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Accounts

Chemically Induced Dynamic Electron Polarization Studies of Photochemical Reactions: Acetone in 2-Propanol and Triethylamine

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The results of Chemically Induced Dynamic Electron Polarization (CIDEP) studies of acetone in 2-propanol and triethylamine are reviewed to show how CIDEP studies can reveal interesting details of the initial processes of photochemical reactions. After a brief description of various mechanisms that give rise to CIDEP, the following topics are discussed: a) spectral pattern and the main reacting state, b) CIDEP mechanisms and the temperature and frequency dependences of the spectra, c) direct EPR observation of the radical pair spectra in solution, d) time-developments of the CIDEP signals and spin and reaction dynamics of the initial processes of photochemical reactions, e) quantitative analyses of the magnitudes of CIDEP in terms of a stochastic Liouville equation, and f) some related applications. An overview of the remaining problems and the future outlook is also presented.

Electron spin systems in radicals created by photochemical reactions are not in thermal equilibrium immediately after reactions. Transient EPR (Electron Paramagnetic Resonance) spectra of these radicals reflect a non-Boltzmann distribution of the spin states and show electron spin polarization called CIDEP (Chemically Induced Dynamic Electron Polarization).1) Transient EPR studies of radicals and radical pairs produced in photochemical reactions in solution often provide valuable information about the details of the initial stages of reactions that cannot be obtained by other methods. First, one can detect and identify short-lived intermediate radicals involved in the reaction and can thus clarify the reaction mechanisms. One can easily tell whether the reaction is taking place from an excited singlet state or a triplet state only by looking the pattern of the spectrum. Second, by analyzing the time developments of transient EPR signals, one can follow the reaction and spin dynamics of radicals. Third, detailed information about radical pairs created in the initial stages of reactions may also be obtained under favorable conditions. Thanks to the developments in the time-resolved EPR (TREPR) spectroscopy,2) considerable progress has been made in this area recently.

In the present review we take CIDEP of acetone as a representative example. We show how these studies can reveal interesting details of the spin and reaction dynamics of photochemical reactions in solution. The CIDEP is produced by the hydrogen abstraction reaction of acetone; the spectrum of the produced 2-hydroxypropan-2-yl radical is very simple and suited for a detailed analysis. Studies of the reactions of acetone under various conditions provide rich information about CIDEP mechanisms, radical pairs, and reaction schemes. Here we focus our attention on the CIDEP obtained by the photolysis of acetone in 2-propanol and triethylamine. The main processes taking place in these systems upon photoexcitation are schematically shown in Fig. 1.

The CIDEP of acetone has been investigated by many groups,3—9) but we mainly discuss the results obtained in our laboratory10—19) and other works particularly related to ours.8,9,20—23) The topics to be covered are: a) spectral pattern and the reacting state, b) CIDEP mechanisms and temperature and frequency dependences of the spectrum, c) direct observation of the radical pair spectrum, d) time-developments of the CIDEP signals and spin and reaction dynamics, e) quantitative

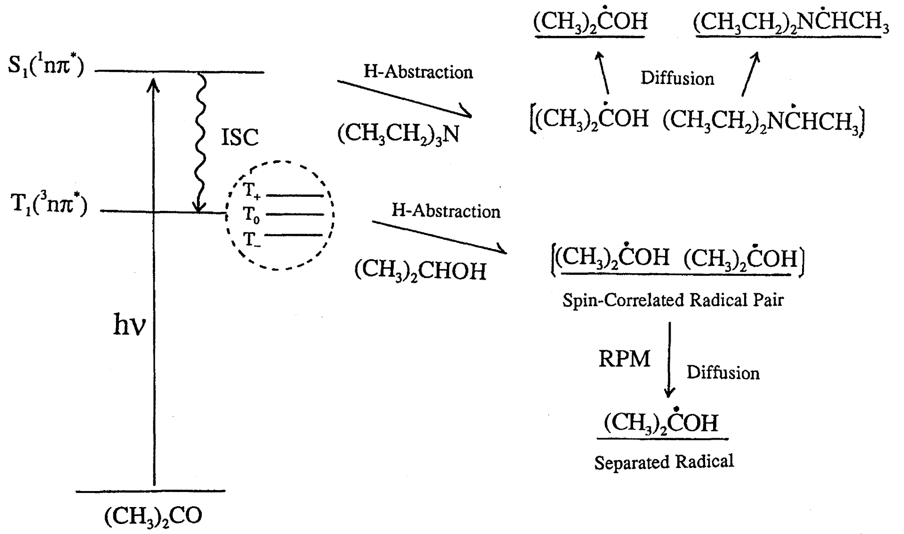

Fig. 1. Overall reaction scheme. Underlined species were detected by TREPR.

analysis of CIDEP, and f) related applications.

