Dual Spin Polarization of CIDEP in Benzil/Quencher Systems

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Dual spin polarization of triplet benzil was investigated by the time-resolved ESR technique. Spin polarization of triplet benzil showed only absorption in rigid matrices at 77 K. However, the phase of CIDEP signals caused by the triplet mechanism showed absorption or emission depending on the concentration of quenchers at room temperature. Both polarizations were generated through a one-photon absorption process. Absorptive polarized radicals were produced from free benzil, whereas emissive polarized radicals were produced from benzil/quencher complex.

Introduction

The photochemistry of carbonyls has been extensively used in model systems during the early development of the photoexcited triplet mechanism (TM) in CIDEP (chemically induced dynamic electron polarization) phenomena.¹ TM polarization arises in sublevel-selective intersystem crossing (ISC) from a photoexcited singlet state to the lowest triplet state to yield a polarized triplet species. This reaction conserves spin alignment to yield polarized radicals providing that certain kinetic requirements are met. A reaction which is fast enough compared to the triplet electron spin-lattice relaxation time gives a polarized TM signal. A number of CIDEP studies have been carried out on carbonyl compounds using time-resolved ESR measurements.^{2,3}

It is well-known that benzil has two rotational isomers. Many studies⁴⁻⁶ have been made on the conformations of benzil. Benzil in the ground state has a nonplanar (skew) conformation in which the central carbonyl-carbonyl bond is twisted at an angle of 111°.7 Therefore, the two benzoyl moieties are not in conjugation with each other. In the excited state, benzil has a trans-planar conformation. Morantz and Wright reported that the skew benzil relaxed to the trans-planar conformation after the excitation.8

Grant and McLauchlan² reported TM polarizations of several carbonyl compounds, in which benzil yielded absorptive TM polarization. On the other hand, Yamauchi et al.³ observed emissive signals in the benzil/2-propanol system. Recently, Mukai et al.⁹ reported that benzil gave both absorptive and emissive TM polarizations in the benzil/triethylamine system, which were explained by reactions from different excited triplet states produced by one- and two-photon absorption.

In this paper, we report dual spin polarization generated by TM from the lowest triplet state in benzil/amine and benzil/phenol systems. It is concluded that free benzil gives an absorptive while benzil-quencher complexes give emissive polarizations.

Experimental Section

Time-resolved ESR measurements were carried out using a Varian E-112 spectrometer at X-band without field modulation. Signals were accumulated in a boxcar integrator (Stanford SR-

250). The gate of the boxcar was opened $1.1-2.1 \ \mu s$ after the laser pulse. A nitrogen laser (Molectron UV-24) or a XeCl excimer laser (Lambda Physik EMG 52 MSC or LPX 100) was used as an excitation light source. The details of the experimental apparatus were described previously.10

In low-temperature experiments, the sample in a quartz ESR tube of 5 mm diameter was thoroughly degassed by multiple freeze-pump-thaw cycles. In room temperature experiments (CIDEP), sample solution was bubbled with nitrogen gas to remove dissolved oxygen and flowed through a quartz flat cell (0.5 mm interior space) at a flow rate of ca. 2 mL/min.

Zone-refined (Kanto Chemicals) and G.R. grade benzil (Tokyo Kasei) were used for low-temperature experiments and CIDEP, respectively. G.R. grade aniline (Yoneyama Yakuhin Kougyo) was purified by distillation under reduced pressure or used without purification. G.R. grade 2-butylamine and N,N-dimethylaniline (Tokyo Kasei) were used without purification. G.R. grade 2,6di-tert-butylphenol (Tokyo Kasei), 2,4,6-trimethylphenol (Kanto Chemicals), and 2,6-dimethylphenol were purified by column chromatography using silica gel, followed by recrystallization from *n*-hexane. Sodium dodecyl sulfate (SDS) obtained from Tokyo Kasei was used without purification.

