CIDEP Study of Radicals Produced Photochemically in the Organic Solution of 9-Acridone and Phenols

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(Received January 26, 1993)

The photoreaction of the solution systems of 9-acridone (or *N*-methyl-9-acridone) and phenols was investigated by optical spectroscopy, ESR, and time-resolved CIDEP techniques. CIDEP signals of acridone semiquinone and phenoxyl radicals were detected together and the hyperfine coupling constants of acridone semiquinone were determined for the first time by simulation method. It was also clarified that radical pair mechanism (RPM) with triplet precursor and triplet mechanism (TM) were the main spin polarization mechanisms in these systems. The results indicate that the excited triplet state of acridone abstracts a hydrogen of phenols. Temperature, phenol concentration, light intensity and time dependence of the phenoxyl CIDEP signal intensity and/or pattern supported the conclusion.

Transient or permanent production of phenoxyl radicals is well-known on radiolysis or photolysis of phenols in solution.$^{1)}$ Among them those with large substituents such as *t*-butyl group at 2- and 6-positions of phenyl ring have a long lifetime owing to their steric protection from reactions. On the other hand, 9-acridone in benzene is subject to disproportionation reaction and gives transiently two different radicals (C radical and N radical) by photoirradiation.$^{2)}$ In pyridine, however, hydrogen transfer occurs from acridone to solvent molecule of pyridine through hydrogen bond to produce N radical and half-reduced pyridine radical.$^{2)}$ Recently *N*-methyl-9-acridone, in the presence of *N*,*N*-dimethylaniline as an electron donor, was found to form the dimer of 9-10-dihydroxy-10-methyl-9-acridinol (via acridone semiquinone radical).$^{3)}$ The reactive state of acridone in these photoreaction has been confirmed to be the lowest excited triplet state. In this paper, the photoprocesses taking place when acridone (or *N*-methylacridone) with phenols is photoirradiated in organic solvent are discussed on the basis of spectroscopic data and CIDEP signals of the related radicals.

Experimental

9-Acridone (G. R. of Tokyo Kasei) and *N*-methyl-9-acridone (MAD) were recrystallized from ethanol. Four phenols, i.e. phenol, 3,5-dimethylphenol, 2,6-di-*t*-butylphenol, and 2,6-di-*t*-butyl-*p*-cresol (DTBPC), were all G. R. grade of Tokyo Kasei and used as received. Solvents, toluene (G. R. of Wako Junyaku) and 2-propanol (IPA) (G. R. of Wako Junyaku) were used without further purification. The sample solution for observation of CIDEP was prepared as [acridone]=0.01 mol dm^{-3} and [phenols]=1 mol dm^{-3} in 2-propanol containing 15% toluene (15T-IPA)$^{4)}$ and degassed by repeating the freeze-pump-thaw cycle several times. In the experiments of flash photolysis and flow-method ESR techniques, oxygen was removed out of the solutions by bubbling nitrogen gas through them.

For CIDEP observation, an ESR spectrometer (JEOL, RE-2XG) equipped with wide band preamprifier (ES-WBPA-2) was used without magnetic field modulation. A digital boxcar integrator (NF, BX-531) was used to record the time-resolved ESR spectra. Averagings were carried out 128 times. An excimer laser (Lambda Physik, LPX-200) with a pulse duration of 28 ns and output power of about 200—300 mJ (λ=308 nm) was used as a light source for this purpose. Light intensity was altered by means of wire-net filters. All these apparatuses were connected to and controlled by a personal computer (NEC, PC-9801-vm2).

Electronic spectra and fluorescence spectra were taken with a spectrophotometer (Hitachi, type 228) and a fluorometer (JASCO, FP-777), respectively. Fluorescence lifetime was measured by the time-correlated single photon counting method using the light source of dye laser excited by mode-lock YAG laser and the detection system of the photomultiplier with microchannel plate (Hamamatsu Photonics R2809U). Transient absorption spectra and their decay rates were measured with the conventional home-made flash photolysis device,$^{5)}$ whose full width of half maximum is ca. 10 μs and flash energy per pulse is ca. 60 J. A 100 W high-pressure mercury lamp (Toshiba, SHL-100UV2) with the filter (Toshiba UV-D36C) was used as a light source for a continuous irradiation of 365 nm light. Its intensity was measured with acridine actinometer$^{6)}$ as 1.10×10^{-8} (mol dm^{-3}) s^{-1} cm^{-1}.