The importance of these topics is summarized as follows. Hydrogen abstraction reactions of carbonyl molecules are usually considered to take place from the lowest excited triplet states, but the CIDEP studies unambiguously establish that the reactions can also take place from singlet states, depending on the condition.[11)] Detailed analyses of the time profiles of the CIDEP signals give useful data on the spin and reaction dynamics.[17,20,21)] The CIDEP spectrum of the 2-hydroxypropan-2-yl radical strongly depends on temperature, indicating that various CIDEP mechanisms are involved.[8—13,16)] Detailed studies on the temperature dependence of the CIDEP spectrum of the 2-hydroxypropan-2-yl radical led to many important findings concerning the CIDEP mechanisms. A particularly important one is the direct observation of the EPR spectra of radical pairs in solution,[8,13,15,16)] because the radical pair and the cage effect are of vital importance for the reaction dynamics in solution. Direct EPR observation may provide a useful means to obtain detailed information on radical pairs. Since the CIDEP spectrum of the 2-hydroxypropan-2-yl radical is very simple, it enables us to make a quantitative theoretical analysis from which one can also gain insight into the nature of the intermediate radical pairs.[16,23,24)]

We started to work on the CIDEP of acetone in 1983 when three of us were in Kyoto. Over a period of more than ten years since then we have been concerned with various aspects of the CIDEP of acetone from time to time. In this account we summarize the results of our work and present our views of the current status and the future outlook.

CIDEP Mechanisms and TREPR Measurements

Before going into the discussion of the CIDEP of acetone, we briefly summarize various mechanisms that give rise to CIDEP. For more details, readers are referred to original papers and review articles.[8,25—32)]

a) Triplet Mechanism (TM).[25—27)] When a reaction takes place from an excited triplet state, the spin polarization of the precursor triplet state is transferred to the produced radical. The spectrum shows either a net emission (E) or absorption (A) of the microwave. The magnitude of the polarization depends on numerous factors, such as the zero field splittings (ZFS) D and E, the ratios (w_x, w_y, w_z) of the intersystem crossing rates into sublevels of the triplet state from the excited singlet state, the spin-lattice relaxation time of the precursor triplet state (T_1^{T}), the reaction rate for the production of the radical (k_{T}), the rotational correlation time (τ_{R}) of the triplet molecule and the microwave frequency (ω_0). To produce a large polarization, k_{T} should not be much smaller than $1/T_1^{\mathrm{T}}$. According to the calculation by Atkins–Evans,[26)] the magnitude of the initial polarization due to TM (P^0_{TM}) in a high magnetic field is given as

$$P^0_{\mathrm{TM}} = \left(\frac{k_{\mathrm{T}}T_1^{\mathrm{T}}}{1+k_{\mathrm{T}}T_1^{\mathrm{T}}}\right)\frac{4}{15}(D\hat{K}+3E\hat{I}) \times\left\{\frac{\omega_0}{\omega_0^2+\tau_{\mathrm{R}}^{-2}}+\frac{4\omega_0}{4\omega_0^2+\tau_{\mathrm{R}}^{-2}}\right\}, \quad (1)$$

$$\frac{1}{T_1^{\mathrm{T}}} = \frac{2}{15}(D^2+3E^2)\left\{\frac{\tau_{\mathrm{R}}^{-1}}{\omega_0^2+\tau_{\mathrm{R}}^{-2}}+\frac{4\tau_{\mathrm{R}}^{-1}}{4\omega_0^2+\tau_{\mathrm{R}}^{-2}}\right\}. \quad (2)$$

$$\hat{K} = \frac{1}{2}(w_x+w_y)-w_z,$$
$$\hat{I} = \frac{1}{2}(w_y-w_x),$$
$$w_i = k_i/k_{\mathrm{total}}.$$

