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Chemically Induced Dynamic Electron Polarization in the Photoreduction of Aromatic Ketones with $\pi\pi^*$-Type Triplet State

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Chemically induced dynamic electron polarization (CIDEP) spectra of radicals produced in the photoreduction reaction of aromatic ketone/triethylamine systems were measured by time resolved ESR method. Anion radicals with net absorption (Abs) CIDEP were produced in ethanol with a base such as KOH, while ketyl type radicals with net emissive (Em) CIDEP have been formed in cyclohexane and benzene. Laser power dependence measurement indicates that net Em CIDEP of ketyl radicals is generated by a two-photon process while the production of ketyl radical itself is by one-photon process. Therefore, it was concluded that net Em CIDEP is generated through radical-triplet pair mechanism (RTPM) between the triplet state aromatic ketone and the produced ketyl radical. While RTPM is reasonably considered as an origin of net Em CIDEP for ketyl radicals, it is difficult to determine the CIDEP mechanism of the net Abs polarization of anion radicals in the present systems. Possible mechanisms were tentatively proposed for the present net Abs CIDEP generation.

Chemically induced dynamic electron polarization (CIDEP) produced on the free radicals has absorbed much interest since the generation of CIDEP strongly related to the dynamics on the initial photochemical stages such as radical–radical interactions and the radical–excited molecule interactions.[1] The study of CIDEP mechanism itself provides the details of the dynamics among paramagnetic species. So far, there exist several CIDEP mechanisms: triplet mechanism (TM),[2] radical pair mechanism (RPM),[3] and radical triplet pair mechanism (RTPM).[4,5] The spin-correlated radical pair discovered recently is one of the interesting intermediates in the photochemistry and was found by detection of CIDEP.[6]

In the last decade, our group has been engaged in studying RTPM to reveal the quenching mechanism of excited molecules by the free radicals from the viewpoint of spin polarization.[5] In most of our studies of the subject, we used nitroxide radical as the triplet quencher and saw how the CIDEP of nitroxide was produced in individual systems with various solvents and triplet species. Recently, the importance of RTPM-induced CIDEP has been argued in the CIDEP studies of general photochemical systems. Some of the photochemical systems have been found to show the CIDEP due to RTPM.[7—11] When the triplet lifetime is relatively long, there is a chance for produced radicals to collide with parent triplet molecules remaining in the system. In such systems, CIDEP through RTPM can be generated on free radicals.

In the present study, we report the CIDEP due to RTPM in the photoreduction of aromatic ketones, 9-fluorenone and 4-benzoylbiphenyl, with triethylamine (TEA). These molecules have the lowest triplet state of $\pi\pi^*$ type character[12] which generally shows relatively slow unimolecular decay and reaction rates compared to $n\pi^*$ type triplet and may have a chance to collide with radicals produced in the system.

Besides the CIDEP generation through RTPM, we found another CIDEP of unknown source in the photoreduction reaction of the same systems. Photoreduction produces anion radicals of corresponding aromatic ketone as well as ketyl radicals with ratio of yields depending on the nature of the solvent. CIDEP of anion shows absorptive (Abs) polarization in the photoreduction systems studied in the present work. This unknown CIDEP should be generated during the process of the anion production. Time profiles of these CIDEP and the decays of the radicals and the triplet molecules have been examined to characterize the reaction and CIDEP mechanisms. Though clear evidence for the origin of the net Abs CIDEP has not been found yet, a tentative conclusion was made based on the conventional CIDEP mechanisms.

Experimental

Time Resolved (TR)-ESR Measurement. TR-ESR detection system consists of an X-band ESR spectrometer (Varian E-112) and a boxcar integrator (Stanford SR-250) to extract transient ESR signal synchronized with laser pulse.[13] The excitation light source was a XeCl excimer laser (Lambda Physik LPX 100) of 20 ns

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duration time and of 100 mJ/pulse laser power or a nitrogen laser (Molectron UV-24) of 10 ns duration time and of 3 mJ/pulse laser power. The laser power was attenuated to be about 30 mJ at the cell in the microwave cavity for CIDEP measurements. The gate of the boxcar integrator was opened from 1.5 to 2.0 μs after each laser pulse unless otherwise mentioned. The signals were collected at the repetition rate of 5 or 10 Hz. The microwave power was usually 15 mW.

Transient Absorption Measurement. A transient absorption detection system has already been described elsewhere.[14] An excitation light source was the XeCl excimer laser used in the TR-ESR measurements.

Samples. All the samples purchased from Tokyo Kasei were used as received. Benzene and ethanol (Tokyo Kasei) were used as solvents for the measurements of TR-ESR spectra of radicals. Sample solutions were degassed by bubbling of nitrogen gas and were flowed through the cell. Sample cells are 1) quartz flat cell with 0.5 mm interior space for CIDEP measurements or 2) ESR quartz cell with 5 mm diameter for triplet measurements at 77 K which are attached in the microwave cavity for TR-ESR measurement and 3) quartz cell with cubic shape of 0.5 cm^3 interior space for transient absorption measurement. The concentration of excited molecules was prepared to be almost the same for both TR-ESR and transient absorption measurements by adjusting the concentration of ground state molecule and the laser power at the excitation spot, when we compared the time profiles of CIDEP and transient absorption of the radicals.

