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CIDEP Study of the Photoreduction of Aromatic Ketones with Alkoxides in Alcohols

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The photoreductions of xanthone and benzophenone with alkoxides in several alcohols were studied by observing CIDEP. The total emission spectra, observed after the photoexcitation, were assigned to the ketone anion radicals having TM spin polarization. The dependence of the spectral line width upon alkoxides indicates the existence of a hyperfine interaction between the ketone anion radical and the alkali metal cation, even in the early stage of the photochemical reaction in an alcoholic media. A careful analysis of the spectral pattern leads to the conclusion that the counter radical of the ketone anion interacting as a geminate pair which is responsible for the RPM polarization, is other than a methoxyl radical in these systems.

ESR studies on the aromatic ketone anions formed by the reduction with alkali metals in ethereal solvents proved the properties of ion pairs between the ketone anion radicals and the alkali metal cations.[1-4] The phenomenon of an 'atom transfer' in the electron-transfer process has also been shown.[5] On the other hand, the photoreduction of aromatic ketones has been investigated in several systems extensively.[6,7] Alkoxides are known to be one of the good reducing agents used in the photoreaction of aromatic ketones in alcoholic media. The primary steps in this photochemical reaction, especially concerning the behavior of the alkali metal cation and the alkoxyl radical, are of great interest, but few studies on this problem has been reported.[1]

The studies on CIDEP (chemically induced dynamic electron polarization) provide information about the primary steps of photochemical reactions, and are powerful tools for studying the reaction dynamics. The time-resolved study of the CIDEP spectra provides information about the chemical exchange and/or electron spin exchange reactions which induce the relaxation processes.[8]

In the present paper, the CIDEP investigation of the photoreduction of aromatic ketones, xanthone (9-xanthenone), and benzophenone (diphenylmethanone), with alkoxides in several alcohols is presented. New information concerning the presence of a weak interaction between the ketone anions and the alkali metal cations in alcoholic media in the early stage of the photochemical reaction is given. To our knowledge, this paper represents the first CIDEP investigation on the ion pairs formed in the photochemical reaction of aromatic ketones and alkoxides in alcoholic solvents.

Experimental

Xanthone and benzophenone were recrystallized repeatedly from acetone. A sodium methoxide ($NaOCH_3$), 28% methanol solution provided by Wako Pure Chemical Industries, Ltd., was used as received. Potassium methoxide ($KOCH_3$) as ca. 10% methanol solution was prepared by the reaction of potassium metal and methanol. The solvents used in this experiment were ethanol, 2-propanol, cyclohexanol, and a 1 : 1 (v/v) mixture of cyclohexanol and isobutyl alcohol (2-methyl-1-propanol). Commercially available special-grade alcohols provided by Wako Pure Chemical Industries, Ltd. were used as received. Throughout most of the present experiment, the concentrations of xanthone and benzophenone were 0.01 and 0.1 mol dm^{-3}, respectively, unless otherwise noted. The mixing ratio of a methanol solution of alkoxide and the other alcoholic solvents was 1 : 9 in volume in most cases. The concentrations of $NaOCH_3$ and $KOCH_3$ in the solution used in the experiment were ca. 0.5 and 0.1 mol dm^{-3}, respectively. The solutions were deoxygenated by bubbling with pure nitrogen gas prior to the CIDEP measurements.

A nitrogen gas laser (λ=337.1 nm, 5 mJ/pulse) was used for the photoexcitation with a repetition rate of 7.5 Hz. Steady-state ESR was observed by an X-band ESR spectrometer using 100-kHz field modulation during the pulsed laser excitation. The CIDEP spectra were measured by a modified X-band ESR spectrometer (time resolution of 60 ns) for the time-resolved measurement using no field modulation. A boxcar integrator was used to record the time-resolved ESR spectra at several fixed gate times after the laser pulse. The gate width of the boxcar integrator was 0.2 or 0.5 μs. The steady-state ESR and CIDEP measurements were carried out at room temperature. The solutions were flowed at a constant rate of ca. 25 ml h^{-1} through a flat quartz cell of 0.3-mm depth in an ESR cavity of TE_{011} mode. The details were similar to those reported before.[9,10]