b) Radical Pair Mechanism.[28—30)] Homolytic cleavage of a chemical bond produces a pair of radicals in which spins are correlated (Spin-Correlated Radical Pair, SCRP). Radicals forming a radical pair separate or re-encounter because of the diffusional motion in solution. When the radicals re-encounter, mixing of the singlet (S) and triplet (T) states takes place during the time interval between the encounters, because of the Zeeman and hyperfine interactions. This mixing and the exchange interaction (J) at the time of re-encounter produce the polarization of the spin state of the radical. This is the polarization due to the geminate radical pair. At a magnetic field employed in the usual X-band EPR measurements, the mixing between the S and T_0 states (ST_0M) is dominant. The magnitude of the polarization is given by the following formula:

$$P^{\mathrm{a}}_{\mathrm{STOM}} \propto \sum_b \mathrm{sign}(Q_{\mathrm{ab}})\sqrt{|Q_{\mathrm{ab}}|}, \tag{3}$$

$$Q_{\mathrm{ab}} = (1/2)\{(g_1 - g_2)\mu_{\mathrm{B}}B + (\sum_i A_{1i}m_{1i} - \sum_j A_{2j}m_{2j})\}.$$

Here $P^{\mathrm{a}}_{\mathrm{ST0M}}$ is the magnitude of the polarization of radical 1 in the overall nuclear spin state a, while i and j refer to different nuclei in the nuclear states a and b of radicals 1 and 2, respectively. The first term in Q_{ab} represents the difference in the Zeeman interactions due to the g-factor difference and the second term represents the difference in hyperfine interactions between the two radicals. It is important to note that the polarization due to ST_0M does not change the total polarization of the radical, but does change the distribution of the α and β spins with respect to the nuclear spin states. Thus different nuclear spin states carry different polarizations, producing a hyperfine dependent CIDEP spectrum. The spectrum shows an absorption on the low field side and an emission on the high field side (A/E) or vice versa (E/A), depending on whether the reaction takes place from an excited singlet state or a triplet state and on the sign of J. When the g difference is small, the sign of the polarization is summarized in a simple formula:

$$\Gamma = \mu J, \tag{4}$$

where μ is taken to be + for a triplet precursor and − for a singlet precursor, respectively, and J is the exchange interaction. Γ is + for an A/E pattern and − for an E/A pattern.

Electron spin polarization due to ST_0M also appears when radicals in solution recombine. When isolated radicals approach to form a radical pair, the spin state of the pair is either in the singlet state or the tripet state. Selective recombination in the singlet state leaves more radical pairs in the triplet state, producing spin polarization with the same qualitative features as those of the triplet geminate pairs. This mechanism is called free pair (F-pair) RPM.

When the hyperfine interaction is large and the viscosity of the solvent is high, mixing between the S and T_{-1} states cannot be neglected ($ST_{-}M$). This mechanism involves simultaneous flips of both electron and nuclear spins. The magnitude of the polarization is proportional to the following term:

$$\begin{aligned} P_{\mathrm{ST-M}} &\propto |< S, I_i, M_i - 1|AS_{+}I_{-}|T_{-}, I_i, M_i >|^2 \\ &= (1/8)A^2[I_i(I_i+1) - M_i(M_i-1)], \end{aligned} \tag{5}$$

where I_i and M_i denote the nuclear spin quantum number and and the magnetic quantum number of the i th nucleus, respectively. The spectrum shows a net emission.

c) Radical Triplet Pair Mechanism (RTPM).[31] This mechanism takes place by the interaction between a radical and a triplet molecule. However, the triplet molecule must be stable enough to encounter the radical and, in the case of triplet of acetone with a lifetime of 10^{-7} s, this mechanism is not likely to be important. The polarization due to this mechanism is predicted to be emissive.

d) Spin-Correlated Radical Pair.[8,32] Spin-correlated radical pairs (SCRP) whose existences are always assumed in the RPM of CIDEP are very important chemical species in understanding the initial processes of chemical reactions, but it is only recently that spectroscopic identification of this species became possible. EPR spectra of SCRP were clearly observed in micelles[32,33] and biradicals,[34,35] but there are only a few cases in which the EPR spectra of SCRP have been obtained in solution.[8,15,16,36] Here we summarize the salient features of the spectra.