Results and Discussion

1) TR-ESR and Transient Absorption Spectra in the Photoreduction of Aromatic Ketones. Figures 1a, 1b, and 1c shows TR-ESR spectra measured in the laser photolysis of 9-fluorenone (20 mM)–TEA (70 mM) (1 M = 1 mol dm^{-3}) systems in a) cyclohexane, b) cyclohexane with ethanol (20% in volume) and c) ethanol with KOH (30 mM). It is interesting that the spectra of free radicals clearly show different CIDEP patterns. The spectrum of radical in Fig. 1a is different from that in Fig. 1c in their *g* values (2.0026 for Fig. 1a and 2.0029 for Fig. 1c) as well as CIDEP pattern, which indicates that there exist two different radicals produced by the photoreaction of 9-fluorenone with TEA, depending on the nature of the solution. The radicals produced in the photolysis may be ketyl and anion radicals, as was case in a number of previous research projects on aromatic ketone–amine photoreactions.[15] Hyperfine coupling constants (hfcc) of both radicals have already been reported[16] and there is a small difference in the hyperfine structures between the two. The broadenings of TR-ESR spectra of these radicals are rather large and, unfortunately the hyperfine structure is not clear. Thus, it is hard to assign the radicals by the simulation.

To assign radicals, we measured transient absorption spectra under the same conditions as those of Figs. 1a, 1b, and

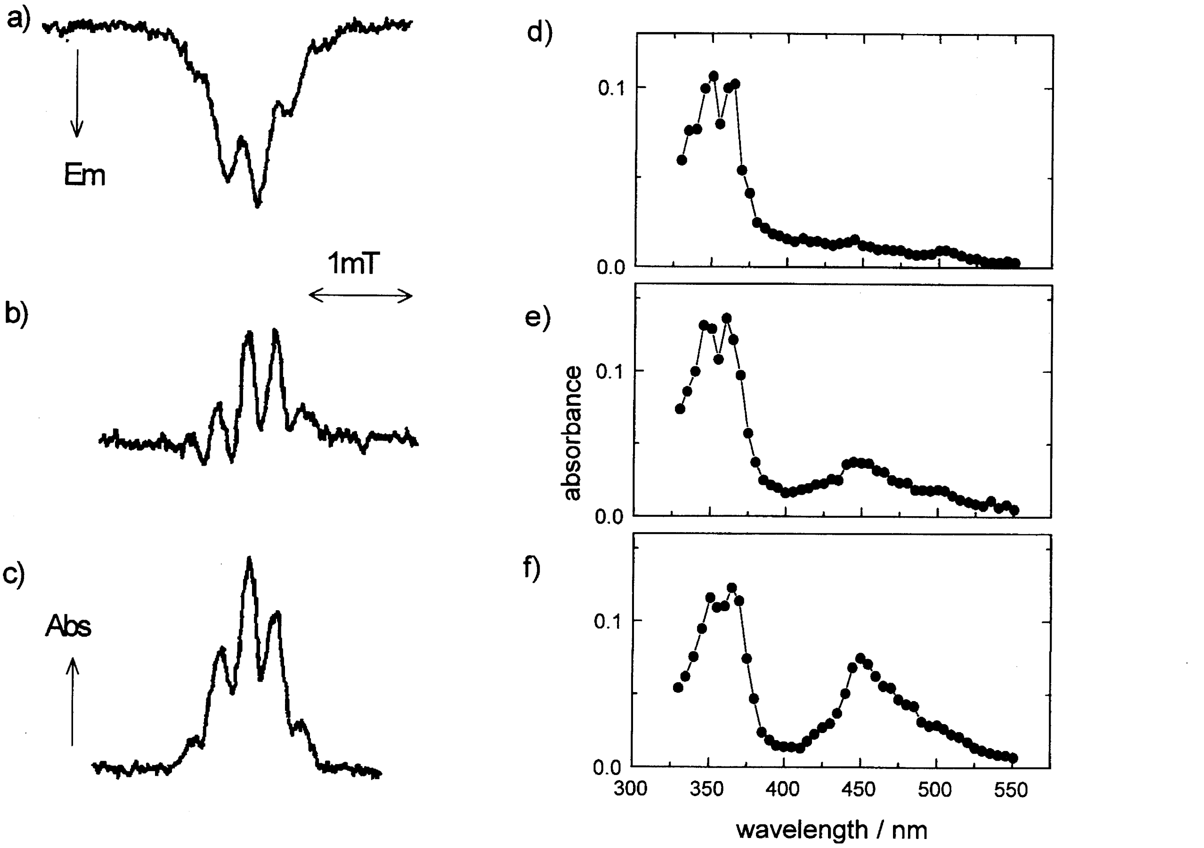

Fig. 1. TR-ESR and transient absorption spectra obtained in the laser photolysis of 9-fluorenone/TEA (70 mM) system in a) and d) cyclohexane, b) and e) cyclohexane/ethanol (5 : 1 in volume) and c) and f) ethanol with KOH (30 mM), respectively. The concentration of 9-fluorenone were 18 and 0.45 mM for TR-ESR and transient absorption measurements, respectively.

