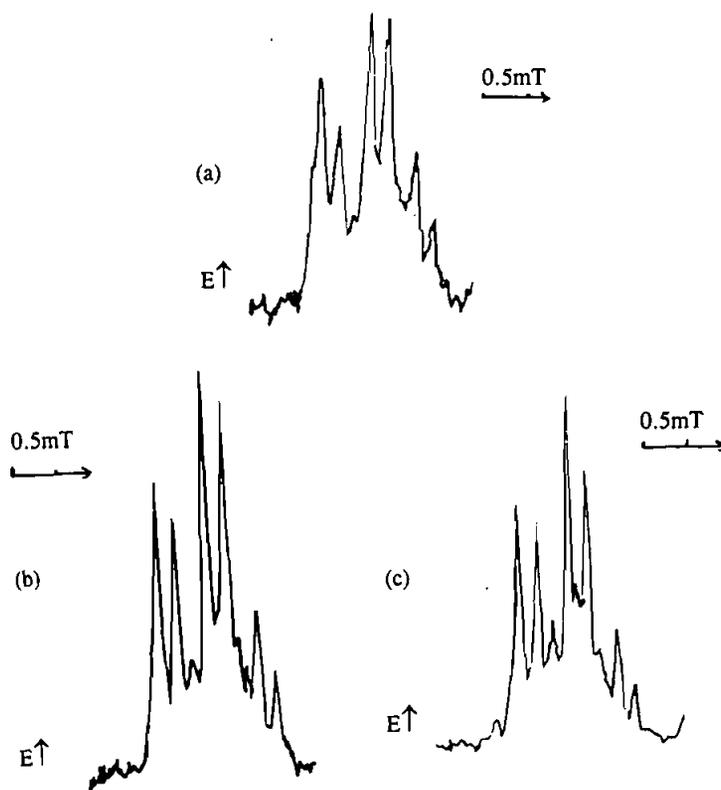


Fig.4 TRESR spectra taken(a) $0.4 \mu s$, (b) $0.8 \mu s$, (c) $1.2 \mu s$ after excitation of PBQ in EG solution of TX-100 with $[TX-100]=0.065 \text{MOLL}^{-1}$.

As to the system with 0.065 mol.l^{-1} TX-100, the TRESR spectra taken at a different time after excitation by laser flash are further studied. As shown in Fig.4, the deviation of intensities between lines in high field and their symmetrical lines in low field increases with time. That is to say, the effect of RPM increases with time, which could be drawn from the data in Table 2.

Table 2 illustrates that proportion of RPM effects on polarization of PBQH[•] in PBQ/TX-100/EG system ($[TX-100]=0.0065 \text{ mol.l}^{-1}$) at a different time after excitation.

Table 2 Proportion of RPM for PBQH[•] at different time

Td/ μ s	0.4	0.8	1.2
RPM%	30.1	33.1	39.3

The phenomena that the effect of RPM increases with time after excitation show that a type of F-pairs RPM has come into being. RPM occurs due to the fact that spin alignment is conserved in the radical creation step and, in this case, a geminate spin-correlated radical pair which is called G-pair is formed. Such correlated pairs are produced by the random encounter of freely diffusing radicals created in separate geminate events, which are called F-pairs, so the type of G-pairs RPM operates instantaneously in the radical creation step and relaxes quite fast where as the F-pairs polarization is generated for as long as reactive radicals persist in the solution, F-pairs are thus observed long after radical creation by photolized P-benzosemiquinone.^[1] The production of G-pair which are PBQH[•] and $\dot{R}(\text{OH})_2$, but the life of the latter is very short (1.5 μ s); therefore a conclusion could be drawn that the random encounter of PBQH[•] radicals after creation forms F-pairs and the effect of F-pairs RPM become more and more apparent with the lapse of time after excitation. In the TX-100 micelle solution, PBQ is solubilized in the poly ethylene glycol chain shell of TX-100 micelles^[10] The hydrogen atom located in-OH-group of PBQH[•] is slightly positively charged because of the attraction of π -bonding of the benzene ring to electrons of-OH-group. The formation of hydrogen bonding between the oxygen atom in polyethylene glycol chain of TX-100 and the above mentioned hydrogen atom of PBQH[•] will effectively hinder the diffusion separation of radicals. On the other hand, the concentration of PBQH[•] radicals is enriched because of their solubilization in TX-100 micelles. Affected by the above two factors, micelle supercargo acts as boundaries which will increase the probability of the formation of F-pairs by the radical's encounter at random. So the effect of F-pairs RPM on the CIDEP of PBQH[•] in TX-100 micelle solution increases in comparison with homogeneous PBQ/EG solution; thus the influence of micelle microenvironment on transient behavior of radicals is shown.

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