

A CIDEP study of photolysis benzophenone radicals in the microheterogeneous phase systems*

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Abstract The chemically induced dynamic electron polarization (CIDEP) of photolyzed benzophenone radicals in the microheterogeneous phase systems has been made by using the time-resolved electron spin resonance (TRESR) spectrometer. In the AEO₉/isopropanol/H₂O/C₈H₁₈ liquid crystal system, the TRESR spectrum of Ph₂COH shows an unusual CIDEP of spin correlation radical pair (SCRPs). The SCRPs formation in these systems resulting from the character microenvironment and the related physical-chemistry property are discussed.

Keywords: CIDEP, TRESR, benzophenone, radicals, lyotropic liquid crystals.

The phenomenon of transient populations of electron spin states differing from the Boltzmann distribution has been known as chemically induced dynamic electron polarization (CIDEP)^[1]. CIDEP serves as a useful method to study the transient behavior and kinetics of radicals. CIDEP is a micro-second signal, so it must be detected by a time-resolved electron spin resonance (TRESR) spectrometer.

Microheterogeneous phases are organized molecular assemblies, such as various association structures of surfactant solution, which can be microenvironment of reaction, too. Turro^[2] pointed out that these systems were good "senior cages" which can not only prolong the life of intermediate-state product, but also affect the physical process and chemical reaction of substances, especially in respects of their possibility, mechanism, rate, etc.

In the ethylene glycol solution for *p*-benzoquinone (PBQ) photolyzed *p*-benzosemiquinon radicals (PBQH[•]), the proton exchange is influenced. It produces the anion radical (PBQ^{•-})^[3,4] in Tx-100 or AOT micells. There are some reports about CIDEP of photolyzed benzophenone radicals. Sakaguchi et al.^[5] discovered the special polarized spectra of CIDEP for the photolyzed benzophenone (BP) SDS micelle, each hyperfine line looking like a differential curve of ESR spectra of steady state, but they did not give satisfactory explanation. Later on Closs et al.^[6] explained the phenomenon excellently by means of spin correlated radical pairs (SCRPs) theory. However, there has been no report yet on the phenomenon in liquid crystal system. SCRPs is a kind of real

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intermediate state of the reacted substance. A profound study of the phenomenon can offer a lot of useful information about radical reaction process and photochemical reaction mechanism. In this paper, the CIDEP of photolyzed benzophenone radicals in several microheterogeneous phase systems is examined. SCRIP phenomenon is found only in the AEO₉/isopropanol/H₂O/C₈H₁₈ liquid crystal system.

1 Experimental

1.1 Instrument

All spectra were determined on a time-resolved ESR spectrometer, which has been illustrated in detail elsewhere^[7,8]. The instrument mainly consists of a conventional X-band ESR spectrometer, an SRS 252 boxcar integrator, a PM 2556 digital oscilloscope and a normal broad-band preamplifier with a response time of 50 ns. An excimer laser was used for the photolysis of the samples. The laser, an LPX 105 (Lambda physik) excimer laser (Xe-HCl gas mixture), operating at 308 nm with a pulse energy of 60 mJ/pulse, is fired at a repetition rate of 20 Hz. The experiments were performed with a flowing system consisting of a flat (interior space: 0.3 mm) cell.

1.2 Materials

The purities of isopropanol, BP, octane and nonionic surfactant dodecanol poly-ethenoxy ether (AEO₉, C₁₂H₂₅O(C₂H₄O)₉H) were all AR grade and they were used without further purification. Water was distilled twice.

2 Results and discussion

2.1 Diagram of AEO₉/H₂O/C₈H₁₈ system

The ternary phase diagram of AEO₉/H₂O/C₈H₁₈ system was determined according to ref. [9]. As shown in fig. 1, there are three regions in the diagram: the liquid crystal (L. C.) region, the microemulsion (ME) region, and the diphasic region (II). The two points A and B in L. C. and ME regions were chosen as the microenvironment systems. The microstructure of system A was examined by a polar microscope and a ²H-NMR spectroscopy. The L. C. phase exhibits distinct textures when observed by a polarizing microscope. The mosaic texture and oily

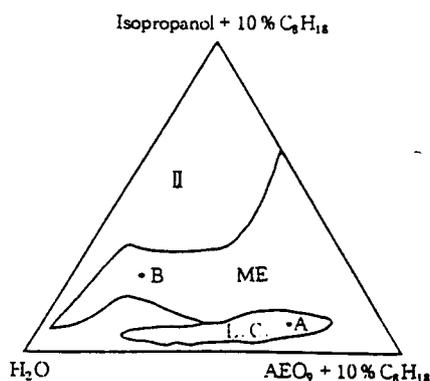


Fig. 1. Ternary phase diagram of AEO₉/(CH₃)₂COH/C₈H₁₈ system. L. C., Liquid crystal; ME, microemulsion; II, two-phase region; A, B, sampling points.

streaks in fig. 2 are best identified as the lamellar phase^[10]. A pair of widely separated (1 kHz) peaks in its ²H-NMR spectrum (see fig. 2(b)) confirms the conclusion that system A is lamellar liquid crystal.