1c. Figures 1d, 1e, and 1f shows transient absorption spectra obtained at delay time of 2 μs in the laser flash photolysis of 9-fluorenone–TEA systems. Triplet–triplet absorption of 9-fluorenone disappeared, with its lifetime of about 1 μs, in the present experimental condition. Therefore, these spectra should be due to product radicals. Assignments of these transient absorption spectra were performed based on the reported spectra of 9-fluorenone ketyl and anion radicals in water by Hayon et al.[17] Absorption spectra of ketyl and anion by Hayon et al. are briefly described as follows. Ketyl radical shows only one intense absorption band from 320 to 380 nm with two peaks at 345 and 360 nm. Anion radical shows two absorption bands; one is from 330 to 375 nm with a peak at 360 nm and the other is from 410 to 530 nm with a peak at 450 nm, and the intensity ratio of the two bands is about 11 (360 nm) to 7 (450 nm). In cyclohexane (Fig. 1d), a strong absorption band with two peaks at 350 and 365 nm was observed and the spectrum is very similar to that of ketyl radical in water. On the other hand, the transient absorption spectrum observed in the ethanol with KOH shows two bands with peaks at 360 and 450 nm. The spectrum in ethanol with KOH is quite similar to that of anion radical. Therefore, we concluded that 9-fluorenone ketyl and anion radicals are produced in cyclohexane and in ethanol with KOH, respectively, and TR-ESR spectra of Figs. 1a and 1c are due to ketyl and anion, respectively. In Fig. 1e, there are two bands around 360 and 450 nm. Since there are clear peaks at 350 and 365 nm on the band around 360 nm, there must be ketyl radical in Fig. 1e. On the other hand, appearance of broad band at 450 nm indicates there is anion radical. This observation lead us to the conclusion that both ketyl and anion radicals appear in Fig. 1e. Thus, the distorted spectrum of Fig. 1b can be understood as the mixture of anion and ketyl radicals. To confirm this assignment, we simulated the spectrum on the assumption that the anion and ketyl with CIDEP of Abs and emission (Em), respectively, coexist together. Figure 2 shows the simulated CIDEP spectrum together with the observed TR-ESR spectrum of 9-fluorenone–TEA system in cyclohexane mixed with ethanol (20% in volume). In the simulation, we used the spectral shapes and g values of anion and ketyl obtained by the simulation of the spectra in Figs. 1a and 1c, respectively. The simulation well reproduced the observed TR-ESR spectrum and confirms that both anion and ketyl are produced in the cyclohexane/ethanol mixture solvent and that their CIDEP is of totally opposite sign of Abs and Em, respectively. We measured time profiles of CIDEP for both ketyl and anion radicals, as shown in Fig. 3. Both profiles show rise component for the first 1 μs, followed by relatively slow single exponential decays. The decay rates are tentatively determined by the fitting of decay parts as $(9.10\pm0.430)\times10^4\ \mathrm{s}^{-1}$ for ketyl and $(6.25\pm0.070)\times10^4\ \mathrm{s}^{-1}$ for anion.

Figure 4a shows TR-ESR spectra of 4-benzoylbiphenyl (6 mM)–TEA (100 mM) systems in benzene without KOH and in ethanol with KOH (0.05 M). The TR-ESR spectrum in benzene consists of the sharp hyperfine structure[18] with E*/A (Em and Abs in higher and lower magnetic field region, re-

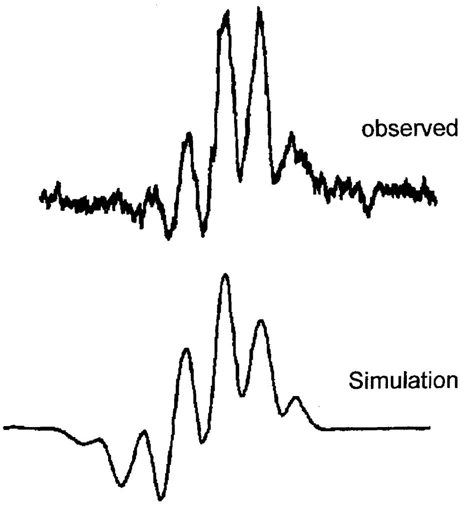

Fig. 2. TR-ESR spectrum of 9-fluorenone/TEA system in cyclohexane/ethanol (5 : 1 in volume) and the simulated spectrum. Simulated spectra of Figs. 1a and 1c were summed with the intensity ratio of 4 : 7 at the center peak. See details in text.