Results and Discussion

Optical Absorption and Fluorescence Spectra. When IPA solution of acridone (5×10^{-5} mol dm^{-3}) and PhOH (2 mol dm^{-3}) was irradated with 365 nm light of 100 W high-pressure mercury lamp, the yield of photoreaction was very low and only 10% diminution of acridone was observed for five or six hour irradiation. However, irradiation with 308 nm pulse of excimer laser for about three minutes (10 Hz, 240 mJ/pulse) gave ca. 75% decrease (DTBPC of 0.5 mol dm^{-3} was used as a reductant in this case). The spectral change of the latter system with irradiation is given in Fig. 1. The isosbestic points appear at 353 and 412 nm, though some small deviation is recognized around 350 nm at initial period of the photoirradiation. The difference spectrum has the absorption maximum at 317 nm, which may correspond to that of the photoproduct (see spectra b's in Fig. 1). Judging from the wavelength of absorption peak, the π-

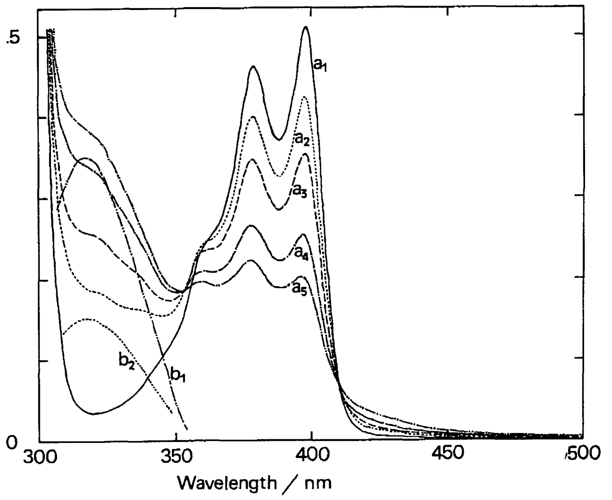

Fig. 1. Change in absorption spectrum with photoirradiation to acridone (5×10^{-5} mol dm^{-3}) and DTBPC (0.5 mol dm^{-3}) in 15T-IPA and the difference spectra. Irradiation times are (a_1) before irradiation, (a_2) 30 s, (a_3) 1 min, (a_4) 2 min, (a_5) 3 min of 308 nm pulses of excemer laser (10 Hz, 240 mJ/pulse). (b_1) and (b_2) are the difference between (a_5) and (a_1) and between (a_2) and (a_1), respectively.

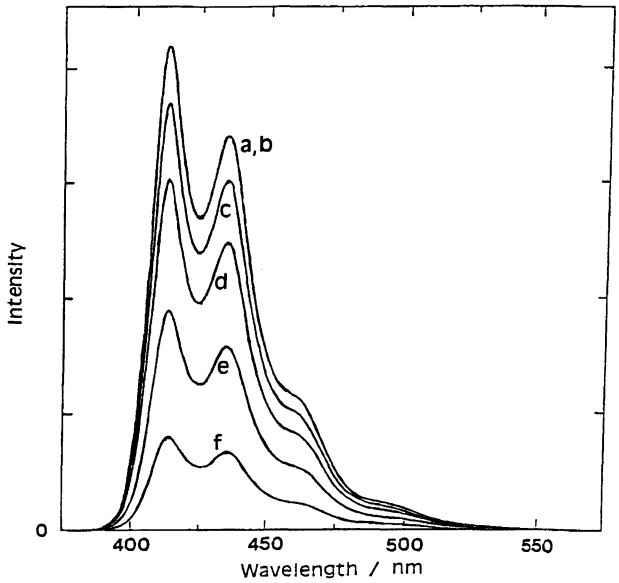

Fig. 2. Change in fluorescence spectrum of acridone (5×10^{-5} mol dm^{-3}) in IPA with PhOH concentration of (a) 0, (b) 0.02, (c) 0.05, (d) 0.1, (e) 0.5, and (f) 1 mol dm^{-3}.