Results and Discussion

1. Triplet Spin Polarization in Low-Temperature Matrices. As stated earlier, benzil has two rotational isomers: the nonplanar (skew) structure in the ground state and the planar one in the excited states. By controlling the rate of cooling, the rotational isomers could be obtained selectively.⁶ When matrices were made with rapid cooling, benzil kept its nonplanar conformation, whereas gradual cooling led to the planar conformation which was stable in polycrystals. Figure 1 shows the TR-ESR spectra of benzil in methylcyclohexane at 77 K. Figure 1a shows the spectrum of a rapidly cooled sample, which was known to contain nonplanar benzil due to its green phosphorescence. Signals are absorptive at H_{\min} near 0.15 T and are absorptive and emissive at magnetic fields lower and higher than H_e , respectively. The ZFS parameters were estimated to be 0.12 cm^{-1} for |D| and 0.027 cm^{-1} for |E| from canonical points of the spectrum. The D and E values obtained are in agreement with those of X-traps of benzil neat crystal reported by Chan and Nelson¹¹ using the ODMR technique (D= 0.1191 cm⁻¹, E = -0.0253 cm⁻¹). Figure 1b shows the spectrum of a slowly cooled sample which emits characteristic orange phosphorescence of the planar conformation.

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Figure 1. TR-ESR spectra of benzil in methylcyclohexane matrices obtained at 77 K and 1.1 μ s after laser pulse: (a) rapidly cooled sample (nonplanar) and (b) slowly cooled sample (planar).



Figure 2. Concentration dependence of the CIDEP spectra on aniline obtained by laser photolysis in benzil $(8 \times 10^{-2} \text{ M})/\text{aniline}$ in benzene. Concentrations of aniline are (a) 10^{-3} M , (b) 10^{-1} M , and (c) 6 M.

Signals at H_{\min} are also absorptive around 0.14 T and those of the $\Delta m_s = 1$ transition are absorptive in fields lower than H_e and emissive in fields higher than H_e . Definitive canonical points were not observed because of the multisite signals of polycrystalline. Since Asano et al.⁶ reported that the rate of ISC to the T_s sublevel was the largest, positive D values seem to be consistent with the observed spectra. Thus, it is concluded that the zero-field T_s spin sublevel is the lowest one and is mostly populated by ISC in both conformation.

If reaction takes place with a rate faster than spin-lattice relaxation from the spin-polarized triplet benzil, radicals with absorption polarization should be produced by TM.

2. CIDEP at Room Temperature. Figure 2 shows the CIDEP spectra obtained in laser photolysis of benzil/aniline systems in



Figure 3. Concentration dependence of the CIDEP spectra on TMP obtained by laser photolysis in benzil $(8 \times 10^{-2} \text{ M})/\text{TMP}$ in benzene. Concentrations of TMP are (a) 4×10^{-3} M and (b) 2×10^{-2} M.

benzene solution at room temperature. The spectra were obtained at a microwave power of 15 mW. The spectrum of Figure 2a obtained at concentrations of 8×10^{-2} M for benzil and 10^{-3} M for aniline consists of resolved hyperfine structures in wide magnetic field and broad emission signal in narrow center field. In this system, phenylaminyl radical is known to be produced by hydrogen abstraction reaction, because the resolved hyperfine structures agree with those of phenylaminyl radical.¹²

$$PhCOCOPh + PhNH_2 \rightarrow PhCOHCOPh + PhNH$$
 (1)

The broad spectrum in the center field is attributed to the counterpart radical, benzil ketyl. The phase of CIDEP in this spectrum is the superposition of total emission and a small contribution of E/A signals. There is little difference in the g value between these two radicals, and both show the same phase in CIDEP. These facts indicate that the net emissive CIDEP signal is produced by TM. Figure 2b shows a CIDEP spectrum in the same system with a high concentration of aniline (0.1 M). The same hyperfine structures are observed, but the phase of CIDEP is quite different from the upper spectrum; the signals of phenylaminyl radical change from E^*/A to E/A^* and the phase of benzil ketyl radical is inverted from emission to absorption. The net absorptive polarization is also interpreted by TM. Furthermore, CIDEP of benzil ketyl again changes its phase to emission at very high concentrations of aniline (6 M) as shown in Figure 2c, where the S/N ratio is low because of lowering of Q value at high concentrations of aniline. The spin polarization in this system shows very complicated behavior; the phase of polarization generated by TM changes from emission to absorption and again back to emission with an increase in the quencher's concentration.

