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A Time-Resolved EPR Study on the Photochemical α-Cleavage of Benzoin and Related Molecules

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The photochemical α-cleavage reactions of benzoin, benzoin methyl ether (BME) and deoxybenzoin (DOB) in methylcyclohexane and benzene have been studied by means of the time-resolved EPR technique. Strong emissive CIDEP spectra of the radicals produced by the α-cleavage reactions are observed in benzoin and BME. From the analysis of the hyperfine splittings they are assigned as benzoyl and α-hydroxybenzyl radicals in the case of benzoin and benzoyl and α-methoxybenzyl radicals in BME. It is clearly shown that the cleavage reaction takes place in the $T_1(n\pi^*)$ states of these carbonyls and the triplet mechanism (TM) is mainly responsible for the CIDEP spectra. From the time profile of the CIDEP signals it is also shown that the produced radicals react almost exclusively with each other. In the case of DOB, the α-cleavage is found to be much less efficient and a hydrogen abstraction reaction is more dominant at room temperature. It is concluded that the cleavage rate constant (k_c) is in the order, k_c (BME)$>k_c$ (benzoin)$\gg k_c$ (DOB).

The photochemical and photophysical dynamics of aromatic carbonyls in condensed media have still continued to be a topic of considerable interest.[1—9] The time-resolved EPR (TREPR) spectroscopy is very powerful in detecting and identifying short-lived intermediate radicals and provides information complimentary to that obtained by other techniques such as transient absorption and NMR.

Recently, we have presented a preliminary report on the photochemical formation of benzaldehyde from benzoin in hydrocarbon solutions at room temperature.[10] The results clearly show that the irradiated benzoin undergoes an α-cleavage reaction via its spin-polarized triplet state, yielding α-hydroxybenzyl and benzoyl radicals between which an efficient H-abstraction reaction takes place to produce benzaldehyde. These radicals have been detected directly by TREPR. Our conclusion for the photochemical process was similar to those derived from the CIDEP (chemically induced dynamic electron polarization) and ENDOR spectra of photolyzed 2,2-dimethoxy-1,2-diphenylethanone by Jaegermann et al.[11] and from the CIDNP (chemically induced dynamic nuclear polarization) spectra of benzoin and benzaldehyde by several investigators.[12,13]

In the present work we have extended our TREPR work further to confirm the proposed reaction mechanism and to examine its applicability to other related molecules. Here we first examine the CIDEP spectra of other related molecules such as benzoin-d_2 (2-hydroxy-*d*-1,2-diphenylethan-2-*d*-one), benzoin methyl ether (hereafter abbreviated as BME) and deoxybenzoin (abbreviated as DOB) to identify the reaction intermediates and to determine the reaction mechanisms. Second, we clarify the nature of the precursor triplet state to ascertain the cleavage mechanism. Third, we investigate the time profiles of the transient EPR signals in detail to obtain information about the dynamics of the intermediate radicals. Finally we compare the order of the cleavage rate constant in these molecules.

Experimental

All the hydrated benzoins were obtained from Tokyo Kasei Co., Ltd. Two of them, BME and DOB (benzyl phenyl ketone), were purified by repeated vacuum sublimation. Benzoin, a reagent of zone-melting grade, was used as received. Two deuterated compounds, benzoin-d_2 (2-hydroxy-*d*-1,2-diphenylethan-2-*d*-one) and DOB-d_2 (1,2-diphenylethan-2,2-d_2-one), were prepared according to the following procedure: (i) shaking a mixture of 3 ml 1% NaOD–D_2O (total D purity 99 atom%) solution and 0.1 g solute in a sealed Pyrex tubing at about 140 °C for 3 h; (ii) filtration of the deuterated compound deposit at room temperature; (iii) sealing another Pyrex tubing containing a freshly prepared mixture of 3 ml 1% NaOD–D_2O solution and all the deposit material loc. cit.; and (iv) repeating the steps (i)—(iii) twice more. Lastly, the obtained deposit was washed with hot (ca. 80 °C) D_2O and dried in a vacuum system. From an NMR spectral analysis, deuterium substitution was found to occur only at the benzylic position and to be almost complete (>98%).