Using the singlet and triplet states of the pair as basis, the eigenstates of the radical pair comprising radicals R_a and R_b are given in terms of the exchange interaction J and the difference between the resonance frequencies of R_a and R_b ($Q = (1/2)(\omega_a - \omega_b)$). The frequencies of the EPR transitions are given as follows:

$$\begin{aligned} \omega_{12} &= (1/2)(\omega_a + \omega_b) + \Omega - J, \\ \omega_{34} &= (1/2)(\omega_a + \omega_b) + \Omega + J, \\ \omega_{13} &= (1/2)(\omega_a + \omega_b) - \Omega - J, \\ \omega_{24} &= (1/2)(\omega_a + \omega_b) - \Omega + J. \end{aligned} \tag{6}$$

The relative intensities of the EPR signals are determined by the population of each state and the transition probability. They are given by the following equation.

$$-I_{12} = I_{34} = -I_{13} = I_{24} \propto Q^2/\Omega^2 \;\; (\Omega^2 = Q^2 + J^2). \tag{7}$$

When $Q \gg J$, these transitions give rise to two doublets separated by Ω, each of which becomes an E/A type peak split by 2 J for a triplet precursor.

e) TREPR Measurements. Transient EPR spectra are taken by means of the time-resolved EPR spectroscopy (TREPR).[2] TREPR experiments are carried out by using both CW- and pulsed microwave. CW-TREPR experiments can be performed easily by slightly modifying a conventional commercial EPR spectrometer, but there are limitations in the time and spectral resolutions. When a commercial X-band spectrometer with a microwave cavity of $Q \simeq 5000$ is employed, the time resolution is limited to ca. 0.1 μs and the spectra taken within 0.5 µs are severely broadened, when intrinsic linewidths are narrow. Furthermore, analysis of the time development of a transient EPR signal is not straightforward because of the constant interaction between the spin system and the microwave. Therefore, in following the early time development of the spin system, pulsed EPR measurements are more advantageous. In the following, we first present the main features of the CIDEP spectra obtained under various experimental conditions and then the time developments of the CIDEP signals together with qualitative interpretations of the results.

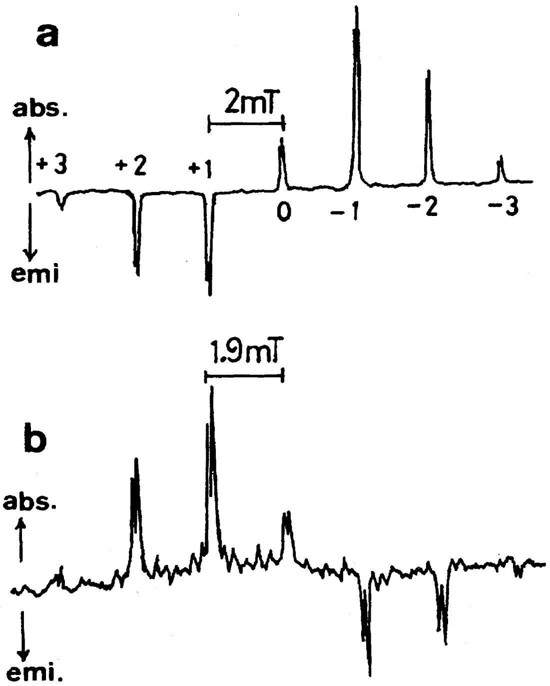

Fig. 2. (a) CIDEP spectrum of 2-hydroxypropan-2-yl radical obtained by the photolysis of acetone in 2-propanol at 25 °C, (b) Spectrum obtained by the photolysis of acetone in triethylamine at 25 °C. Both spectra were taken at 1 µs after the laser pulse.