This interesting phenomenon was observed not only in the benzil/aniline system, but also in other benzil/amine and benzil/phenol systems. The amines used were 2-butylamine and N_iN -dimethylaniline and the phenols used were 2,6-dimethylphenol (DMP), 2,6-di-*tert*-butylphenol (DTBP), and 2,4,6-trimethylphenol (TMP). For example, Figure 3 shows the CIDEP spectra obtained in benzil/TMP in benzene. It was reported that aromatic carbonyl compounds in the triplet state abstracted hydrogen atom from phenols and produced ketyl and phenoxy radicals.² In our system, hydrogen atom is abstracted from TMP.

 $PhCOCOPh + Ph-OH \rightarrow PhCOHCOPh + Ph-O$ (2)

The resolved hyperfine structures in wide magnetic field were attributed to 2,4,6-trimethylphenoxy radical and broad signals in the center field were assigned to benzil ketyl radical. In this

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Figure 4. Laser power dependence of the CIDEP signals for absorptive (\Box) and emissive (O) benzil ketyl radicals. Both plots indicate first-order dependence with laser power.



Figure 5. Dependence of the CIDEP spectra on the concentration of benzil obtained in benzil/aniline $(3 \times 10^{-2} \text{ M})$ in benzene. The concentrations are (a) $1.6 \times 10^{-2} \text{ M}$ and (b) $1.6 \times 10^{-1} \text{ M}$.

system, emissive TM polarization of the ketyl radical at low concentration is inverted to absorption at high concentration.

According to TM, the polarization of produced radicals reflects that of triplet precursor. Though the triplet state of benzil has absorptive character as known from the low-temperature experiments, the produced ketyl radicals in our system show emissive and absorptive polarizations depending on experimental conditions. This requires dual-faced polarization of the triplet benzil. No molecule other than benzil has been known to exhibit such kind of behavior. Why does the polarization of the triplet benzil change?

Mukai et al. also observed a TEA concentration dependent inversion of the TM polarization produced in the benzil/triethylamine (TEA) system:⁹ absorptive polarized radical was produced at high concentrations of TEA and emissive benzil ketyl radicals at low concentrations. The switching of polarization was interpreted with the reactions of different excited triplet states of benzil. Laser power dependence showed that the absorptive anion was produced from the lowest triplet state T_1 , whereas the higher triplet states led to emissive radicals. We examined the laser power dependence of the CIDEP signals in the benzil/aniline system in Figure 2, a and b. The logarithmic plots of benzil ketyl radical CIDEP signals (I) vs laser power (P) are shown in Figure 4. The values of laser power dependence were 1.0 for both emissive and absorptive signals. It was, therefore, concluded that their proposed mechanism was not operative and the lowest triplet







Figure 7. CIDEP spectra of benzil $(3 \times 10^{-3} \text{ M})/\text{aniline} (3 \times 10^{-2} \text{ M})$ in aqueous solution containing SDS $(8 \times 10^{-2} \text{ M})$. See text for details.

state was the reacting state in our system.

Next, we examined the concentration dependence of benzil. The spectrum shown in Figure 5a was obtained at concentrations of 1.6×10^{-2} M for benzil and 3×10^{-2} M for aniline. The E/A pattern produced by radical pair mechanism (RPM) was also observed and the contribution of TM polarization was very weak. An increase in benzil concentration leads to an enhancement of emissive TM signal as seen in Figure 5b where the concentration of benzil was 1.6×10^{-1} M. This indicates that spin polarization generated in this system depends not only on the quencher concentration but also on the benzil concentration. These results suggest that the complex formation between benzil and aniline in the ground state would influence the spin polarization of the triplet state.