The solvents, methylcyclohexane (MCH) and benzene (both Dotite spectroscopic grade reagents), were used without further purification. The concentrations were usually 1—3×10^{-3} mol dm^{-3} unless otherwise stated. The sample solutions were deaerated by blowing helium gas and allowed to flow into a quartz tubing of 2.5 mm i.d. at a rate of 0.3 ml min^{-1}. The TREPR spectra were obtained by feeding an output of a modified preamplifier of a microwave unit of an EPR spectrometer (JEOL FX3X) to a PAR 160 boxcar integrator. The signal gate width of the boxcar integrator was usually set to 0.2 μs throughout the work. Decay curves of the transient EPR signals were monitored by a transient memory (Kawasaki Electronika MR50E) and accumulated on a HP

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9816 computer. In obtaining decay curves microwave power was kept as low as possible (<0.1 mW) to avoid the effect of Torrey oscillation. Other experimental details were similar to those described previously.[5,14]

Results and Discussion

According to the results reported previously, the photoreactions of benzoin are shown as follows. The α-cleavage reaction producing α-hydroxybenzyl and benzoyl radicals[10,15,16] occurs through the excited triplet state of benzoin. These radicals react with each other to produce benzaldehyde, namely,

$$\text{Ph-COCH(OH)-Ph} \longrightarrow {}^{3}(\text{Ph-COCH(OH)-Ph})^{*} \quad (1)$$

$$^{3}(\text{Ph-COCH(OH)-Ph})^{*} \longrightarrow \text{Ph-}\dot{\text{C}}\text{O} + \text{Ph-}\dot{\text{C}}\text{H(OH)} \quad (2)$$

$$\text{Ph-}\dot{\text{C}}\text{O} + \text{Ph-}\dot{\text{C}}\text{H(OH)} \longrightarrow \text{Ph-COCH(OH)-Ph} \quad (3)$$

$$\text{Ph-}\dot{\text{C}}\text{O} + \text{Ph-}\dot{\text{C}}\text{H(OH)} \longrightarrow 2\ \text{Ph-CHO} \quad (4)$$

These are the major reactions that seemingly do not involve any other reactions because only the two relevant radicals are detected in the CIDEP spectra and only benzaldehyde peaks appear in the absorption spectrum after photolysis.[10]

Occurrence of the primary α-cleavage reactions in benzoin and BME is confirmed by the analysis of the CIDEP spectra of the produced radicals. Figure 1 shows the spectra obtained by the photolysis of benzoin derivatives, benzoin-d_2 and BME. The spectra obtained at 0.4 or 0.6 μs after the laser excitation consist of the spectra of two radicals. One is an emissive signal of the benzoyl radical with $g=2.0009$[17] which decays very rapidly and disappears at 1.0 μs after excitation. Since the relative intensity of the benzoyl radical peak is much stronger in the case of BME, this peak dominates the spectrum (Fig. 1b). In the case of benzoin-d_2 the spectral range is much narrower because of the effect of deuteration. The hyperfine structures of the spectra of other radicals are broadened at this time, but they are sharpened up at 1.0 μs after excitation. The hyperfine splittings of these radicals are determined from the simulation of the spectra shown in Fig. 2. Agreement between the observed and simulated spectra for each case is considered to be satisfactory. From the comparison with the values in literature[18-20] they are assigned as α-hydroxybenzyl and α-methoxybenzyl radicals, respectively.

The hfcc obtained for the α-hydroxybenzyl radicals derived from benzoin and benzoin-d_2 in MCH and in benzene are summarized in Table 1 together with the data by Fischer et al. who studied the EPR spectrum

Fig. 1. CIDEP spectra of irradiated benzoin derivatives in MCH at room temperature. Observed spectra of (a) benzoin-d_2 at 0.4 μs and (b) BME at 0.6 μs.