Main Spectral Features

1. Pattern of the Spectrum and the Reacting State.[11,13] The main photochemical reaction of acetone in solution is the hydrogen abstraction reaction from solvent, though the importance of other side-reactions such as the Norrish type I bond cleavage in understanding the CIDEP spectra has been pointed out.[37] In a solution of 2-propanol, the main reaction of acetone is given as,

$$(CH_3)_2C{=}O + (CH_3)_2CHOH \rightarrow 2(CH_3)_2\dot{C}OH$$

The CIDEP spectrum of acetone changes remarkably depending on the solvent and temperature. In Fig. 2a, the spectrum obtained by the photolysis in 2-propanol at room temperature is shown. The spectrum consisting of seven main peaks separated by 1.97 mT due to the hyperfine interactions with six methyl protons confirms the assignment that the radical is 2-hydroxypropan-2-yl. Each main component is further split into two lines by the hydroxyl proton. The spectrum shows an E/A* (emission on the low field side and absorption on the high field side with an additional total absorptive component) type pattern. The E/A pattern is due to the ST_0M of RPM, which immediately shows that the reaction takes place mainly from the excited triplet state, provided that J is negative. On the other hand, in triethylamine (TEA) the spectrum shows an opposite A*/E type pattern, as shown in Fig. 2b, though the same 2-hydroxypropan-2-yl radical is responsible for the spectrum, as indicated by the following reaction scheme: [11]

$$(CH_3)_2CO + N(C_2H_5)_3 \rightarrow (CH_3)_2\dot{C}OH + (C_2H_5)_2N\dot{C}HCH_3$$

This indicates that the reaction in TEA now takes place dominantly from the excited singlet state. In mixed solvents of TEA and benzene, the CIDEP pattern actually changes from A*/E to E/A* as the concentration of TEA is decreased. This observation is explained in terms of the competition between the singlet reaction and the triplet reaction. The intersystem crossing (ISC) rate from the excited singlet state to the triplet state is estimated to be ca. 10^8 s^{-1}. In pure TEA the hydrogen abstraction rate in the singlet state is faster than this rate, preventing the ISC. Then the predominant singlet reaction is observed. As the concentration of TEA is decreased, ISC gradually takes over, making the triplet reaction dominant. This is the first clear example that the reaction in the excited singlet state was shown to be dominant in the hydrogen abstraction reaction in carbonyls. This example quite clearly shows the power of the CIDEP in identifying the reacting state.

2. Temperature and Frequency Dependences and the CIDEP Mechanism.[8–14] The CIDEP spectrum of acetone in 2-propanol exhibits notable temperature dependence. As shown in Fig. 3, the pattern of the spectrum changes from E/A* at room temperature to E/A at around −45 °C, and to E*/A at lower temperatures.[10,13] The total absorptive component observed at higher temperature was originally ascribed to TM on the basis of the temperature dependence and the polarization measurements.[12,13] However, the assignment of this component has been a matter of considerable dispute and alternative interpretations have been suggested.[20,37,38] A comparison of the time profiles of the net absorptive signal and RPM signal contributions led Levstein and van Willigen to the conclusion that the absorptive signal cannot be due to TM.[20] They suggested that the transfer of polarization from triplet precursors at thermal equilibrium to doublet radical products gives rise to the absorptive signal. McLauchlan and co-workers[37] favored the TM involv-

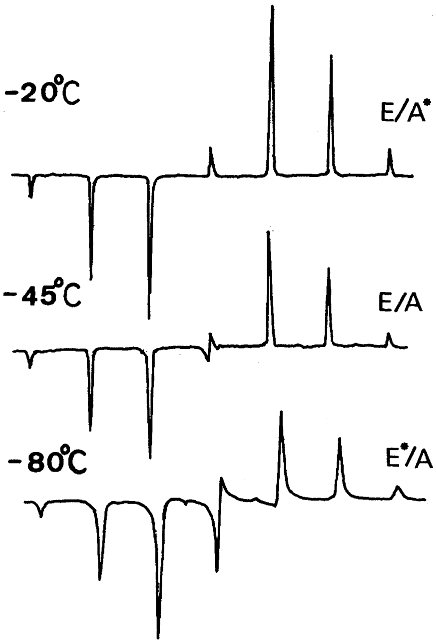

Fig. 3. Temperature dependence of the CIDEP spectrum of the 2-hydroxypropan-2-yl radical in 2-propanol observed at 0.8 μs after the laser pulse.

ing the secondary reaction following bond breaking as well as the hydrogen abstraction reaction. On the other hand, Shkrob and Wan[38)] attributed the net absorption to a TM contribution originating in the triplet state of the enol tautomer. It appears that a complete agreement has not been reached as yet.