Miyata et al. reported that benzil formed complexes with propionitrile and several alcohols in the ground state.¹³ The absorption spectra in the benzil/aniline system were obtained by varying the aniline concentration and are shown in Figure 6. The absorbance gradually increased with an increase in aniline con centration, which indicates complex formation between benzil and aniline in the ground state. Similar complex formation was also observed in the benzil/DMP system. On the other hand, complex formation was not observed in the benzil/TEA system in which benzil anion did not show an inversion of CIDEP by a one-photon process. Only in the systems where complexes were formed, the inversion of CIDEP was observed by varying the quencher's concentration. Therefore, emissive TM polarizations are expected to be produced by the reaction of complexes. We tried to measure

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TR-ESR spectra of benzil/aniline and benzil/DMP complexes in methylcyclohexane matrices at 77 K, but did not succeed because of the fast reaction of the triplet benzil in the complexes.

To determine the polarization of products from the triplet complexes, we examined the CIDEP of the benzil/aniline system in SDS_{aq} using a flow system. Two types of experiments were carried out. In the first experiment, benzil was dissolved in the SDS_{aq} solution and then aniline was added, and thus benzil and aniline were isolated from each other. Figure 7a shows the CIDEP spectrum obtained in this solution. Benzil ketyl radical was observed with absorptive polarization, but no phenylaminyl radical, which indicated isolation of the solutes. This absorptive polarization reflects that of the bare triplet benzil. Next, we prepared the same system in a different way: Benzil was first dissolved in neat aniline, and then this solution was dissolved in SDS_{aq}. The complexes formed in the first step are expected to survive in the SDS_{aq} solution where they are surrounded by SDS. Figure 7b shows the CIDEP spectrum of this solution. Benzil ketyl and phenylaminyl radicals were observed with emissive spin polarization. Thus we conclude the complexes yield photoproducts with emissive TM polarization.

3. Kinetic Analysis of CIDEP. We carried out a kinetic treatment in an attempt to reveal the mechanism responsible for spin polarization inversion. In our system, there are two chromophores due to chemical equilibrium of the ground-state molecules

$$\mathbf{B} + \mathbf{Q}\mathbf{H} \rightleftharpoons \mathbf{B} - \mathbf{Q}\mathbf{H} \tag{3}$$

where B is benzil and QH is the quencher. Free benzil gives absorptive CIDEP by TM, whereas complexes of benzil yield emissive CIDEP, which is opposite to the spin polarization of the triplet state measured at 77 K.

First we will discuss the absorptive CIDEP intensity of ketyl, I^A , produced by free triplet benzil. Polarized benzil ketyl is produced by the reaction scheme in eqs 4–7, where BH and Q

$$B \xrightarrow{h\nu} {}^{1}B$$
 (4)

$${}^{1}\mathbf{B} \xrightarrow{\mathbf{ISC}} {}^{3}\mathbf{B}_{sp}$$
 (5)

$${}^{3}B_{sp} \xrightarrow{k_{1}} {}^{3}B$$
 (6)

$${}^{3}B_{sp} + QH \xrightarrow{\kappa_{2}} BH_{sp} + Q$$
 (7)

are benzil ketyl and the dehydrated quencher radical, respectively. The superscript indicates the spin multiplicity of benzil, and the subscript represents the spin-polarized species. The excited singlet state yields polarized triplet benzil, ${}^{3}B_{sp}$, within 2 ns after laser excitation.¹⁴ Therefore, the formation rate of ${}^{3}B_{sp}$ was excluded from the rate equations. ${}^{3}B_{sp}$ decays via two channels, by spin-lattice relaxation to a Boltzmann distribution and by reaction with the quencher to produce absorptive polarized benzil ketyl. Spin-lattice relaxation and reactions of polarized radicals are neglected in the time range studied here because of their slow rate. In order to evaluate the contribution of BH_{sp}, the rate equations are written as follows