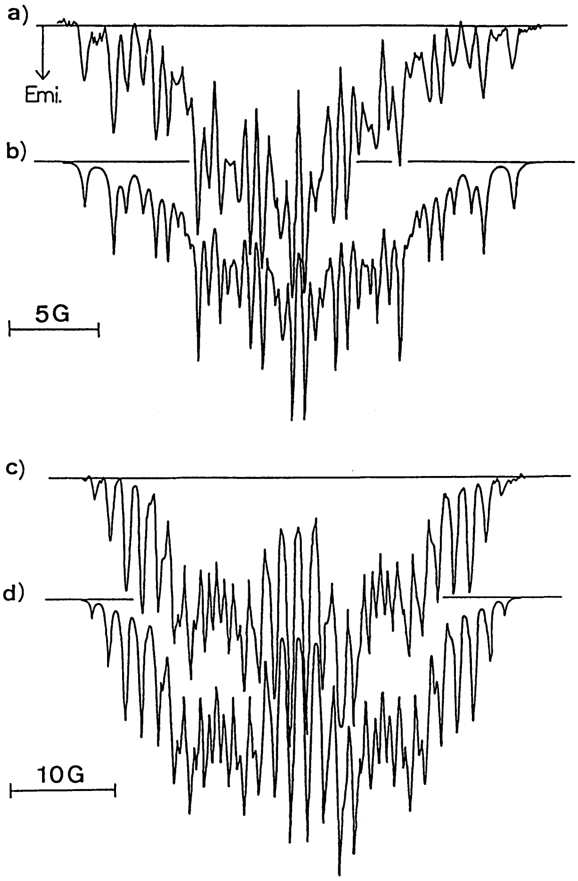
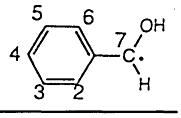


Fig. 2. CIDEP spectra of irradiated benzoin derivatives in MCH at room temperature. (a) Observed spectrum of benzoin-d_2 at 1.0 μs after laser excitation and (b) simulated one. (c) Observed spectrum of BME and (d) simulated one.

Table 1. Hyperfine Coupling Constants of α-Hydroxybenzyl Radical[a)]



H. Fischer[b)]		Present work	
		in $C_6H_{11}CH_3$	in C_6H_6
a(7)	15.17	15.71 (2.41)[c)]	15.65
a(2)	4.62	4.62	4.62
a(3)	1.63	1.64	1.64
a(4)	5.88	6.04	5.98
a(5)	1.63	1.64	1.64
a(6)	5.17	5.18	5.20
a(OH)	<0.47	0.33 (0.03)[c,d)]	0.33

a) In G units . b) Taken from Ref. 18. c) Values in parentheses indicate the corresponding a(D) values which are employed for simulating Fig. 2b. d) In a high resolution spectrum, the splittings due to the O–H proton are observable.

Table 2. Hyperfine Constants of α-Methoxybenzyl Radical[a)]

	SSS[b)] in C_6H_6	KKCB[c)] in cyclopropane	Present work in MCH
a(7)	15.10	15.24	15.38
a(2)	5.03	5.04	4.65[d)]
a(3)	1.65	1.51	1.64[e)]
a(4)	5.73	5.75	5.82
a(5)	1.55	1.51	1.68[e)]
a(6)	4.52	4.52	5.15[d)]
a(CH_3)	1.40	1.51	1.36

a) In G units. b) Taken from Ref. 19. c) Taken from Ref. 20. d,e) Reversed assignment of a(2) and a(6) (a(3) and a(5)) is in the same line as those by SSS and KKCB. However, the atomic numberings are not necessarily definite in their assignments. The present assignment is more compatible with that of benzoin (see Table 1). It is also consistent with the result of the calculation on benzaldehyde anion by Miertus and Kysel.[30)]

during the reaction of phenylacetic acid with the OH radical.[18)] Although several other data have been reported on this radical in various environments,[21)] all these are close to Fischer's. However, there is a small difference between Fischer's and ours: e.g., 2.7 and 3.6% increases in the coupling constants of a(4) and a(7) (and also slight increases in a(2) and a(6)) on going from Fischer's to ours. (Here the numbering of the atoms is the same as used by Fischer.) The hfcc for α-methoxybenzyl radical produced from BME are given in Table 2 together with the literature values.[19,20)] Small differences in the coupling constants of the α-methoxybenzyl radical are found between Steeken et al.'s[19)] and ours. Thus the hfcc's of these radicals seem to be somewhat dependent on the environment.

The CIDEP patterns are of nearly net emission with a small contribution of an E/A (Here E and A denote an emission and an absorption of the microwave, respectively) component. This suggests that the α-cleavage reaction occurs in the excited triplet state of benzoin,