Results and Discussion

(I) Xanthone. Figure 1 shows typical results of the steady-state ESR spectra observed during the in situ laser photolysis in the systems of xanthone/$NaOCH_3$ and xanthone/$KOCH_3$ in the mixture of cyclohexanol and isobutyl alcohol (HB). These spectra were assigned to xanthone anion radical from their hyperfine structure (hfs). Other radical species could not be detected. The hyperfine coupling constants (hfc) were in good agreement with those reported in the literature.[11] The line width of the spectra observed using $NaOCH_3$ was much broader than those observed using $KOCH_3$. The change in the concentration of

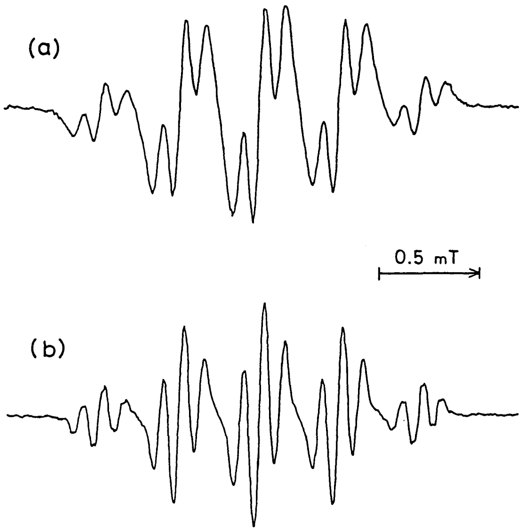

Fig. 1. Steady state ESR spectra observed during the in situ laser photolysis of (a) xanthone/NaOCH$_3$ and (b) xanthone/KOCH$_3$ in HB.

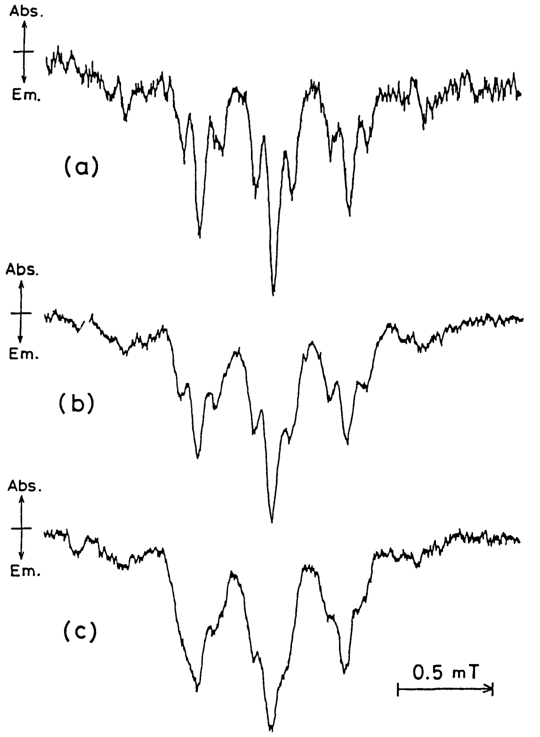

Fig. 2. Time resolved ESR spectra observed in the systems of xanthone and NaOCH$_3$ (a) in ethanol, (b) in 2-propanol and (c) in HB with the gate opening time from 1.0 to 1.2 μs after the laser pulse.

xanthone and alkoxides did not affect the respective spectral patterns and the line width, though it did affect the signal intensities. These results imply the existence of a certain interaction which affects the line width of the ESR spectra between the alkali metal cation and the radical anion in alcoholic media. The line width of the spectra observed using NaOCH$_3$ drastically varied with the solvent alcohol. This effect also appeared weakly in a system containing KOCH$_3$.