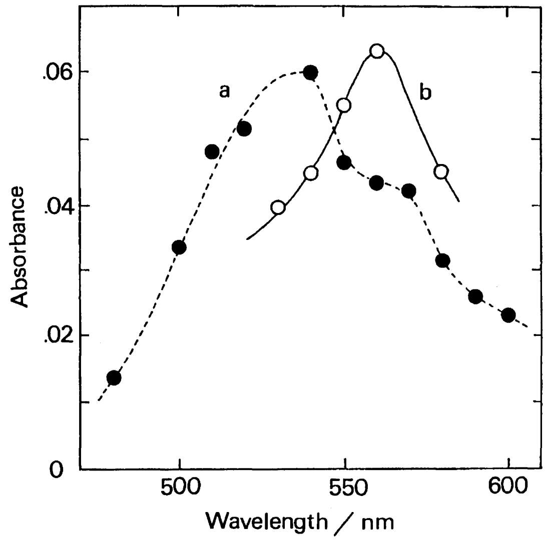

Fig. 3. Transient absorption spectra observed in benzene solution of acridone (saturated) at 50 µs after flashing (a) without DTBPC and (b) with DTBPC (4.2×10^{-3} mol dm^{-3}).

conjugation between N-C_ϕ and/or C_9-C_ϕ (C_ϕ : phenyl ring carbon) bonds in acridone may be broken in the photoproduct molecule. As no new absorpion band appears when acridone and one of phenols are mixed with each other in a solution, these molecules have no special interactions in their ground state. Acridone has strong blue fluorescence in polar sovents. The fluorescence in IPA was found to be quenched by PhOH, as shown in Fig. 2. This is the collisional quenching and the Stern–Volmer polt of their intensities gave a straight line. The quenching constant was obtained from the slope of the line as 3.6 dm^3 mol^{-1}. Taking account of the lifetime of the acridone fluorescence in IPA (10.3 ns, 350 nm excitation and 430 nm monitoring), the rate constant of the process that the excited singlet state of acrdone is deactivated by PhOH molecule, k_q, is evaluated as 3.5×10^8 dm^3 mol^{-1} s^{-1}. The value is one or two order less than that of the diffusion controlled process. Thus, the reaction of the lowest excited triplet state of acridone may be ensured even under the addition of 1 mol dm^{-3} of PhOH since the intersystem crossing rate from the exited singlet to the lowest excited trplet state might be of the order of 10^9 s^{-1}.[2)]

Flash Photolysis Studies. We observed spectra of intermediates of the photoreaction by flash technique. To simplify the reaction system, we chose benzene as solvent innert photochemically. As a reductant, DTBPC was adopted. Acridone is saturated (8.2×10^{-5} mol dm^{-3}). Figure 3 shows the spectra of reaction intermediates obtained at 50 µs after fashing (a) without DTBPC and (b) with DTBPC (4.2×10^{-3} mol dm^{-3}). Oxygen was removed from both solutions. These spectra are different from the T–T absorption of acridone.[7)] The spectrum a is similar to the result obtained by Fushimi et al.[2)] in shape and is much broader than the spectrum b. This may imply that two species are present in the former system. The decay of spectra a and b was of the second order and rate constants of their decay, k_d/ε's, were 5×10^6 cm s^{-1} (at 540 nm) and 1.2×10^7 cm s^{-1} (at 560 nm), respectively. In order to help to identify species formed, flash photoylsis was carried out on the system of MAD instead of acridone. Since MAD has no hydrogen atom to be readily abstracted, the photoreaction mechanism may be more simplified. It is known that no signal other than T–T absorption ($\lambda_{\max}$=630 nm) appears in the system of O_2 free MAD–benzene solution by flash irradiation.[3,7] When the O_2 free benzene solution of MAD (7.3×10^{-5} mol dm^{-3}) containing DTBPC (4.2×10^{-3} mol dm^{-3}) was flashed, the spectrum of the intermediate similar to that in Fig. 3b was observed 75 μs after flashing, as shown in Fig. 4. The intermediate has the absorption maximum at 560 nm and decays with the second order reaction ($k_d/\varepsilon=6.2\times10^6$ cm s^{-1}). This value is comparable with that of MADH•, 4.7×10^6 cm s^{-1} (at 560 nm), detected in the system of MAD and *N*,*N*-dimethylaniline (as a reductant) in benzene.[3] This appears neither in the air-saturated system of MAD–DTBPC nor in the O_2-free system of DTBPC. Taking the results on ESR investigation into account (see below), we are forced to identify both intermediates with $\lambda_{\max}$=560 nm (appearing in the systems of acridone–DTBPC and of MAD–DTBPC) to semiquinone radicals of acridone and MAD, ADH•, and MADH•, respectively.