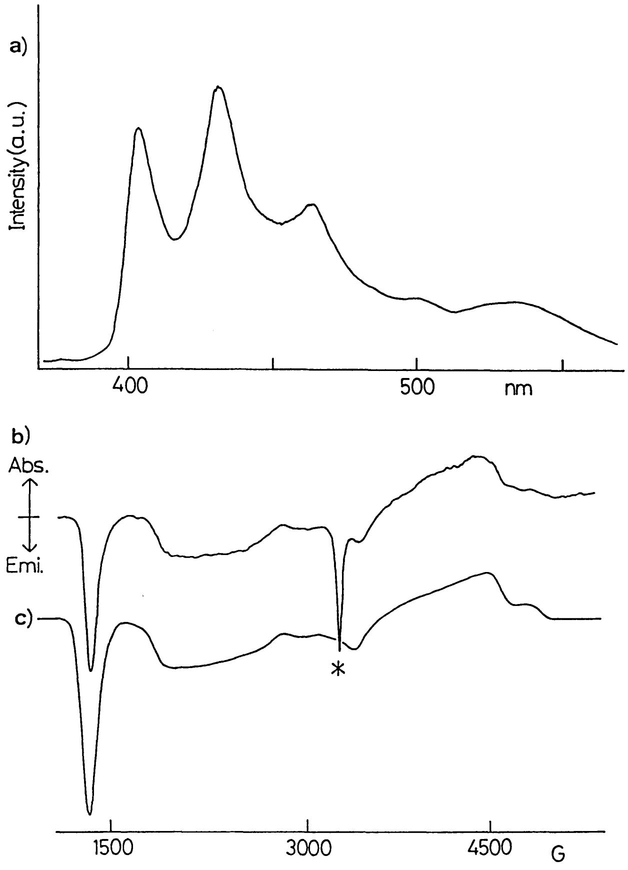


Fig. 3. (a) Phosphorescence spectrum of benzoin in MCH at 77 K. (b) Time-resolved EPR spectrum of T_1 state of benzoin in benzene at 77 K and (c) simulated one of T_1 state. A sharp emissive signal indicated by * in (b) is due to the radical produced by photolysis.

because a net emissive pattern is due to the triplet mechanism (TM) of CIDEP. The signal intensity is linearly dependent on the laser power within experimental error, indicating that the reacting state is excited by a one-photon process. Therefore, the precursory triplet state is considered to be the lowest excited triplet (T_1) state of benzoin. The phosphorescence spectrum of benzoin observed in MCH at 77 K is shown in Fig. 3a. The spectrum shows a progression of the C=O stretching vibration (403, 432, and 465 nm) which is characteristic of a $^3n\pi^*$ aromatic carbonyl. The phosphorescence lifetime is about 1.2 ms when measured with laser excitation. This lifetime is also consistent with the $n\pi^*$ assignment. The emissive CIDEP spectra of the produced radicals indicate that upper spin-sublevels are more populated in the reacting triplet states. Since the most populated sublevel is the uppermost one (Z sublevel with the Z axis along the C=O direction) in a $^3n\pi^*$ aromatic carbonyl, this is also consistent with the $^3n\pi^*$ assignment of the reacting state.

The TREPR spectrum of the T_1 state of benzoin further confirms this. Figures 3b and 3c show the observed spectrum of T_1 benzoin in benzene obtained at

77 K and the simulated one. The spectral pattern of E, EEA/EAA suggests that the uppermost sublevel is more populated than the lower sublevels. The zero field splitting (zfs) parameters and the relative populations used for the spectrum simulation are given in Table 3. They are reasonable for a $^3n\pi^*$ aromatic carbonyl. From these results, it is clearly seen that the T_1 state of benzoin has a negative D ($D=-3/2Z$) value and the largest population is in the uppermost sublevel as in the cases of many other aromatic carbonyls.[22–25] So the emissive spectral patterns of the produced radicals are explained in terms of the TM for the reaction from the T_1 ($n\pi^*$) state.

The above result that the α-cleavage reaction occurs in the T_1 state via one-photon process contrasts with the case of benzil in which the α-cleavage reaction occurs in a higher excited triplet state via two-photon process and the T_1 state is not reactive.[26] Benzil which is an α-dicarbonyl molecule has a *s*-trans planar structure in the T_1 state and the C–C bond has a partial double bond character. Therefore, the C–C bond of benzil is stronger than that of benzoin and more energy is needed for the α-cleavage of benzil than benzoin.

The radicals produced by the α-cleavage reaction form a geminate pair in a solvent cage. Then the RPM (radical pair mechanism) due to geminate pairs may be expected to contribute to the CIDEP spectra. A significant contribution of the RPM is clearly observed in the benzoin spectrum at 1.0 µs in which the intensities of the signals on the low field side of the center are considerably stronger than those on the high field side. In the case of BME the contribution of the RPM is smaller and the CIDEP spectrum becomes more symmetric.