Figure 2 shows the time-resolved ESR spectra observed in a system of xanthone and NaOCH$_3$ in various alcohols with the gate opening time from 1.0 to 1.2 μs after the laser pulse. In all the time-resolved ESR spectra shown in the present paper, the downward signals show the microwave emission. These spectra were assigned to the xanthone anion radical; other radical species could not be detected. The spectral hfs were the same as those observed in the steady-state ESR.

The total emission pattern of these spectra clearly shows the feature of the triplet mechanism (TM) of CIDEP; namely, the photochemical reaction is much faster than the spin-lattice relaxation process of the spin polarized triplet state of precursor xanthone. The intensity of hyperfine (hf) lines in the lower field was slightly stronger than that of the corresponding $|M_I|$ lines in the higher field. This fact suggests a slight superposition of emission on the lower-field side and absorption on the higher-field side (E/A pattern), which is due to the radical pair mechanism (RPM) between the geminately produced radicals. The CIDEP signals decayed in some tens of microseconds, depending upon the experimental conditions. This signal decay does not reflect the chemical reaction but, rather, CIDEP relaxation, since the steady state ESR measurement provides the equilibrated spectrum of the anion radical. The line width of the CIDEP spectra varied with the solvent. It became broader with an increase in the molecular weight of the alcohols used in this experiment.

Figure 3 shows the CIDEP spectra observed using

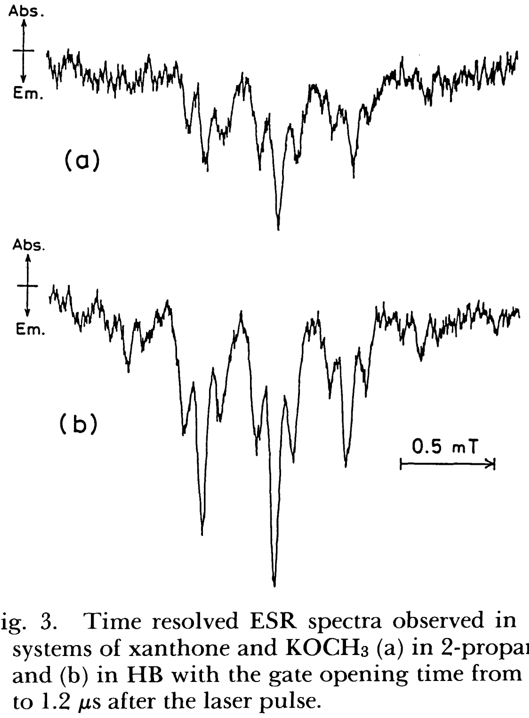

Fig. 3. Time resolved ESR spectra observed in the systems of xanthone and KOCH$_3$ (a) in 2-propanol and (b) in HB with the gate opening time from 1.0 to 1.2 μs after the laser pulse.

$KOCH_3$ in 2-propanol and HB. The spectral hfs and the total emission pattern are almost the same as those observed using $NaOCH_3$. The line width observed in this system is much sharper than that observed in the system containing $NaOCH_3$, as it is clearly demonstrated by comparing Figs. 2 and 3. The solvent effect on the line width, similar to the system of $NaOCH_3$, also appeared weakly. The dependence of the line width upon the solvents and alkoxides observed in the CIDEP study is similar to the result of the steady-state ESR observation described above. Even immediately (0.1 μs) after the photoexcitation, the CIDEP spectra were essentially identical to those observed in the later region, except for the line width. This line-broadening in the early period usually occurs in CIDEP measurements.[12,13] These results clearly demonstrate that the same interaction as that observed in the steady-state ESR takes place even in the period earlier than 10^{-7}s after the photoexcitation.