ESR Studies. By irradiation of 308 nm light, every system of acridone in 15T-IPA solution containing each of four phenols gave the superposition of CIDEP signals of two kinds of radicals, which were assigned to ADH• and the corresponding phenoxyl radical on the basis of their spectra. When MAD was used instead of acridone, the CIDEP signal of MADH• was detected. In the absence of acridone (or MAD), the ordinary ESR signal with the similar intensity was observed but the CIDEP signal was not detected at all.[8] The CIDEP spectra as well as their simulation are illustrated in Fig. 5. According to the CIDEP spectra, *g*-value and *hf* coupling constant of the phenoxyl radicals were evaluated and listed in Table 1. Simulation of CIDEP spectra of phenoxyl radicals was successfully performed by superposing the E*/A type signal owing to radical pair mechanism (RPM) via S–T_0 mixing in the triplet radical-pair precursor on the totally emissive signal of triplet mechanism (TM). It should be noted that these two kinds of CIDEP both originated from the excited triplet state of acridone. The ratio of TM signal intensity to the total one (TM+RPM) at the position of the maximum absolute CIDEP intensity is also written in Table 1 as TM% value. The data show high TM contribution unlike the system of naphthalene and DTBPC in 15T-IPA.[8] The CIDEP signal of ADH• appears overlapping with that of the phenoxyl radicals and also consists of contributions from two mechanisms, TM and RPM (S–T_0 mixing), the latter being clearly of A*/E pattern (see Fig. 6-Obs). This feature is recognized remarkably in the CIDEP spectrum of MADH•. The trend toward A*/E pattern is consistent with the fact that ADH• or MADH• is formed as the counterpart of the phenoxyl radical, which tends toward the E*/A pattern. The center of the CIDEP spectra (e.g. mark a in Fig. 6) was determined by taking account of the whole CIDEP spectra of these semiquinones and phenoxyl radicals. Then *g*-values of ADH• and MADH• were evaluated as 2.0040_1 and 2.0040_6, respectively. In the case of acridone/DTBPC system, CIDEP signal of the ADH• was well-resolved and disclosed from the signal of the phenoxyl radical enough for us to analyze it by simulation, as illustrated in Fig. 6-Obs. The hf coupling constants of ADH• were estimated from parameters for simulation (see Fig. 6-Sim). The values are given in Fig. 7 with the calculated coupling constants using the McLachlan's method based on the simple LCAO–MO approximation. The parameters used to estimate the coupling constants are the same ones that used for the calculation for those of acridine anion radical.[9]

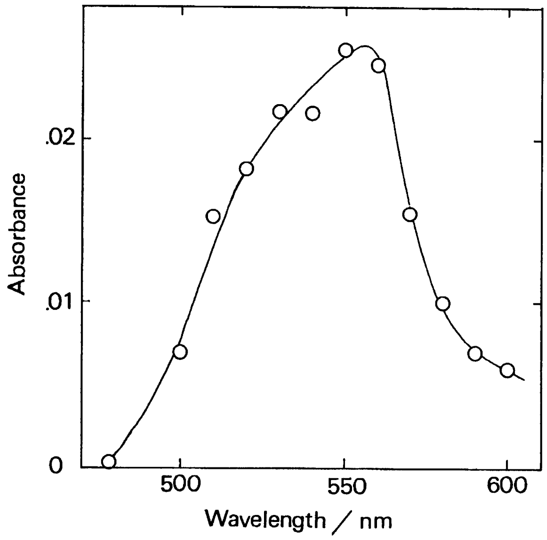

Fig. 4. Transient absorption spectrum observed in benzene solution of MAD (7.3×10^{-5} mol dm^{-3}) containing DTBPC (4.2×10^{-3} mol dm^{-3}) at 75 μs after flashing.