When a small amount of BP was put into system A and B, the microstructure of the systems did not change: the former was liquid crystal and the latter was microemulsion. Fig. 2(c) shows a schematic diagram of liquid crystal.

2.2 CIDEP study of photolyzed BP in isopropanol

The CIDEP spectrum of BP in isopropanol was obtained after BP was irradiated by laser for 0.6 μs ($T_d = 0.6 \mu s$, see fig. 3). There were separately three hyperfine lines on the two sides of the magnetic field: emis-

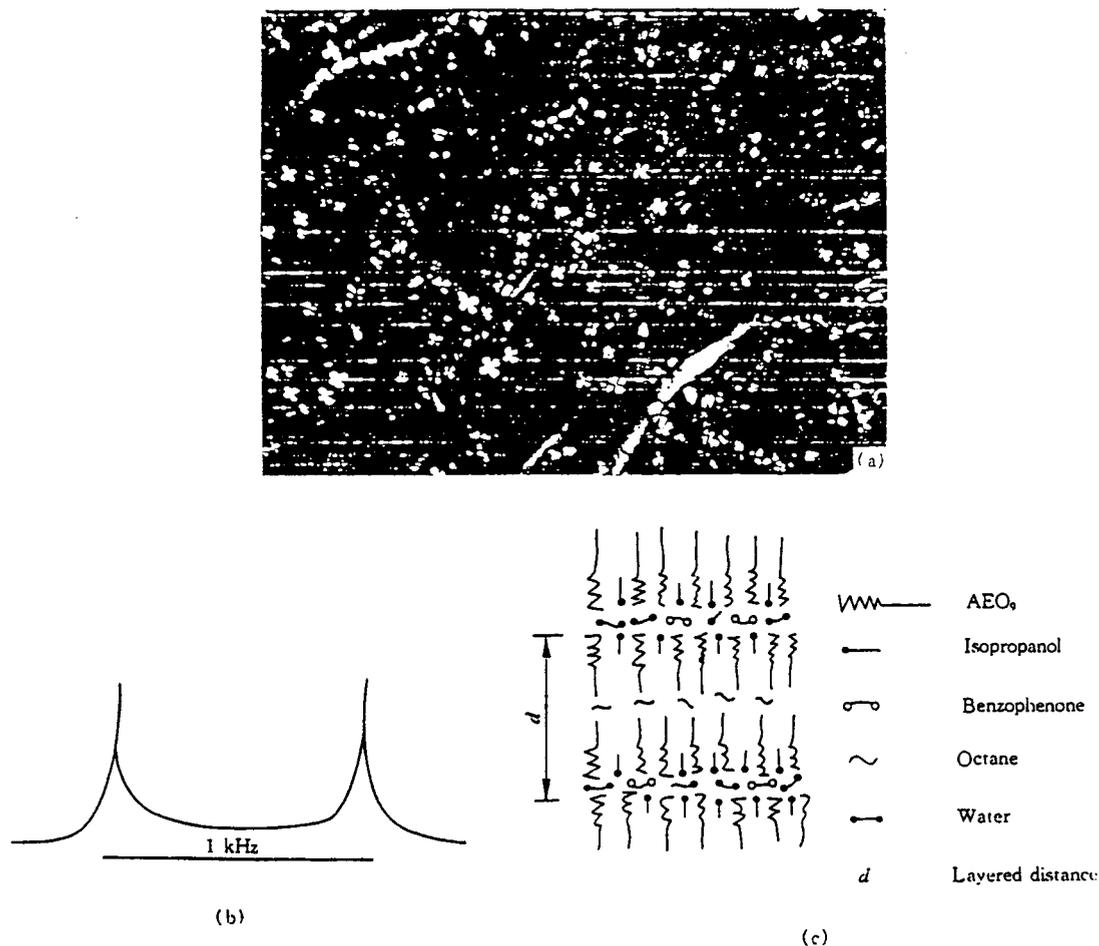


Fig. 2. The characteristic diagram. (a) Texture of liquid crystal; (b) ^2H -NMR spectroscopy of liquid crystal; (c) schematic diagram of lamellar liquid crystal.

sion lines were on the lower field, absorbent lines were on the higher field. The six lines belonged to $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radicals. Its polarizing process took place through single state (S)-triplet state (T_0) mixed radical pair mechanism (RPM). The wide peak at the center of the spectrum belonged to $\text{Ph}_2\dot{\text{C}}\text{OH}$ radicals, which contained several overlapping weak emission lines. Increasing time T_d did not bring about any changes in the shape of lines, except that the strength became weak. The phenomenon has already been reported^[11].