The photoreduction of xanthone with alkoxides can be represented as follows:

$$\mathrm{Xn}+h\nu \longrightarrow \mathrm{Xn(S_1)^*} \xrightarrow{\mathrm{ISC}} \mathrm{Xn(T_1)^*} \tag{1}$$

$$\mathrm{Xn(T_1)^*}+\mathrm{MOCH_3} \longrightarrow \mathrm{Xn^{\cdot-}}+\mathrm{M^+}+{}^{\cdot}\mathrm{OCH_3}, \tag{2}$$

where M denotes alkali metal and the asterisks represent the electronic excited states. Xanthone is excited by a laser pulse to the excited singlet state (S_1), and the spin-selective intersystem crossing (ISC) induces spin polarization in the triplet state (T_1): namely, the uppermost spin-sublevel is exclusively populated.[14,15] This excited triplet state reacts with alkoxides very quickly while the spin polarization is conserved. Therefore, the product anion radical, preserving the spin polarization, shows the total emission spectra. This xanthone anion radical and the alkali metal cation form the ion pair soon after the photochemical reaction in the alcoholic solvents. This ion-pair formation is considered to be analogous to that reported in the system of alkali metal reduction of aromatic ketones in ethereal solvents.[1–3] Although the methoxyl radical carrying TM spin polarization may be produced by this photoreduction, we could not detect this particular radical. Alcohol radicals which may be produced by a secondary reaction of this radical were not observed either. The failure to detect these radical species may be explained by the rapid relaxation of the spin polarization of the methoxyl radical.

The line width of these CIDEP spectra is considered to be caused by a hyperfine interaction between the alkali metal cation and the radical anion; therefore, the hfc of sodium nuclei is larger than that of potassium. This is analogous to the results in an ethereal solution, reported in the literature.[1,2,11] However, this hyperfine interaction in alcoholic solvents is much weaker than that in ethereal solvents. Thus, the solvent effect on the line width may also be explained by a variation of the hyperfine interaction, possibly due to the polarity of the solvent. This means that the hyperfine interaction between the radical anion and the alkali metal cation becomes stronger with a decrease in the polarity of the solvent.

The existence of the paramagnetic dimer of ketone anion radicals was reported,[16] which might obscure the hfs of the ESR spectrum. In the present experiment, however, this contribution to the line width may be negligible since the concentration of radicals in our observing systems, probably less than 10^{-4} mol dm^{-3}, was scarce enough not to form the dimer.

In ordinary steady-state ESR, the variation of spin-spin relaxation time by electron transfer between radical species and its parent molecule is one of the causes of line-broadening. In the time-resolved ESR studies, however, it is known that such an exchange reaction sensitively affects the time evolution of the CIDEP spectrum.[8,13,17] In the presence of the electron-transfer process, the effective relaxation time of CIDEP signals is dependent upon the line degeneracy D_i, microwave field strength ω_1, and the concentration of parent molecule $[A]$. The apparent spin-spin and spin-lattice relaxation times (T_{2i}^{ET} and T_{1i}^{ET}) for a line i at low ω_1 are as follows:

$$\frac{1}{T_{2\,i}^{\mathrm{ET}}} = \frac{1}{T_2} + \frac{(D-D_i)}{D}\,k_{\mathrm{ET}}[A] \tag{3}$$

and

$$\frac{1}{T_{1\,i}^{\mathrm{ET}}} = \frac{1}{T_1} + \omega_1{}^2\left(\frac{1}{T_{2\,i}^{\mathrm{ET}}} - \frac{1}{T_1}\right)^{-1} \tag{4}$$

where D is the total line degeneracy and k_{ET} is the rate constant of the electron-transfer reaction.

The CIDEP spectra observed in systems of $NaOCH_3$ with xanthone of different concentrations and by shifting the gate opening time of the boxcar integrator are shown in Fig. 4. The hfs of spectra, its total emission pattern and the line width were not seriously affected by the concentration of xanthone and the gate-opening time. On the other hand, the observable spin-lattice relaxation time of the spin polarization on each hf line was different. The center line of the respective triplet ones of the spectra decayed faster than its neighboring lines. This result can be considered to demonstrate the dependence of the effective relaxation times upon the line degeneracy.