Dependency of the CIDEP signal intensity on excitation-light intensity was investigated using the solution of acridone (0.01 mol dm^{-3}) and DTBPC (1 mol dm^{-3}) in 15T-IPA. CIDEP spectra observed at three levels of the light intensity were found to be almost the same pattern with each other. Thus, the contribution ratios between CIDEP generation mechanisms may not change with the light intensity. The CIDEP signal intensities at the maximum emission 0.5—0.6 μs after laser pulse were plotted against the light (laser pulse) intensities and found that they were in linear relation with each other (see Fig. 8), again unlike the system of naphthalene and DTBPC in 15T-IPA.[8] Thus, no biphotonic process may be involved in this photoreaction.

Temperature and phenol-concentration dependence of the CIDEP signal intensity and pattern was examined together on the system of acridone (0.01 mol dm^{-3}) and DTBPC in 15T-IPA. The observation clearly shows that the emission intensity was increased with both temperature (−40, −20, and 20 °C)

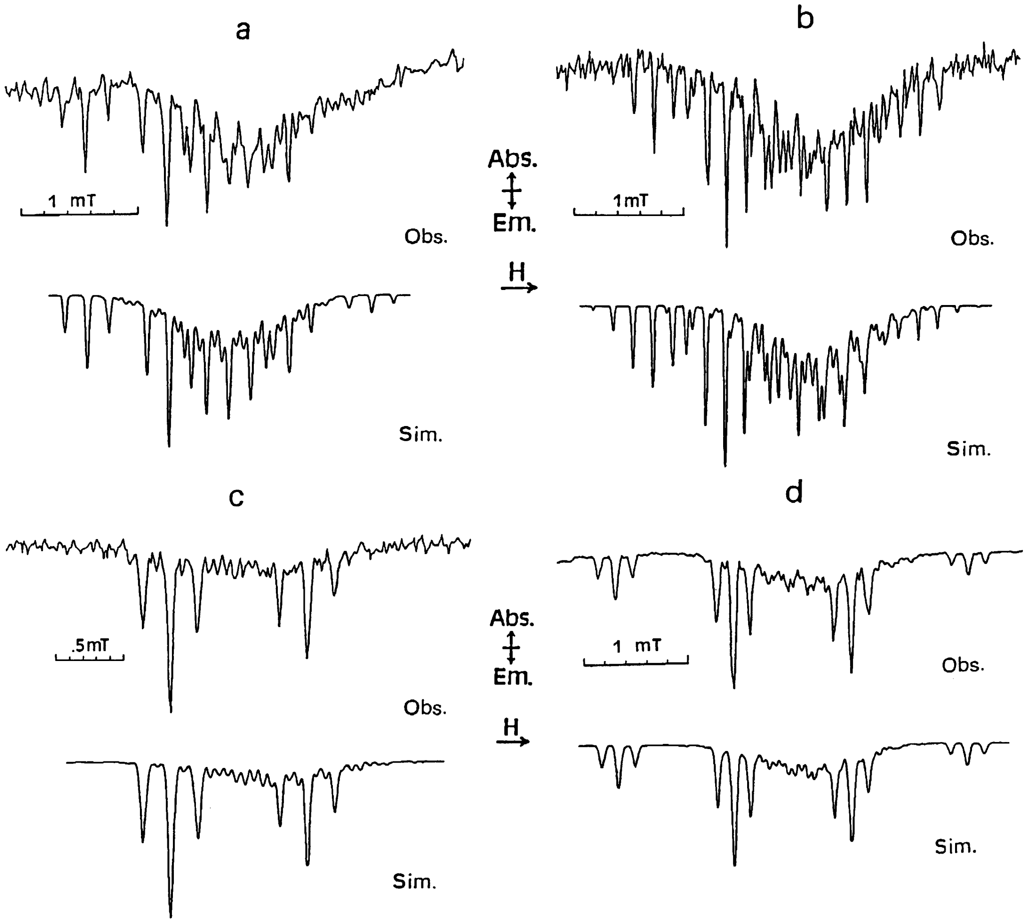

Fig. 5. CIDEP spectra observed on irradiation to the systems of acridone (0.01 mol dm^{-3}) containing (a-Obs.) PhOH (2 mol dm^{-3}) in IPA, (b-Obs.) 3,5-dimethylphenol (1 mol dm^{-3}) in 15T-IPA, (c-Obs.) 2,6-di-t-butylphenol (1 mol dm^{-3}) in 15T-IPA, and (d-Obs.) DTBPC (1 mol dm^{-3}) in 15T-IPA, and their simulation (a—d-Sim.) Measurement was carried out (a-Obs.) 0.6—0.8 μs after laser pulse at 10 °C, (b-Obs.) 0.75—0.85 μs after laser pulse at 21 °C, (c-Obs.) 0.8—0.9 μs after laser pulse at 10 °C, and (d-Obs.) 0.5—0.6 μs after laser pulse at 27 °C.