The total emissive component observed at lower temperatures has been assigned to ST_-M of RPM.[9,13)] The increased viscosity of the solvent and the relatively large hyperfine splitting of the methyl proton make this mechanism important. Since the polarization due to this mechanism arises from the mixing between the S and T_- states, the relative importance of ST_-M with respect to ST_0M is expected to increase at lower microwave frequencies (or low magnetic fields). This has been confirmed experimentally by Terazima et al.[14,39)] Figure 4 shows the spectra in the L-band (1.5 GHz). Here the spectra are of E^*/A type at all temperatures, indicating that total emissive components are now drastically enhanced. At low temperatures where the viscosity of the solvent is very high, polarization due to ST_-M is quite strong even in the X-band.[13)]

The second-order hyperfine splittings are also clearly resolved in the L-band spectra, as shown in Fig. 4. Since the off-diagonal matrix elements are responsible for both the second-order hyperfine splittings and the ST_-M mechanism, it is interesting to study the polarization on each resolved component. It was hoped that new information about the interactions in radicals and radical pairs might be obtained from such a study. Buckley and McLauchlan suggested[9)] that there are two mechanisms that give rise to ST_-M polarization, so-called hyperfine dependent and hyperfine independent mechanisms. In the former case hyperfine interaction between the unpaired electron and the nuclei in the same radical is important, while in the latter case the unpaired electron interacts with all the nuclei in the radicals comprising the pair. It is possible to distinguish the two mechanisms from the analysis of the peak intensities of the center group peaks.[14,39)] Experimentally, the relative intensities of these peaks were found to vary considerably, depending on the temperature.[14)] This observation was qualitatively explained in terms of the increased stability of the pair at lower temperatures. However, complete understanding of the low frequency CIDEP spectra is rather complicated and remains as a future problem.[14,40)]

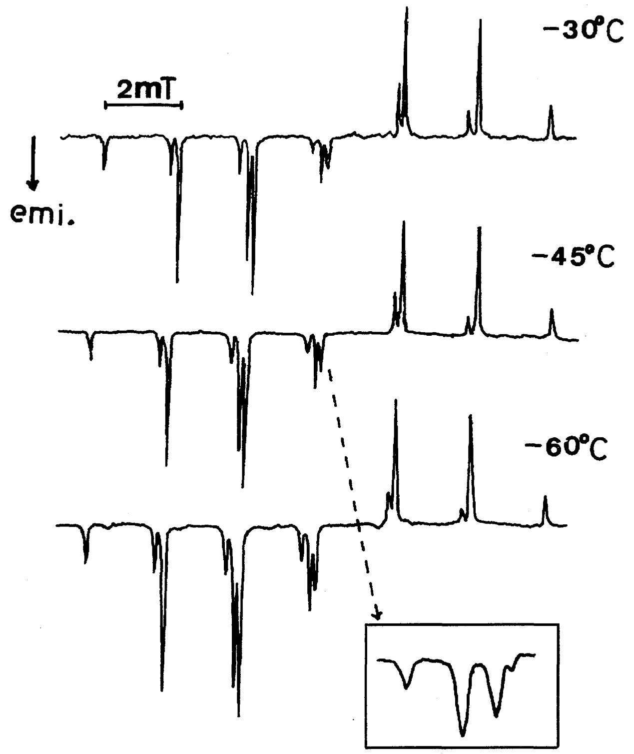

Fig. 4. L-band (1.5 GHz) CIDEP spectrum of the 2-hydroxypropan-2-yl radical in 2-propanol at various temperatures. The spectrum in the insert shows the center group peaks.