The concentration dependence of the signal decay is clearly demonstrated by a comparison of Figs. 4a and 4b. The observed decay rate of the CIDEP signals increases with a decrease in the concentration of xanthone. This may be explained by the term $k_{\mathrm{ET}}[A]$, which affects the observed values of the relaxation time in Eqs. 3 and 4. A system using potassium methoxide provided similar results.

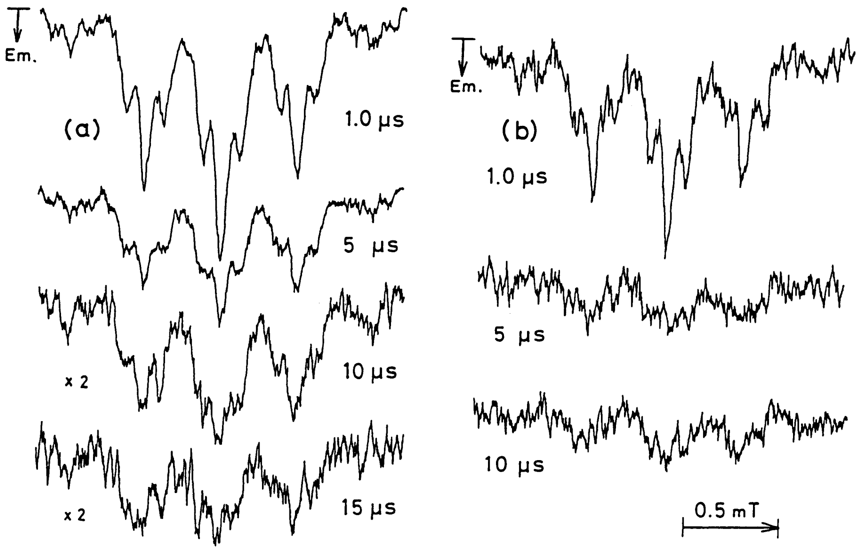

Fig. 4. Time evolution of CIDEP spectra observed by shifting gate opening time (fixed gate width of 0.5 μs) of the boxcar integrator in the system of xanthone/NaOCH$_3$ in 2-propanol. The concentration of xanthone is (a) 6.9×10^{-3} mol dm^{-3} and (b) 1.9×10^{-3} mol dm^{-3}.

These results seem to suggest that the electron-transfer reaction from a xanthone anion radical to its parent molecule takes place. The rate of the electron-transfer reaction is reported to be slow (k_{ET} is ca. 10^7 mol^{-1} dm^3 s^{-1}) in the case of fluorenone anion radical in alcoholic media.[18] If this value is adopted in the present system, the contribution of the electron-transfer reaction to the result shown in Fig. 4 is thought not to be very significant. On the other hand, the excitation by the attenuated laser light provided data concerning a fast decay, compared with the one excited by intense light. This result suggests that the concentration of radicals also affects the apparent decay rate of the spin polarization: that is, the relaxation mechanism such as the electron spin-exchange reaction must also be taken into account in this particular system. In this case, the apparent relaxation rate of hf line i may also be expressed in an identical form to that used in Eqs. 3, where the spin-exchange rate and the radical concentration must be used, instead of k_{ET} and $[A]$,[13] respectively.

After all, it was suggested that the spin-exchange reaction between anion radicals and the electron transfer from the xanthone anion radical to its parent molecule takes place in the early period after photoreduction, and the interaction of the ion pair continues