Table 1. Physical Constants of Phenoxyl Radicals Used for Simulation of Their CIDEP Spectra

Radical	g-Value	hf Coupling constants (mT)			TM%[a]	ADH·%[b]
PhO·	2.0048	a_p=1.020	a_o= .699	a_m= .189	66	36
Me$_2$C$_6$H$_4$O·	2.0049	a_p=1.108	a_o= .690	a_{CH_3}= .187	68	35
t-Bu$_2$C$_6$H$_4$O·	2.0046	a_p= .973	–	a_m= .194	87	14
DTBPC·[c]	2.0044	a_{CH_3}=1.134	–	a_m= .162	79	23

a) Percentage of the contribution from TM at the maximum position of the observed CIDEP spectrum. b) Percentage of the superposed CIDEP intensity of ADH· on that of phenoxyls when compared at each signal maximum. c) 2,6-di-t-butyl-4-methylphenoxyl radical.

and DTBPC concentration (0.1 and 1 mol dm^{-3}) while the absorption intensity appeared to decrease, where the attention was focussed only on the phenoxyl radical. The temperature dependence observed in the system containing 0.1 mol dm^{-3} of DTBPC is given in Fig. 9. The trend is quite the reverse of the case on the naphtalene-DTBPC in 15T-IPA, where the emission was stronger at lower temperature and phenol concentration.[8] These CIDEP spectra are well simulated by adjusting the relative amount of the contribution from the two CIDEP-generation mechanisms, i.e. TM (E) and RPM (E*/A),[10] the separation of these contribution being listed in Table 2 with the raw data of the CIDEP intensity. The results indicate that the contribution ratio of RPM to TM is larger at lower temperature and at lower concentration of DTBPC. This temperature dependence may be caused by the change in flexibility of the solvent cage around the radical pair, ^{3}(ADH· ΦO·)*. The lifetime of the radical pair may increase with viscosity of the solvent and decrease with temperature so that the S–T$_0$ mixing can take place more efficiently and in turn the contribution of RPM

Table 2. Temperature and DTBPC-Concentration Effect on CIDEP Intensity of DTBPC·[a] and Relative Contribution of Two CIDEP-Generation Mechanisms[b]

	[DTBPC] and conditions					
	1 mol dm^{-3} {0.2 mW[c], 160 mJ[d]}			0.15 mol dm^{-3} {2 mW[c], 130 mJ[d]}		
Temp/°C	Total	TM[E]	RPM[E*/A]	Total	TM[E]	RPM[E*/A]
20	18.0	15.4 (85%)	2.6 (15%)	21.1	8.8 (42%)	12.3 (58%)
−20	27.4	16.9 (62%)	10.5 (38%)	30.6	9.0 (30%)	21.6 (70%)
−40	15.7	9.0 (58%)	6.7 (42%)	19.5	3.2 (16%)	16.3 (84%)

a) 2,6-di-*t*-butyl-4-methylphenoxyl radical. b) The numerical values in this table are CIDEP intensity in cm unit on chart at the field position of the maximum emission. c) Microwave power. d) Laser power per pulse.