3. Spectra of Spin-Correlated Radical Pair.[8,15,16)] The EPR spectra of SCRP have been observed in micelles[32,33)] and biradicals,[34,35)] but it has been considered that direct EPR detection of SCRP in solution is difficult because of its short lifetime. As shown in Fig. 3, the spectrum of the 2-hydroxypropan-2-yl radical in 2-propanol shows a small central peak of E/A type by itself at −45 °C, as well as a peculiar distortion of the lineshape at very low temperatures. This E/A type peak and the distortion become much more evident in the spectrum of the deuterated 2-hydroxypropan-2-yl radical, in which the intensities due to ST_0M are much weaker because of smaller hyperfine splittings in the deuterated radical.[12] Here at very low temperatures, many hyperfine lines show first derivative-like lineshapes (Fig. 5). The central E/A type lines and the distortions of the lineshapes were successfully explained in terms of a superposition of the spectra of separate radicals and radical pairs. The radical pairs give rise to the spectra whose hyperfine lines show E/A lineshapes, as observed in biradicals and micelles. Direct EPR detection of a radical pair is usually difficult, because of its short lifetime and low concentration, but the lifetime of the pair of the 2-hydroxypropan-2-yl radical in 2-propanol at low temperatures is apparently on the order of a microsecond which is long enough to allow direct EPR observation. A large spin polarization expected for a radical pair also helps EPR detection. From the analysis of the decay of the SCRP signal, the lifetime of the pair was estimated to be longer than 2 µs at −80 °C.[13] It was thought that at low temperatures long-lived microscopic solvent structures develop to trap the radical pair. This seems to be a characteristic feature of alcohol which makes it possible to observe the EPR spectra of the radical pairs.

There are two notable observations about the spectra of the radical pairs. First, the linewidths of the hyperfine components of the SCRP spectrum of the 2-hydroxypropan-2-yl radical strongly depend on the magnetic quantum number of the methyl proton M_I.[13,16] This dependence is considered to be mainly due to the anisotropy of the hyperfine interactions which are incompletely averaged by a slow rotational motion.[41] The M_I dependence is much smaller in the deuterated radical, supporting this interpretation. The M_I dependence of the linewidth ($\Delta\omega(M_\mathrm{I})$) is expressed as

$$\Delta\omega(M_\mathrm{I}) = A + BM_\mathrm{I} + CM_\mathrm{I}^2. \qquad (8)$$

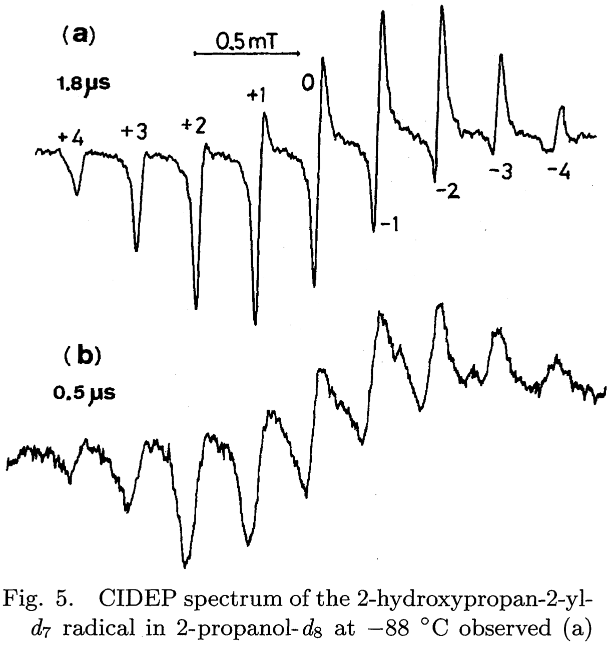

Fig. 5. CIDEP spectrum of the 2-hydroxypropan-2-yl-d_7 radical in 2-propanol-d_8 at −88 °C observed (a) at 1.8 µs and (b) at 0.5 µs after the laser excitation.

Here the constants B and C are proportional to the rotational correlation time. The rotational correlation time of the radical pair was estimated to be about ten times longer than that of the separated radical. This seems to mean that SCRP is a stable entity that exists in a more rigid environment produced by the microscopic solvent structure.[16]

Second, as shown in Fig. 6, there appears a very broad E/A background signal at early times in the low temperature spectrum. This signal disappears within 1 µs at −82 °C, but the decay time becomes somewhat longer at further lower temperatures. This broad component may arise from radical pairs with smaller radical–radical separations and stronger exchange and dipole–dipole interactions. The decay may represent structural changes of the radical pair.