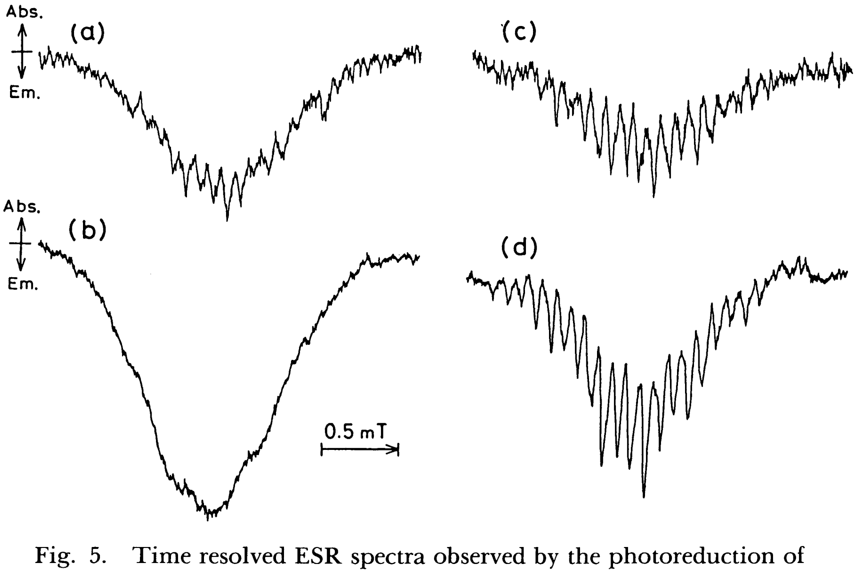

Fig. 5. Time resolved ESR spectra observed by the photoreduction of benzophenone with alkoxides in various alcohols with gate opening time from 1.0 to 1.2 μs. (a) NaOCH$_3$/2-propanol, (b) NaOCH$_3$/HB, (c) KOCH$_3$/2-propanol, and (d) KOCH$_3$/HB.

during these processes. The transfer of the alkali metal cation takes place along with the electron-transfer reaction, which is known as an 'atom transfer'.[5)]

(II) Benzophenone. Figure 5 shows the CIDEP spectra observed in the photolysis of benzophenone instead of xanthone in alcoholic solvents containing $NaOCH_3$ or $KOCH_3$. These spectra, having a total emission pattern of TM, are assigned to benzophenone anion radical by an analysis of the hfs,[1,2)] which clearly appeared in the system of potassium methoxide. No other species, such as the alcohol radical, was detected. The spectral change with the solvent and the alkoxide showed a similar tendency to that observed using xanthone. The change in the concentration of benzophenone did not affect the spectral pattern or line width seriously, though the decay of the signal became fast upon diluting the concentration. This situation was also the same as that observed using xanthone. Steady-state ESR measurements also provided an ordinary ESR spectrum of the anion radical during the laser photolysis. Consequently, the photochemical primary reaction and successive processes in the system of benzophenone are very similar to those of xanthone: namely, there exists a hyperfine interaction between the benzophenone anion and the alkali metal cation; solvation also affects the interaction.

Concerning the contribution of RPM to the total emission spectra observed in both xanthone and benzophenone systems, a unique and important feature of this reaction is obtained. Usually, RPM provides the E/A character by S-T_0 mixing of the two geminately produced radicals having nearly the same g-value. In the present experimental systems, the counter radical of the ketone anion is predicted to be a methoxyl radical which must be produced in the early stage of this reaction. The methoxyl radical is known to have a larger g-value,[19,20)] $g_{iso}=2.029$,[21)] while the ketone anion radicals have a g-value of 2.0036,[22)] which is close to that of a free electron. This larger difference of the g-values almost gives a symmetrical total absorption spectrum of the ketone anion through S-T_0 mixing.[23-25)]

The simulated CIDEP spectra of the ketone anion radical of pure TM polarization and of pure RPM regarding the above-mentioned assumption in the case of benzophenone, are shown in Figs. 6a and 6b, respectively. The hfc of $A(\mathrm{o})=0.280$ mT, $A(\mathrm{m})=0.100$ mT, $A(\mathrm{p})=0.354$ mT and the line width of 0.030 mT (FWHM) are employed for the anion radical. These hfc values, which are obtained from the observed CIDEP spectrum, are in good agreement with those reported before.[1,2)] In order to reproduce the observed spectra of the distorted total emission pattern, the contribution of TM must be slightly stronger than that of RPM. This situation hardly takes place due to the following two reasons. The signal intensity might be very weak owing to a cancellation of the emission and absorption components under the condition assumed above, though the observed signal intensity was almost comparable with the ordinary TM spectrum observed in several systems. Secondly, since the spin-lattice relaxation of triplet ketones competes with its chemical reactions, the spectral pattern could be sensitively influenced by such experimental