2.3 CIDEP study of photolyzed BP in liquid crystal system

BP in AEO₉/isopropanol/ C_8H_{18} liquid crystal system (point A in fig. 1) was irradiated by

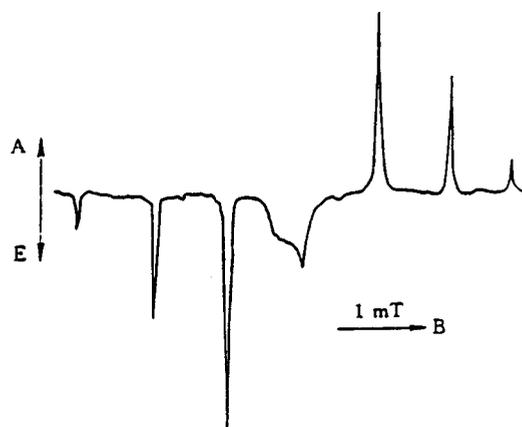


Fig. 3. TRESR spectrum of photolyzed benzophenone in isopropanol. $[\text{BP}] = 0.05 \text{ mol} \cdot \text{L}^{-1}$, boxcar width = $0.3 \mu\text{s}$, $T_d = 0.4 \mu\text{s}$.

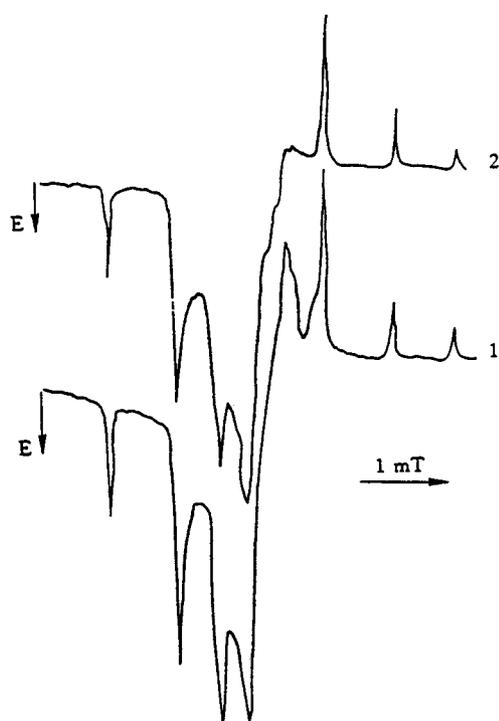


Fig. 4. TRESR spectra of photolyzed benzophenone in $\text{AEO}_9/\text{isopropanol}/\text{C}_8\text{H}_{18}$ liquid crystal system. $[\text{BP}] = 0.05 \text{ mol}\cdot\text{L}^{-1}$, boxcar width = $0.3 \mu\text{s}$, $T_d(1) = 0.6 \mu\text{s}$, $T_d(2) = 1.0 \mu\text{s}$.

BP was irradiated by laser in $\text{AEO}_9/\text{isopropanol}/\text{C}_8\text{H}_{18}$ microemulsion system (point B in fig. 1), and CIDEP spectrum was then obtained (see fig. 5). The six hyperfine lines of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ became wider compared with those in fig. 3, but the signal of $\text{Ph}_2\dot{\text{C}}\text{OH}$ was strong and the absorbent peak near the emissive peak did not appear. These phenomena belonged to the radical pair mechanism (RPM).

2.5 Discussion

Various CIDEP spectra of BP were obtained respectively in isopropanol, liquid crystal and microemulsion system. Irradiated by laser at wavelength of 308 nm, such a photochemical and photophysical process of BP could occur. BP molecule changes from ground state to single excited state after absorbing photon, and then in the process of intersystem crossing changes from the single excited state into excited triplet state, and in the mean time captures hydrogen. The spin correlation radical pair existed for a very short time, and disappeared along with diffusion of radicals. So the normal RPM polarization was accomplished through production, diffusion and recombination of the radical pair. If radicals are produced in special systems such as liquid crystal, the diffusion and separation of radicals may be limited, their spin correlation life can be delayed. So liquid crystal proves to be a special condition for the polarization of the radical pair.