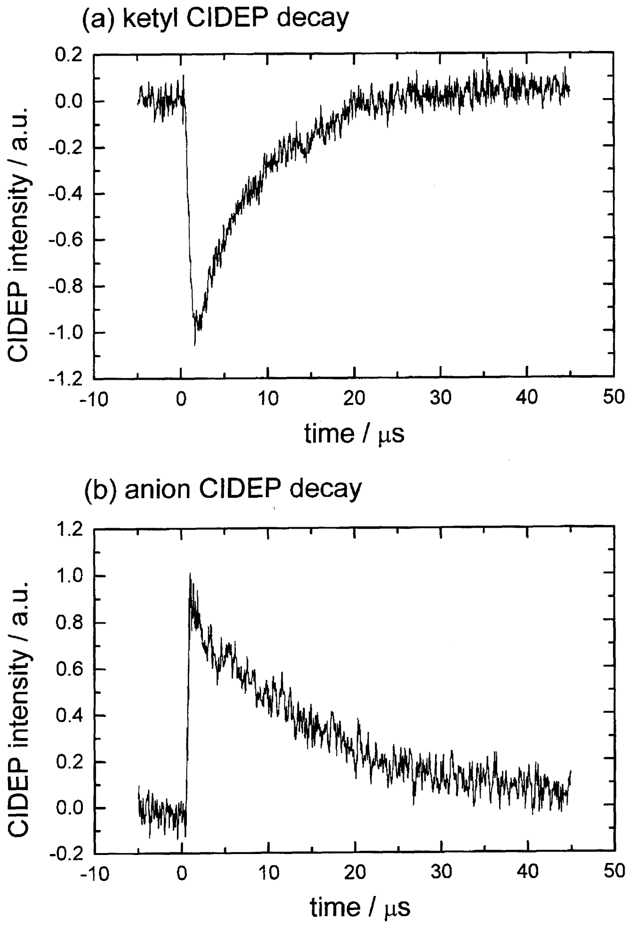

Fig. 3. Time profiles of CIDEP signal of a) 9-fluorenone ketyl radical in cyclohexane and b) 9-fluorenone anion in ethanol with KOH. Microwave power were a) 10 mW and b) 20 mW.

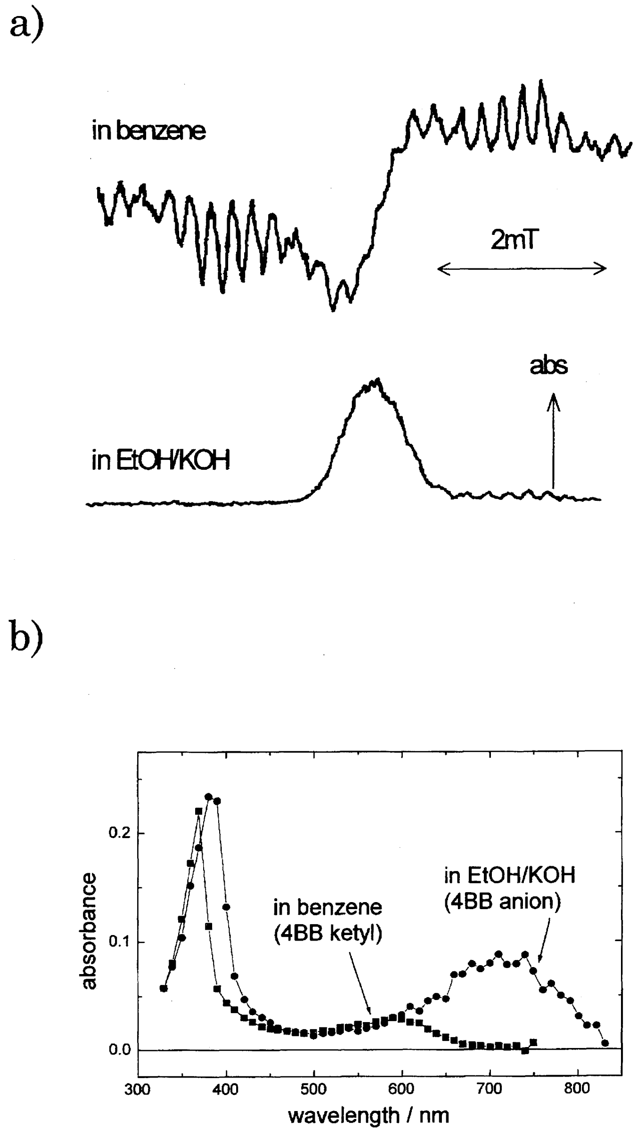

Fig. 4. a) TR-ESR and b) transient absorption spectra of 4BB/TEA (100 mM) system in benzene and in ethanol with KOH (30 mM) measured at 2.0 μs after 308 nm laser photolysis. The concentration of 4BB were 13 and 0.33 mM for TR-ESR and transient absorption measurements, respectively.