The time dependence of the spectrum is shown in Fig. 4. The emissive signal of the benzoyl radical disappears almost completely within 1 µs, but an absorptive signal reappears later. This means that the spin-lattice relaxation time of the benzoyl radical is very short and the spin states of the radical are thermally equilibrated within 2.5 µs. The absorptive signal is considered to be

Table 3. Zero Field Splitting Parameters and Relative Populating Rate of the T_1 State of Benzoin at 77 K in Benzene

	zfs (GHz)	Population ratio
X_1 (Z)	2.51	0.9
X_2 (Y)	0.54	0.1
X_3 (X)	−3.05	0.0

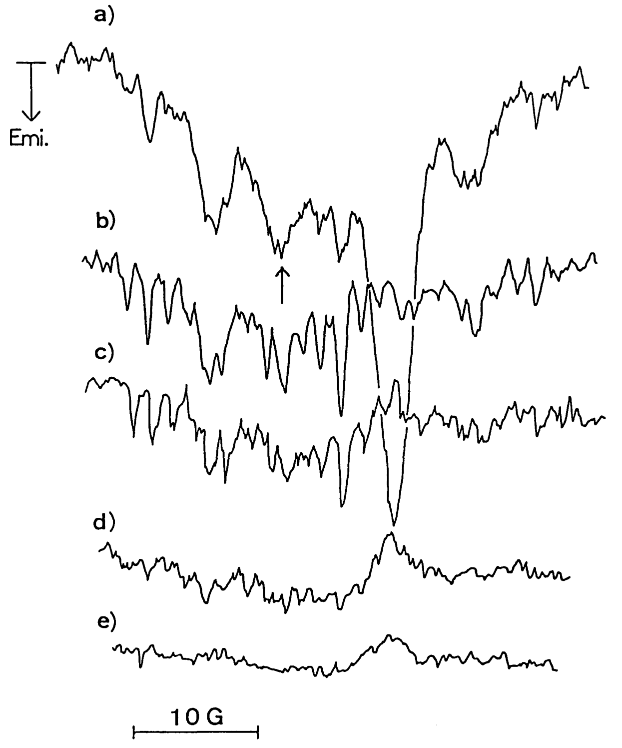


Fig. 4. Time dependence of CIDEP spectra of benzoin in MCH at room temperature. Time delays (in µs units) are (a) 0.4, (b) 1.0, (c) 1.5, (d) 2.5, and (e) 5.0.

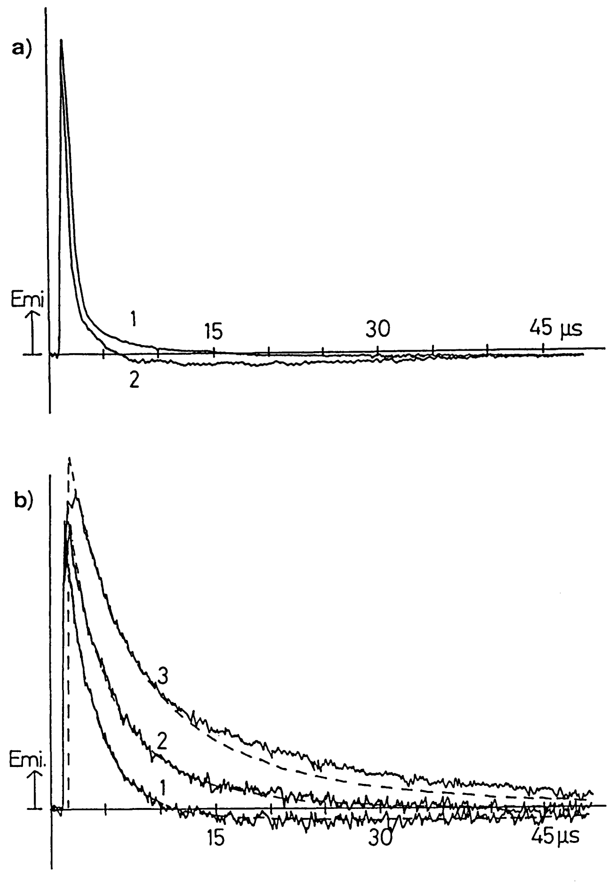


Fig. 5. Time profiles of the CIDEP signals of radicals produced from benzoin in MCH at different temperatures. (a) benzoyl at (1) −60 and (2) −10 °C and (b) α-hydroxybenzyl radical at (1) 20, (2) −10, and (3) −40 °C. The time profiles were obtained at the peak indicated by an arrow in Fig. 4a. The dotted curves were obtained by Eq. 5 with the following parameters (1) $k_2[R_0]=2\times10^5\,s^{-1}$, $T_1=5$ µs (2) $k_2[R_0]=1.5\times10^5\,s^{-1}$, $T_1=8$ µs and (3) $k_2[R_0]=1.1\times10^5\,s^{-1}$, $T_1=18$ µs.