In order to understand the phenomenon of spin correlation radical pair polarization^[6], a supposition is made first that the interaction between two radicals is very weak, so that the resonance spectra of the centers of pairs are two lines of ω_1 and ω_2 and the exchange interaction energy of

laser for $0.6 \mu\text{s}$ or $1.0 \mu\text{s}$, and two spectra were obtained (see fig. 4, curves 1 and 2). The signal of $\text{Ph}_2\dot{\text{C}}\text{OH}$ radicals at the center of the spectrum strengthened clearly compared with that in fig. 3, and was stronger than the six hyperfine lines of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radicals. It proved that the concentration of $\text{Ph}_2\dot{\text{C}}\text{OH}$ radicals increased greatly. The reasons may well be as follows: (i) according to reaction ${}^3\text{Ph}_2\text{CO} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{Ph}_2\dot{\text{C}}\text{OH} + (\text{CH}_3)_2\dot{\text{C}}\text{OH}$, the triplet state of photolyzed molecule ${}^3\text{Ph}_2\text{CO}$ captured hydrogen from isopropanol molecule, producing these two kinds of radicals; (ii) ${}^3\text{Ph}_2\text{CO}$ also captured hydrogen from surfactant molecule to get $\text{Ph}_2\dot{\text{C}}\text{OH}$. When $T_d = 0.6 \mu\text{s}$, a new absorbent peak as shown in fig. 4, curve 1, appeared near the emissive peak on the side of the higher field. When $T_d = 1.0 \mu\text{s}$ this new absorbent peak disappeared as shown in fig. 4, curve 2, but the strength of these emissive peaks did not change. The phenomenon will be explained as follows by using SCR theory.

2.4 CIDEP study of photolyzed BP in microemulsion

the unpaired electron $J(r)$ is far smaller than the difference of resonance frequencies of two radicals $\Delta\omega = (\omega_1 - \omega_2)$. If there had not been the hyperfine structure, the radical pairs would have split into four states T_+ , T_0 , T_- and S . Because of the Zeeman effect in the magnetic field, The energy of T_+ state is the highest. That of T_- is the lowest and those of T_0 , S stand in the middle, because T_0 and S are in the degenerate mixed states. The radical pairs produce four new states $\Psi_1, \Psi_2, \Psi_3, \Psi_4$ under spin correlation condition. By using one-order approximation, the four states of radicals could be indicated as

$$\begin{aligned}\Psi_1 &= T_+ = \alpha_1\alpha_2, \\ \Psi_2 &= \alpha_1\beta_2 + \kappa\beta_1\alpha_2, \\ \Psi_3 &= \beta_1\alpha_2 + \kappa\alpha_2\beta_2, \\ \Psi_4 &= T_- = \beta_1\beta_2,\end{aligned}$$

where κ is the mix constant and related to

$J(r)$. $\alpha_1, \alpha_2, \beta_1, \beta_2$ represent the unpaired

electron spin states of both radicals, respectively. If the radicals are in the triplet state at the beginning, the distributed energies of $\Psi_1(T_+)$, $\Psi_4(T_-)$ and T_0 are 1/3, respectively. Because T_0 and S mix, Ψ_2 and Ψ_3 account for only 1/3. If $J(r) < 0$, there are both radical pairs of permitted jump among the four states. For example, the first radical pair is from ω_1 to ω_3 (emissive jump), the second radical pair is from ω_4 to ω_2 (adsorptive jump). Therefore, the original line of ω_1 splits into a pair of lines of emission/adsorption. Because the $J(r)$ value is very small, the two lines are very near and are like a differentiation curve of a stable state ESR spectrum.

In this experiment, the first spin correlated radical pair is composed of $\text{Ph}_2\dot{\text{C}}\text{OH}$ and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ (fig. 4, curve 1). Its emissive peak and adsorptive peak which is near the high field form the two lines of emission/adsorption of SCRCP, notwithstanding the spectrum is also due to a little RPM. The second spin correlated radical pair contains $\text{Ph}_2\dot{\text{C}}\text{OH}$ and another radical, which may be a surfactant molecule (AEO_9) that has lost hydrogen. The above-mentioned result demonstrates that the signal of benzophenone radical ($\text{Ph}_2\dot{\text{C}}\text{OH}$) in the liquid crystal (fig. 4, curve 1) is stronger than that in the isopropanol solution (fig. 3). Because the relaxation rate of surfactant radical is fast, the surfactant radical cannot be checked up in the experiment.