spectively, and asterisk means Em is stronger than Abs) type CIDEP and the broad peak in the center of the spectrum with net Em CIDEP. The former is assigned to dehydrogenated TEA radical ($CH_3CHN(C_2H_5)_2$) and the latter to counterparted 4-benzoylbiphenyl (4BB) ketyl radical. On the other hand, the broad peak with net Abs CIDEP dominantly appeared and only a trace of dehydrogenated TEA radical was recognized in ethanol with KOH. This broad spectrum may be due to 4BB anion. To confirm this assignment, we measured transient absorption spectra of 4BB-TEA systems in benzene without KOH and in ethanol with KOH as shown in Fig. 4b. The transient absorption spectrum in these systems changes drastically with the concentration of the base, KOH. In benzene, the spectrum shows a broad weak absorption band in the spectral range of 550 to 650 nm as well as a strong absorption band around 370 nm. On the other hand, a fairly strong broad band appears from 550 to 800 nm as well as a strong band around 380 nm in ethanol with KOH. This discrepancy in the spectral shape clearly indicates the formation of different products. Aromatic ketyl radicals are generally a weak acid because they have a phenol-type OH group; thus, they are in equilibrium with the corresponding base form, namely anion radical, in water solution.[17] In the photoreduction of aromatic ketones by amines, an aromatic ketone anion/amine-cation pair is produced in the encounter pair and then ketyl/dehydrogenated amine radical pair is produced by proton transfer from amine-cation to aromatic ketone anion.[15] Thus, the proton transfer is very important for the branching ratio of ketyl and anion yields. When the concentration of base is very high, there is a chance for the base to remove a proton from the aromatic ketone anion/amine cation pair. Therefore, the base such as KOH and TEA in the solution may decrease the relative yield of 4BB ketyl to anion in the photoreduction of 4BB. In the case of 9-fluorenone, ketyl is formed in the absence of base while anion becomes major product in the presence of KOH as shown in the Fig. 1. This result is in good consistence with the mechanism described above. Therefore, we assigned the transient product of the photoreduction of 4BB in benzene to 4BB ketyl and that in ethanol with KOH to 4BB anion radical. From this observation, we confirm the assignments for TR-ESR spectra in benzene and in ethanol with KOH.

2) CIDEP Mechanisms. In the photoreductions of 9-fluorenone and 4BB, ketyl radicals show net Em CIDEP while anions show net Abs CIDEP. A similar result has already been reported by Mukai et al.[19] for CIDEP in the photoreduction of benzil; benzil produced anion, ketyl, and benzoyl radicals at TEA concentration of 10^{-2} M but mostly anion radical at TEA concentration of 1 M. In their TR-ESR spectra, ketyl shows net Em CIDEP while anion exhibits net Abs CIDEP. Since CIDEP time profiles of 9-fluorenone ketyl and anion radicals show quite rapid rises followed by single exponential decays, these net Em and Abs CIDEP may be produced at the early stage and decay with spin lattice relaxation rate. First, we discuss the net Em CIDEP mechanism for ketyl radicals.

Net Emission CIDEP. Possible mechanisms for net Em CIDEP are TM, spin-orbit induced CIDEP mechanism (SOM),[20] and RTPM. To assign the mechanism, laser power dependences of radical production and CIDEP generation were examined. Figure 5 shows laser power dependences of the intensity of net Em CIDEP and the relative yield of ketyl radical in the 9-fluorenone–TEA system measured by TR-ESR and transient absorption methods, respectively. The plot for the CIDEP intensity indicates a two-photon process while that for the relative yield indicates a one-photon process. The production of the ketyl radical is due to hydrogen abstraction reaction of triplet 9-fluorenone from TEA and thus, should be a one-photon process. This is in good agreement with the present laser power dependence. In the two-photon process of the net Em CIDEP generation, one photon should be

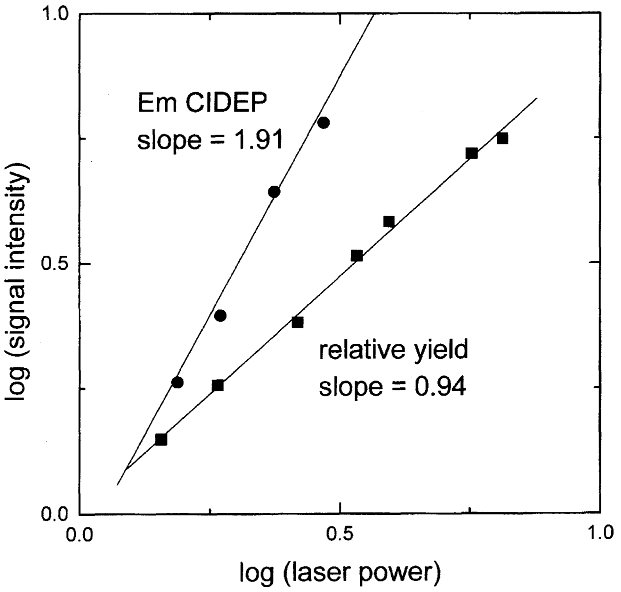

Fig. 5. Laser power dependence of relative yield and emissive CIDEP intensity of 9-fluorenone ketyl radical observed in the laser photolysis of 9-fluorenone (18 mM)/TEA (70 mM) system in cyclohexane.