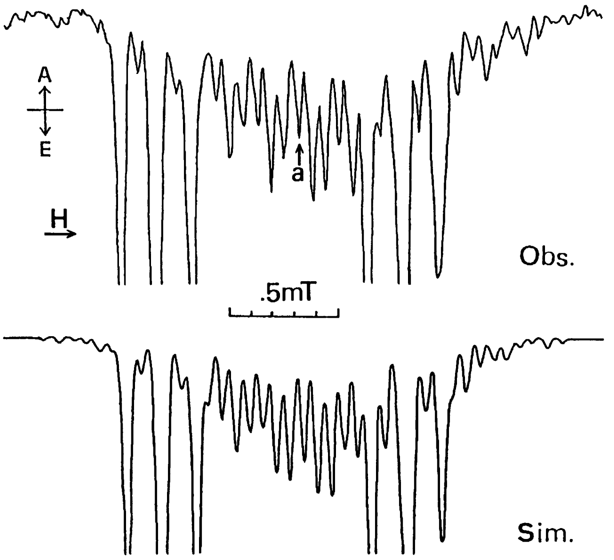

Fig. 6. CIDEP spectrum of ADH· observed 0.75—0.85 μs after pulse irradiation to the system of acridone (0.01 mol dm^{-3}) and DTBPC (1 mol dm^{-3}) in 15T-IPA at 28 °C and its simulation.

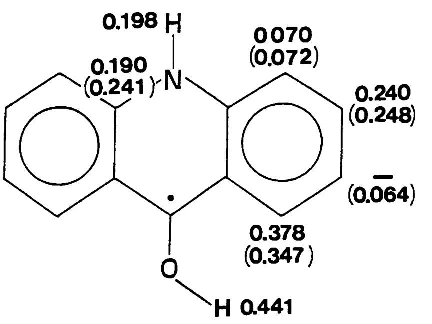

Fig. 7. Hf coupling constants (in mT unit) of nitrogen and protons in ADH· radical. The values in parentheses are those calculated using the relations, $a_H = Q_C \rho_C$ and $a_N = 2.0\rho_N + \Sigma 0.7\rho_{C(next)}]$, where a_H, a_N, are hf coupling constant of proton and nitrogen in mT unit, respectively. And ρ_C, ρ_N, and $\rho_{C(next)}$ are the unpaired spin densities on carbon atoms next to the protons, on nitrogen atom and on carbon atoms next to the nitrogen, respectively. $Q_C = 2.8$ mT is used.

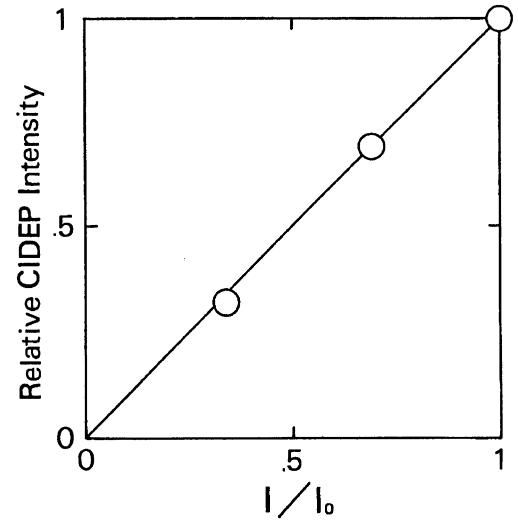

Fig. 8. Light intensity dependence of the CIDEP signal intensities.

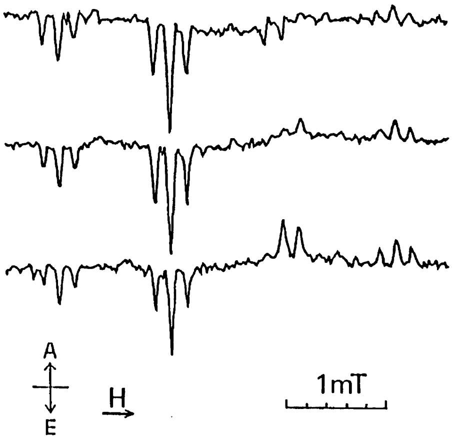

Fig. 9. Temperature effect on CIDEP signal pattern. The signals a to c are those of acridone (0.01 mol dm^{-3}) and DTBPC (0.15 mol dm^{-3}) in 15T-IPA (a) 0.5—0.6 μs after pulse at 20 °C, (b) 0.5—0.6 μs after pulse at −20 °C and (c) 0.8—0.9 μs after pulse at −40 °C. (See Table 2.)

process may prevail at lower temperature. As for the phenol-concentration dependence, TM contribution is determined by the relative importance of the hydrogen-