$$-d[^{3}B_{sp}]/dt = (k_{1} + k_{2}[QH])[^{3}B_{sp}]$$
(8)

$$-d[QH]/dt = k_2[^3B][QH]$$
(9)

$$d[BH_{sp}]/dt = k_2[^3B_{sp}][QH]$$
(10)

where [QH] was handled as a variable. ³B decay is slow in comparison to the spin-lattice relaxation rate k_1 allowing [³B] to be treated as a constant. The values of [BH_{sp}] were obtained as a functions of the initial concentration [QH]₀ by solving above equations numerically assuming $k_1/k_2 = 2$ M and [³B]/[³B_{sp}]_{t=0} = 10. These parameters were selected so that the pseudo-first-



Figure 8. Kinetic simulation of CIDEP intensities as a function of initial quencher concentration. Absorptive polarization generated from free benzil is indicated by the broken lines, emissive polarization from the complex is indicated by the dotted lines, and total polarization is indicated by the solid lines.

order approximation failed at very low [QH].

Emissive CIDEP intensity (I^{E}) resulting from the complex is produced by the following reaction scheme

$$B-QH \xrightarrow{n_{\nu}} {}^{1}B-QH \qquad (11)$$

$$^{1}B-QH \xrightarrow{ISC} {}^{3}B-QH_{sp}$$
 (12)

$${}^{3}B-QH_{sp} \rightarrow BH_{sp} + Q_{sp}$$
 (13)

Since these processes are completed at a much shorter time region than the time resolution of the apparatus, the emissive signal is proportional to the concentration of the spin polarized triplet of the complex

$$I^{E} \propto {}^{3}[B-QH_{sp}]$$

= $I_{abs}\Phi_{ISC}Y\epsilon_{2}[B-QH]/(\epsilon_{1}[B] + \epsilon_{2}[B-QH])$
= $I_{abs}\Phi_{ISC}Y\epsilon_{2}K[B][QH]/(\epsilon_{1}[B] + \epsilon_{2}K[B][QH])$ (14)

where $\epsilon_2[B-QH]/(\epsilon_1[B] + \epsilon_2[B-QH])$ is the correction factor for light absorption, Φ_{ISC} is the triplet quantum yield of the complex, and Y is a spin polarization factor. Estimated absorptive and emissive intensities are plotted as a function of the quencher concentration in Figure 8.

The total spin polarization, that is, the sum of absorptive and emissive intensities, is illustrated in Figure 8 as solid lines. The simulated results qualitatively reproduce the inconceivable behavior of the observed spin polarization inversions: emission at very low [QH], the change to absorption with an increase in [QH], and the second inversion to emission at very high [QH]. This kinetic model confirms the spin polarization inversion in the triplet state of the complexes. This result can be understood intuitively as follows. First, at very low concentration of QH, where pseudofirst-order approximation fails for [QH], benzil reacts with QH after spin polarization of triplet benzil is lost by the spin-lattice relaxation. Therefore, absorptive TM signal is very weak. On the other hand, the triplet complex yields radicals much faster than the spin relaxation and hence produces a strong emissive TM

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polarization. Although the complex is a minor species in the system, it makes a larger contribution to TM signals than free benzil. Next, at the intermediate concentration of QH, where benzil can react with QH before it loses absorptive spin polarization, TM polarization produced from free benzil becomes dominant. At very high concentrations of QH, where complex is a major species in the system, emissive TM polarization is observed.