consumed for the production of the ketyl radical; hence, the other photon may be for the CIDEP generation. The TM and SOM require one photon to produce spin polarized radicals. Thus, TM and SOM are ruled out as CIDEP mechanism in the present case. The recently proposed RTPM generates CIDEP through the interaction between radical and triplet molecule and requires two photons in the present system: one for radical production and the other for triplet formation. The laser power dependence of the present CIDEP is interpreted well by RTPM. For CIDEP generation through RTPM, collisions between ketyl and triplet molecule are necessary. The triplet quenching rate constant in the 9-fluorenone–TEA system[21] is 1×10^7 M^{-1} s^{-1} and the corresponding rate in the present system is about 7×10^5 s^{-1}. If the concentration of produced ketyl radical is more than 0.1 mM, the collision rate between ketyl and triplet is roughly estimated to be more than 6.7×10^6 s^{-1} with a diffusion rate constant, 6.7×10^9 M^{-1} s^{-1}, in cyclohexane.[22] This is fast enough to compete with the triplet decay rate. In the experiment, it is estimated that about 1.5 mM of excited 9-fluorenone is prepared in the ESR cell by ca. 30 mJ of 308 nm laser pulse. Thus, the concentration of higher than 0.1 mM is very reasonable for the ketyl radical. Therefore, it is expected that triplet 9-fluorenone survives in the system until the gate of TR-ESR is opened and there is a chance for produced ketyl radicals to collide with triplet molecules to generate CIDEP due to RTPM. Since the decay of triplet 9-fluorenone is faster than the decay rate of net Em CIDEP ($(9.10\pm0.43)\times10^4$ s^{-1}), the decay of net Em CIDEP is controlled by spin lattice relaxation but not the triplet quenching by 9-fluorenone ketyl. Judging from the results above, we suppose net Em CIDEP of ketyl is due to RTPM between 9-fluorenone triplet and ketyl. RTPM yields net CIDEP in the triplet quenching by radicals with quartet–doublet state mixing through zero-field-splitting interaction of triplet molecule; the sign of CIDEP depends on the sign of exchange interaction (J) of the triplet-radical encounter pair.[4,5,7,8] Net Em and Abs CIDEP are produced in negative and positive J, respectively. Most radical–triplet encounter pairs show negative J value[7—9] and thus, J of 9-fluorenone triplet–ketyl pair is expected to be negative, which means that RTPM must produce net Em CIDEP on 9-fluorenone ketyl. Therefore, it can be concluded that net Em CIDEP is due to RTPM.

We did not obtain net Em CIDEP decay of 4BB because the intense peak of TEA radical prevented us from measuring reliable decay of 4BB ketyl. The T_1 quenching rate by TEA is $(9.11\pm0.68)\times10^6$ M^{-1} s^{-1} which was determined from Stern–Volmer analysis of decay rates of 4BB triplet–triplet absorption; thus, the corresponding quenching rate was 9.11×10^5 s^{-1} under the present experimental condition. Triplet spin relaxation times, T_1^T of many organic molecules in fluid solution are expected to be in nanosecond range according to a theory by Atkins et al.[23] and there are some experimental reports of T_1^T values: T_1^T of duroquione and zinc tetraphenylporphyrin are 20 and 28 ns in ethanol, respectively.[24] Thus, it is reasonably expected that the T_1^T of 4BB may be in a few ten nanoseconds. Since the quenching rate of the present 4BB/TEA system is much smaller than expected triplet spin relaxation rate of 4BB, TM is not likely a dominant process in the CIDEP generation. Therefore, we suppose that RTPM contributes to the net Em CIDEP of 4BB ketyl.

For a long time, TM has been considered as a mechanism of net CIDEP generation in many photochemical systems. Recently proposed RTPM has been recognized as another important CIDEP source in general photochemical systems; the photoreductions of benzil–TEA,[7] benzil–phenol,[8] azaaromatic compounds-2-propanol,[9] unimolecular dissociation of naphthols[8] and relaxation of metalloporphyrin heterodimers.[10] Present systems provide additional evidence for the CIDEP generation through RTPM in ordinary photochemical systems. We believe that CIDEP generation due to RTPM is a very general phenomenon in photochemical systems with high concentrations of triplet and radical species.

Net Absorption CIDEP. Second, we discuss net Abs CIDEP for anion radical. For net Abs CIDEP generation, the following are considered as possible mechanisms: TM, TM with Boltzman distributed triplet molecule (BTM),[24] TM in the complex (CTM),[25] SOM, and RTPM. Occasionally, Boltzman distributed radical itself also gives an absorption signal in the TR-ESR spectra. First, we examined whether the Abs signal was due to CIDEP or the Boltzman distribution of anion radical. Figure 6 shows CIDEP and transient absorption decays of 9-fluorenone and 4BB anions. As is clearly seen from the decay curves, anions decay much slower than CIDEP. Hence, it is concluded that these net Abs signals are truly due to the CIDEP and not to the Boltzman distribution among unpaired electron spin states of anion. TM could provide net Abs CIDEP on anion radicals, if the precursor triplet states have Abs polarization. Thus, we measured TR-ESR