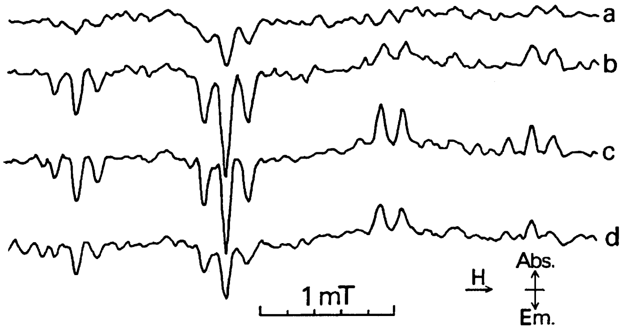

Fig. 10. Time dependence of CIDEP signal pattern when the system of acridone (0.01 mol dm^{-1}) and DTBPC (0.15 mol dm^{-3}) in 15T-IPA was irradiated at −40 °C. The signals a to d are those observed (a) 0.35—0.45 μs, (b) 0.5—0.6 μs, (c) 0.75—0.85 μs, and (d) 2.0—2.1 μs after laser pulse.

abstraction process to the spin-lattice relaxaion process of ^{3}AD*. It is natural that TM/RPM contribution ratio increases with phenol concentration. In the system containing 0.15 mol dm^{-3} of DTBPC, larger contribution of RPM relative to TM was seen (Table 2). As Δg of the initial pair is not so large (=0.0004), the spectral difference between E*/A pattern and E/A pattern (Δg=0 for the F-pair) is very small. The E/A type CIDEP of the phenoxy radical has been observed in the system of naphthalene/DTBPC in 15T-IPA.[8] Thus, it is reasonable to consider the additional participation of the F-pair polarization process at lower DTBPC concentration.

The above results can be summerized by the following schemes:

$$\mathrm{AD} \xrightarrow{h\nu} {}^1\mathrm{AD}^* \tag{1}$$

$$ {}^1\mathrm{AD}^* \rightarrow \mathrm{AD} + h\nu' \tag{2}$$

$$ {}^1\mathrm{AD}^* + \Phi\mathrm{OH} \rightarrow \mathrm{AD} + \Phi\mathrm{OH} \tag{3}$$

$$ {}^1\mathrm{AD}^* \rightarrow {}^3\mathrm{AD}^* \tag{4}$$

$$ {}^3\mathrm{AD}^* + \Phi\mathrm{OH} \rightarrow {}^3(\mathrm{ADH}\cdot\ \Phi\mathrm{O}\cdot)^* \rightarrow \mathrm{ADH}\cdot^* + \Phi\mathrm{O}\cdot^* \tag{5}$$

$$ 2\Phi\mathrm{O}\cdot \rightarrow {}^3(\Phi\mathrm{O}\cdot\ \Phi\mathrm{O}\cdot)^* \rightarrow 2\Phi\mathrm{O}\cdot^* \tag{6}$$

Here, AD, ΦOH, and ΦO· represent acridone, DTBPC (or other phenol) molecule and the corresponding phenoxy radical, respectively. Molecules marked with * are in their electronic excited states and radicals with * in their spin polarized states. The processes of the polarization generation (i.e. TM and RPM) are involved in the process (5).

Time dependence of CIDEP-signal pattern was investigated first on the system of acridone (0.01 mol dm^{-3}) and DTBPC (1 mol dm^{-3}) in 15T-IPA. Little change in the pattern was seen over the time range from 0.35 to 2.0 μs at three temperatures (i.e. 27, −20, and −40 °C). Thus, during the measurement the polarization is to be generated in the same way, i.e. mainly through TM and RPM with constant ratio of contribution. In this case it is not necessary to consider the participation of F-pair polarization and no remarkable variation in the relaxation of electron polarization is conceivable to be present for each nuclear spin state. On the other hand, at the lower concentration of DTBPC (0.15 mol dm^{-3}) perceptible change in the pattern was detected over the time range from 0.2 to 1.5 μs, as shown in Fig. 10. The relative CIDEP intensity of absorption to emission was found to increase with time. This may be explained by taking the process (6) into account, viz., the relative contribution of the process (6) to the process (5) may increase with the time.

The authors wish to thank Dr. S. Murata of National Institute of Materials and Chemical Research for the measurement of the fluorescence lifetime.

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10) Here we assumed that all the E/A type CIDEP were generated by S–T$_0$ mixing in the triplet radical pair which is produced with the reaction between the excited triplet state of acridone and a DTBPC molecule.