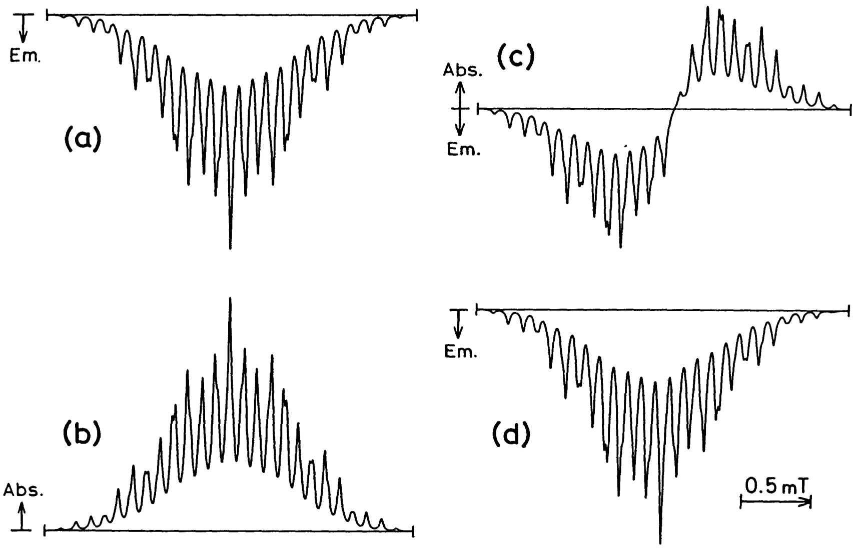

Fig. 6. Simulated CIDEP spectra of benzophenone anion radical in the cases of (a) pure TM, (b) pure RPM assuming the counter radical is methoxyl radical having a hfc of 5.2 mT,[19)] and (c) pure RPM assuming the counter radical is methanol radical having a g-factor of 2.0032 and hfc's of $A_{CH}=1.75$ mT and $A_{OH}=0.100$ mT.[26)] (d) Mixed spectrum of 80% of (a) and 20% of (c), whose intensities are normalized previously.

conditions as the viscosity of the solution or the concentration of solutes, though no such effect has been observed.

Figure 6c shows the simulated CIDEP spectrum of pure RPM obtained by assuming an alcohol radical (hydroxymethyl radical) as the counter one. Figure 6d shows the hybrid spectrum of Figs. 6a and 6c, where the predominant contribution of TM is assumed. In the system of xanthone, similar results were obtained by simulation. Therefore, it was tentatively concluded that the counter radical interacting as a geminate pair is not methoxyl but, perhaps an alcohol radical such as the hydroxymethyl radical produced by a secondary reaction with the solvent or by a fast isomerization of the methoxyl radical.[20] The lifetime of the methoxyl radical would be shorter than the time required for S-T_0 mixing (10^{-9}—10^{-7} s).[23-25]

In conclusion, the photoreduction of xanthone and benzophenone in alcoholic solvents was investigated by CIDEP. The product anion radical and the alkali metal cation form the ion pair soon after the photochemical reaction. The time-resolved ESR study demonstrated that the hyperfine interaction of the ion pair exists, even in the early stage of the photoreaction. It was also suggested that the electron spin-exchange process between the ketone anion radicals possibly occurs along with an electron-transfer reaction. The E/A distortion component of the total emission spectrum could be explained by the contribution of the geminate pair RPM; also, the counter radical of the anion radical of ketones in the geminate cage was shown to be other than the alkoxyl radical.

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