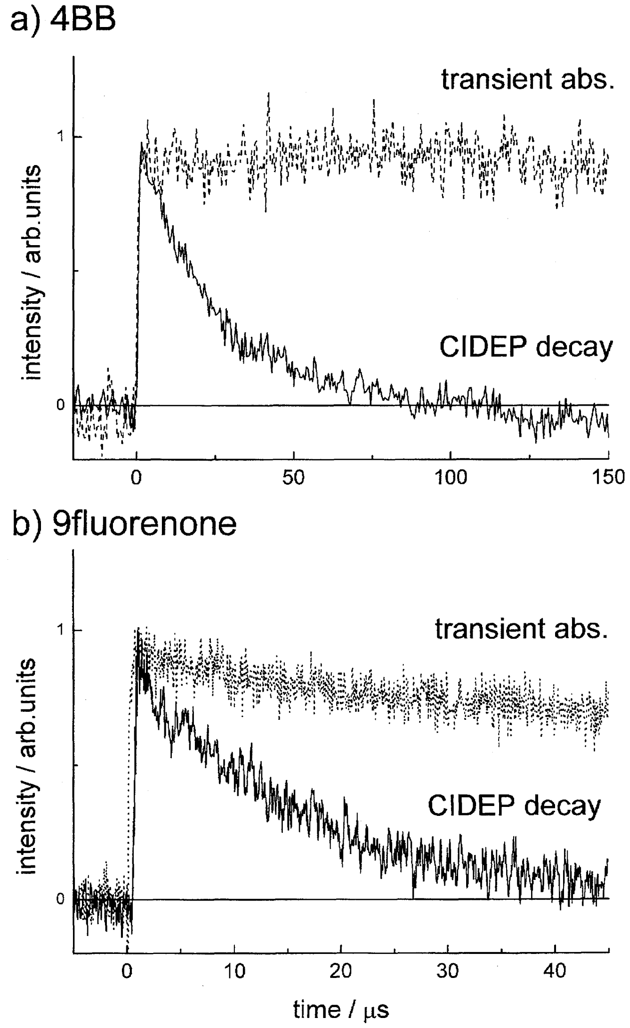

Fig. 6. Decay profiles of CIDEP and transient absorption of a) 4BB anion and b) 9-fluorenone anion radicals in ethanol with KOH.

spectra of triplet 4BB and 9-fluorenone in glass solution at 77 K, as shown in Figs. 7a) and 7b). The peaks corresponding to $\Delta M\mathrm{s} = 2$ show a clear emissive signal, which suggests that the triplet states of 9-fluorenone and 4BB have Em polarization. This result immediately rules out the possibility of net Abs CIDEP due to TM.

It has been known that aromatic ketones such as benzophenone, benzil, and so on, form complexes with amines. Therefore, it can be considered that 9-fluorenone and 4BB form complexes with TEA and that intracomplex electron transfer reaction produces 9-fluorenone anion radical. This is quite a similar mechanism to that of the intracomplex reaction in benzil/aniline systems.[25] If the anisotropy of intersystem crossing of 9-fluorenone and 4BB in the complex is different from that of unimolecular intersystem crossing and produces triplets with Abs polarization, product anions should have net Abs CIDEP due to CTM. To examine this mechanism, a trial experiment to measure TR-ESR spectrum of the triplet 9-fluorenone/TEA complex was carried out as shown in Fig. 7c. In this measurement, TEA/ethanol (9 : 1 in volume) solution was used because it is expected that most 9-fluorenone forms complexes with TEA at such high concentrations of TEA. Similar to the spectrum in ethanol (Fig. 7b), the peak corresponding to $\Delta M\mathrm{s} = 2$ shows a clear Em signal, which suggests that the triplet state of 9-fluorenone also has Em polarization in TEA/ethanol glass. Obtained results can be interpreted as follows: 1) intersystem crossing of 9-fluorenone/TEA complex produced Em polarized triplet state or 2) a trace amount of monomer 9-fluorenone which remained was detected in the spectrum but the complexes were not detected, probably due to the fast intracomplex quenching such as charge transfer quenching of the triplet in TEA/ethanol solvent. Though we could not obtain clear evidence for Abs triplet states in complexes, CTM might be ruled out because of the following reason. In 9-fluorenone/TEA in cyclohexane and 4BB/TEA in benzene systems, only net Em signals due to RTPM were observed on ketyl radicals, as shown in Figs. 1a and 4a, and there was no evidence for the inversion