due to the thermalized benzoyl radical. On the other hand, the decay of the α-hydroxybenzyl radical is much slower. However, the spectrum becomes more and more assymmetric with time (Fig. 4c). This seems to indicate that the F-pair RPM makes a small contribution making the spectrum less symmetric with time. This is reasonable because the formation of benzaldehyde from the radicals proceeds by making a radical pair (F-pair).

In order to obtain further information about the dynamics of the radicals we have studied the time profiles of the transient radicals in more detail. Figure 5 shows the time profiles of the signals at different temperatures. Notable results may be summarized as follows.

1) The fast decay of the benzoyl radical is not so temperature dependent, but the slower decay of the α-hydroxybenzyl radical is much more temperature dependent.

2) The signals of both radicals show polarization inversion and become absorptive at longer times at higher temperatures. The absorptive signals are very long-lived, indicating that the produced radicals are rather stable.

3) The decay of the α-hydoroxybenzyl radical is nearly exponential at room temperature, but at lower temperatures it deviates from a single exponential decay significantly with a faster decay component initially.

The observation 2) shows that the radicals are long-lived. This means that these radicals do not react with solvent molecules in the present systems, though the reaction of the benzoyl radical with MCH to form a methylcyclohexyl radical ($\dot{C}_6H_{10}CH_3$) has been widely accepted by photochemists.[27)]

The spin-lattice relaxation time (T_1) of the α-hydroxybenzyl radical becomes long at low temperatures. Therefore, the faster initial decays observed at lower temperatures are likely due to the second order radical reactions to form benzaldehyde and benzoin ((3) and (4) of the reaction scheme). The rigorous solution of the appropriate Bloch-kinetic equation is rather complex, but it can be approximated by Eq. 5 under the assumption of on resonance and very weak microwave field,[28)]

$$I(t) \propto (k_2[\mathrm{R_o}]t+1)^{-1}\{A \exp(-t/T_1)+1\}, \qquad (5)$$

where $I(t)$ is the intensity of the transient EPR signal, k_2 is the second order rate constant for the radical reaction and $[\mathrm{R_0}]$ is the initial radical concentration. A is given by P_0/P_{eq} where P_0 is the initial polarization and P_{eq} is the equilibrium polarization. Here the radical decays are assumed to follow the second-order kinetics, because the pseudo-first-order reaction with solvent molecules is not important. We have tried to simulate the observed time profiles by this equation. As shown in Fig. 5 the time profiles observed at 20 °C and −10 °C are reproduced quite well by this equation, but at low temperatures the agreement becomes poorer at longer times. This is probably due to the contribution by the F-pair RPM. From the simulation we obtain $k_2[\mathrm{R_0}]$ to be 2×10^5, 1.5×10^5, and $1.1\times10^5\ \mathrm{s^{-1}}$ at 20, −10, and −40 °C, respectively. The concentration of benzoin was 2×10^{-3} M (1 M=1 mol dm^{-3}). If 50% of benzoin is photolyzed, $[\mathrm{R_0}]$ is 10^{-3} M. With the assumption of $[\mathrm{R_0}]=10^{-3}$ M, k_2 is estimated to be $2\times10^8\ \mathrm{M^{-1}\,s^{-1}}$ at 20 °C. This value is considerably smaller than the diffusion controlled rate constant, but is considered to be reasonable for the second order rate constant for the radical reaction. The value of P_0/P_{eq} is estimated to be 30 for the benzoyl and α-hydroxybenzyl radical.