4. Mechanism of CIDEP Inversion. There are other plausible mechanisms for interpreting the spin polarization inversion. The first is a conformation change in the triplet manifold. Roy et al. measured the time-resolved phosphorescence spectra in ethanol at temperatures near the melting point and reported the shift of the peak from 530 to 570 nm within 1 ms after the excitation.¹⁵ The shift was attributed to the relaxation from the nonplanar conformation, which was stable in the ground state to the planar conformation. The conformation change in the triplet state would bring about the spin polarization inversion. This mechanism is, however, ruled out due to the following facts. The fluorescence lifetime of benzil is 2 ns at room temperature.¹⁴ This relatively long S_1 lifetime is sufficient to allow relaxation to the stable conformation in the singlet manifold. Actually, the conformational relaxation in the S_1 state was reported to be completed within a few picoseconds.¹⁶ The conformational change is not, therefore, expected in the triplet state at room temperature.

Another plausible interpretation of the polarization inversion is the radical-triplet pair mechanism (RTPM) reported by Blätter et al.¹⁷ They observed emissive CIDEP of radicals in benzil/ di-*tert*-butyl radical and benzil/benzyl radical systems. According to RTPM, radicals always show emissive polarization because of the doublet-triplet interaction, regardless of the triplet polarization. The emissive polarization observed at the dilute aniline concentration (Figure 2a) could be caused by RTPM. Although the interaction between triplet benzil and the product radical would require second-order dependence on the excitation laser power, our experimental results showed first-order dependence. Moreover, the second inversion observed at very high aniline concentration (Figure 2c) cannot be explained by RTPM. Thus, this mechanism is not operative in our systems.

Summary

Inconceivable behavior was observed for CIDEP of benzil ketyl and its counterpart radicals produced in benzil/quencher systems. The phase of polarization changed from emission to absorption and again back to emission with increasing aniline concentration. The E/A pattern by RPM observed in the benzil/aniline system changed to enhanced emission with an increase of benzil concentration. We resolved this double-faced polarization of triplet benzil by kinetic analysis: free benzil and benzil/quencher complex yielded radicals with absorptive and emissive polarizations, respectively. Emissive CIDEP of products from the complex was confirmed with the experiment in SDS_{ag} solution.

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Registry No. Benzil, 134-81-6; aniline, 62-53-3; 2-butylamine, 13952-84-6; *N*,*N*-dimethylaniline, 121-69-7; 2,6-di-*tert*-butylphenol, 128-39-2; 2,4,6-trimethylphenol, 527-60-6; 2,6-dimethylphenol, 576-26-1.

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Synthesis and Luminescence Properties of Eu³⁺-Intercalated Cd₂P₂S₆

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 Eu^{3+} cations have been intercalated by a cation-exchange procedure into the layered lattice of $Cd_2P_2S_6$. Highly hydrated intercalate cations initially insert into the interlamellar interstices. The water of hydration may be completely removed by heating to ≈ 80 °C. Upon long standing at room temperature or upon heating at about 40 °C, some of the Eu^{3+} cations shift to Cd^{2+} vacancy sites in the host lattice. The coordination of the Eu^{3+} was examined by photoluminescence and photoexcitation spectroscopy. Analysis of the spectra indicates a low-coordination geometry, consistent with the formation of paired cation-vacancy centers required for charge compensation. Lattice photoluminescence was found to be activated by energy transfer from the intercalate.

Introduction

 $M_2P_2S_6$ compounds, where M is typically a dipositive transition-metal ion, form a family of layered materials that possess a very versatile intercalation chemistry. They can undergo topotactical redox reactions¹ and thereby insert electron donor species such as cobaltocene or lithium. They can also undergo cationexchange reactions and insert a large variety of species.^{2,3} The

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latter scheme provides a strategy to design many air-stable composites having new properties with respect to the separated components. For example, molecular ferromagnets with unusually high Curie temperature have been recently synthesized by this scheme.⁴ Several $M_2P_2S_6$ (M = Zn, Mn, Cd) are transparent to light. Therefore, it was tempting to insert luminescent centers in such host lattices and examine the possibility of guest-host electron or energy transfer; efficient transfer properties might lead

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