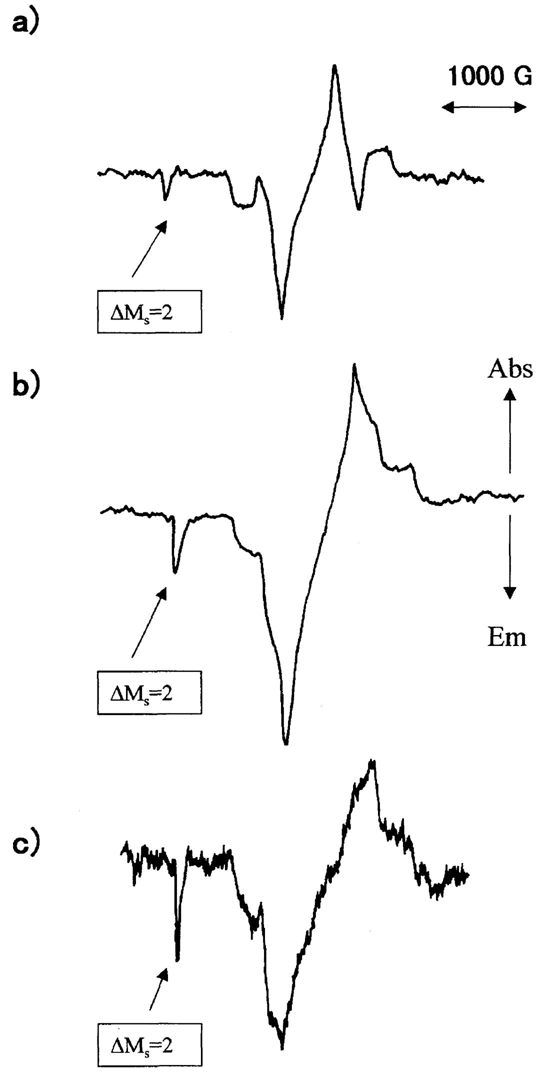

Fig. 7. TR-ESR spectra of the triplet states of a) 4BB in ethanol, b) 9-fluorenone in ethanol and c) 9-fluorenone in TEA/ethanol (9 : 1 in volume) mixture measured at 77 K with gate time of 1.0—2.0 μs. The excitation laser was a nitrogen laser (337 nm) with repetition rate of 5 Hz.

of anisotropic intersystem crossing in the complex.

RTPM could generate net Abs CIDEP on an anion radical in two different cases: (1) S_1 quenching by radical, yielding radical–triplet pair with negative J value and (2) T_1 quenching by radical with positive J value. The CIDEP generation in the former case is due to RTPM with doublet precursor and has been observed only for the excited molecules with relatively long S_1 lifetime (50 ns <) with radical concentration of ca. 1 mM.[8] According to the present experimental condition as discussed above, the estimated concentration of anion radical is at most 1.5 mM and besides, the S_1 lifetime of 9-fluorenone and 4BB are very short (10 ns >). For such systems, the S_1 quenching by anion radical must be a very minor process. Thus, mechanism (1) is excluded for net Abs CIDEP of anions. The latter mechanism is more likely to be operative because there are much more chances for long lived T_1 molecules than S_1 molecules to be quenched by a produced anion radical. So far, there are no reports concerning a positive J value of radical–triplet encounter pairs and thus, it is rather hard to prove that the present anion–triplet pairs have a positive J value. Recently, the positive J value of radical ion pairs has been reasonably explained by an effect of solvent reorganization energy of the pair[26] and positive J values of radical–triplet linked pairs have been reported.[27] These studies suggest the possibility that J value of anion–triplet pair unusually shows positive J value.

Another plausible mechanisms for the net Abs CIDEP of anion radicals is SOM, recently proposed by Tero and his co-workers.[20] In the 9-fluorenone and 4BB–TEA systems, ion pairs could exist immediately after photoreaction, and anisotropic back electron transfer generating Abs CIDEP might occur in the pair due to spin orbit interaction. To confirm this CIDEP mechanism in the present system, the back electron transfer process should be measured somehow to find the anisotropy of this process. BTM could also produce net Abs CIDEP on the product radicals; the energy difference between T_{+1} and T_{-1} states of triplet state is twice as large as that between α and β states of radicals and the spin polarizations of Boltzman populated triplet and radical molecules are different, which results in the net Abs CIDEP generation on radicals.[24] This mechanism may be one of the possibilities for net Abs CIDEP generation in 9-fluorenone– and 4BB–TEA systems. It is rather hard to distinguish BTM from SOM in the present systems because both mechanisms are operative in the reaction of Boltzman populated triplet molecules.

Though no ultimate conclusion is obtained for the present net abs CIDEP of anions, at least we can conclude that photoreduction of aromatic ketones produces an anion radical with net Abs CIDEP which may be produced by RTPM with positive J value, spin-orbit or Boltzman distributed triplet mechanisms.

Summary. We measured TR-ESR and transient absorption spectra in the photoreduction of 9-fluorenone–TEA and 4BB–TEA systems, which we chose as examples of photoreduction systems of $\pi\pi^*$-type triplet state. Ketyl and anion radicals were produced depending on the nature of solvent. CIDEP of ketyl shows net Em due to RTPM while, that of anion shows net Abs. Efficient production of net Em CIDEP due to RTPM suggests the importance of RTPM as one of the mechanisms for CIDEP generation in conventional photochemical systems. For net Abs CIDEP of anions, RTPM with positive J value, spin-orbit mechanisms, and Boltzman distributed triplet mechanism were tentatively proposed according to TR-ESR and transient absorption measurements.

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