We have also studied the CIDEP spectra of DOB in MCH to see whether or not similar CIDEP spectra are obtained in this system. We have not detected any emissive signals of the radicals produced by the α-cleavage at room temperature. Since the phosphorescence spectrum of DOB also shows its $^3n\pi^*$ character, this observation indicates that the rate of the α-cleavage reaction from the T_1 state is much slower in DOB. However, a very weak spectrum with an E/A pattern shown in Fig. 6 was obtained with a signal intensity of about two orders of magnitude less than those of benzoin and BME. The locations of the peaks marked by solid circles are similar to those of the methylcyclohexyl radical,[29)] suggesting that the following hydrogen abstraction reaction takes place from the triplet DOB as in many $n\pi^*$ aromatic carbonyls.

$$\mathrm{Ph\text{-}CH_2\text{-}CO\text{-}Ph} + \mathrm{C_6H_{11}CH_3} \longrightarrow \mathrm{Ph\text{-}CH_2\text{-}\dot{C}(OH)\text{-}Ph} + \mathrm{\dot{C}_6H_{10}CH_3}$$

At low temperatures a weak emissive signal of the benzoyl radical is observable, indicating that the α-cleavage reaction does occur (Fig. 6d). This observation is rationalized in the following way. As the temperature is lowered the rate of the hydrogen abstrac-

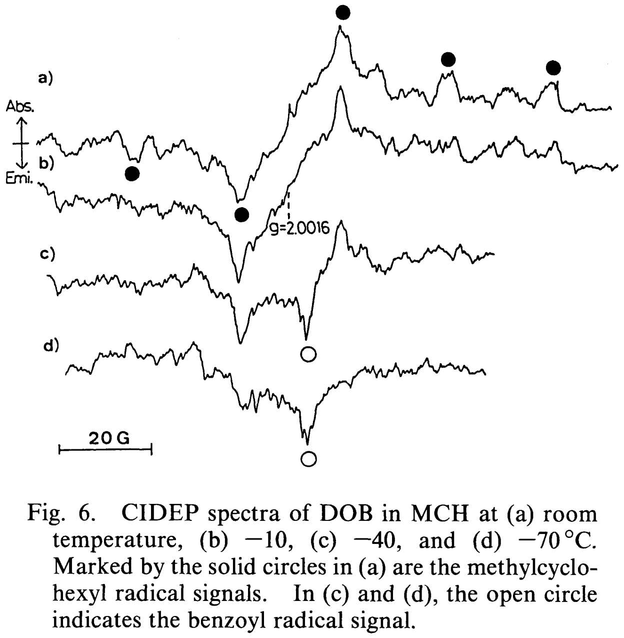


Fig. 6. CIDEP spectra of DOB in MCH at (a) room temperature, (b) −10, (c) −40, and (d) −70 °C. Marked by the solid circles in (a) are the methylcyclohexyl radical signals. In (c) and (d), the open circle indicates the benzoyl radical signal.

tion decreases. On the other hand, the TM polarization due to the α-cleavage is enhanced at a low temperature because of a longer spin-lattice relaxation time of the precursor triplet state of DOB.

Since the relative magnitudes of the polarizations due to the TM and RPM depend on a number of factors such as the reaction rate constant, the spin-lattice relaxation time of the triplet state, the hyperfine splitting and the exchange interaction in the geminate pair, it is difficult to make a quantitative discussion of the cleavage rate. However, the observation of strong TM signals in benzoin and BME indicates that the reaction rate constants must be faster or comparable to the inverse of the spin-lattice relaxation times of the T_1 states (ca. $10^9\,s^{-1}$). The fact that BME spectrum is more symmetric means that the rate constant is larger in BME. On the other hand, the α-cleavage rate constant of DOB is much smaller. Thus from the CIDEP spectra we can conclude that the order of the cleavage rate constant (k_c) is k_c(BME)>k_c(benzoin)≫k_c(DOB). This order is in complete agreement with the result obtained by Lewis et al.[16] who estimated $k_c(\text{BME})>k_c(\text{benzoin})=1.2\times10^9\,s^{-1} \gg k_c(\text{DOB})$ from quenching experiments. These authors rationalized the remarkable dependence of the α-cleavage rate constant on the structure in terms of the ionic character of the transition states.

Conclusion

We have studied the α-cleavage reactions of benzoin and its derivatives by TREPR. The hfcc of the intermediate radicals were determined and the radical species were identified. It was confirmed that the cleavage takes place from the $T_1(n\pi^*)$ state by a one-photon process. A detailed analysis of the time profiles of the transient signals was made. The CIDEP spectra indicate that the order of the cleavage rate constant k_c is in the order, k_c(BME)>k_c(benzoin)≫k_c(DOB).

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