When the time (T_d) was prolonged to 1.0 μs , the radical pair diffused and separated. Therefore the SCRCP polarization changed into a normal RPM polarization, as is shown in fig. 4, curve 2.

Laser photolyzed process often produces radical pairs which can exhibit the spin correlation in the special condition because of the law of conservation of spin. The phenomenon is called the spin

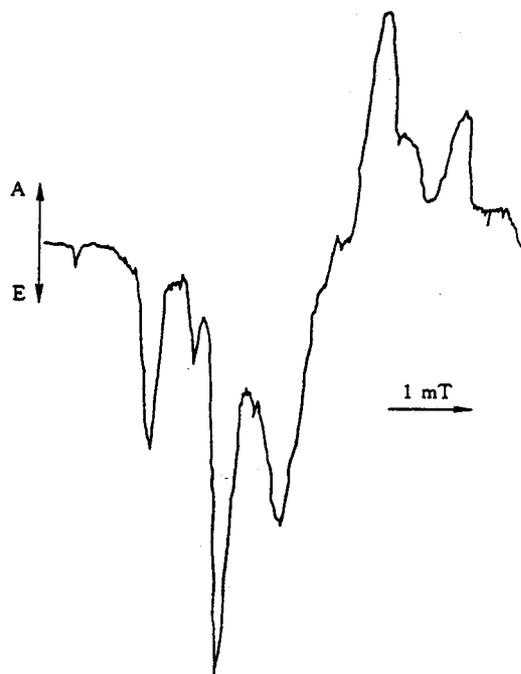


Fig. 5. TRESR spectrum of photolyzed benzophenone in $\text{AEO}_9/\text{isopropanol}/\text{C}_6\text{H}_{18}$ microemulsion system. $[\text{BP}] = 0.05 \text{ mol}\cdot\text{L}^{-1}$, boxcar width = 0.3 μs , $T_d = 0.4 \mu\text{s}$.

correlative radical pair.

Lytropic liquid crystal is a kind of anisotropic association structure system which contains surfactant, oil, water and cosurfactant. The system is orderly in long range but disorderly in short range, and has high viscosity. The system can solubilize oil and water at the same time, so it is a "excellent cage", which can hinder the diffusible separation of radicals. This is the first time we have observed the phenomenon of polarized spin correlated radical pair in liquid crystal system.

The interface membrane of lyotropic liquid crystal system in this paper contains ordered AEO₉ and a part of isopropanol molecules. Other isopropanol, water and benzophenone molecules are solubilized between the two surfactant polar head layers, while oil is solubilized between the two hydrocarbon chain tail layers. Triplet state molecule (³Ph₂CO) of photolyzed BP could capture hydrogen from an isopropanol or surfactant molecule in the surfactant polar head layers, and only produce (CH₃)₂ĊOH and Ph₂ĊOH radical pairs, because surfactant radical has a fast relaxation rate. The volume of a (CH₃)₂ĊOH is very small, so that it can diffuse out of the cage and become a free single radical, and then normal RPM polar spectrum could be got. But most (CH₃)₂ĊOH radicals produce spin correlated radical pairs with Ph₂ĊOH. In fact the spectrum is the reflection of common result of SCRCP and normal RPM polarization. In the systems studied in the paper, the maintainable time of spin correlation radical pair is limited. After 1.0 μs the two kinds of radical pairs are separated through diffusion and the normal CIDEP spectrum can be obtained.

In the microemulsion point B, the spectrum line of Ph₂ĊOH does not split into a derivation curve, which shows that not all the microheterogeneous phase systems can efficiently hinder the diffusible separation of radicals and prolong the existing time of the spin correlated radical pair. The viscosity of microemulsion is small, and part of isopropanol and polar organic BP is solubilized in the interphase of microemulsion^[11], Ph₂ĊOH and (CH₃)₃ĊOH diffuse out of the cages easily for the above reason. It proves that spin correlated radical pair could not be produced easily in microemulsion systems. In fig. 5 the line width is greater and its ratio of signal/voice is smaller. The facts mentioned above show that the movement and rotation of molecule are fast in the low viscosity microemulsion systems.

3 Conclusion

CIDEP processes of photolyzed BP in various systems are different, RPM polarized spectrum has been obtained in isopropanol. The spin correlated radical pairs are gotten. In fact the spectra are the result of the common action of SCRCP and RPM polarization, and turn back into the normal RPM polarized spectrum if the time is increased to 1.0 μs. The RPM polarized spectrum has been obtained in microemulsion systems, too.

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