Though the spectrum of SCRP is only observed at low temperatures in the CW experiments, it is possible to detect a short-lived SCRP using FT-EPR even at room temperature.[20,21,36] In an FT-experiment, the microwave pulse $H_1(//x)$ tips the magnetizations of the radicals in the SCRP with opposite directions (M_z, $-M_z$) into the xy-plane to produce the magnetizations M_y and $-M_y$. These magnetizations start to precess around the z axis. The in-phase (M_y) components disappear before observation because of their short lifetimes. In contrast, after the free precession starts, these magnetizations produce out-of-phase (dispersive) components, which are carried over to the separated radicals upon the dissociation of the radical pair. Therefore, even if the lifetime of the pair itself is short, detection of the pair becomes possible by observing the dispersive component of the separated radical signal.[36] In this way, Levstein and van Willigen[20] detected the SCRP spectrum of the 2-hydroxypropan-2-yl radical at room temperature where the lifetime is on the order of 10 ns. For deuterated acetone and 2-propanol, the rate constants of the formation and decay of the SCRP were estimated to be 5×10^7 and 7.5×10^6 s^{-1}, respectively.

Another novel usage of FT-EPR in studying SCRP was recently developed by Iwaizumi and co-workers as two-dimensional (2D) nutation spectroscopy.[42,43] They intended to give a definitive assignment for the SCRP and to separate the spectrum of the SCRP from that of the radical. As the angles of nutation due to microwave are different for the SCRP and the separated radical[36] they examined the nutation frequency dependence of the free induction decay (FID) signals. FID's (t_2) are observed by changing the pulse-width (t_1) of the applied microwave and are Fourier-transformed with respect to both t_1 and t_2, giving the 2D spectra. It was shown theoretically that the nutation frequencies of $\omega_\mathrm{a}+\omega_\mathrm{b}$ newly appear in the SCRP spectra, ω_a and ω_b being the Larmor frequencies of radicals a and b which make up the SCRP. The 2D spectra obtained at two different delay times are shown in Fig. 6. The existence of both the separated radical and the SCRP is shown at 0.5 µs,

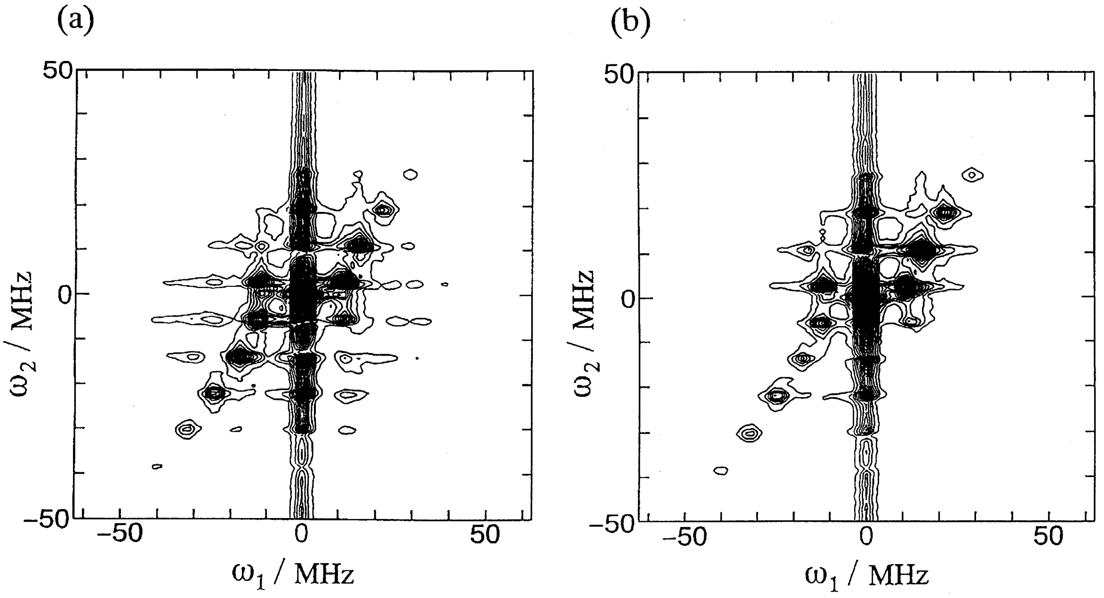

Fig. 6. Contour plots of 2D FT nutation spectra of the 2-hydroxypropan-2-yl-d_7 radical in 2-propanol-d_8 observed at a) 0.5 μs and b) 8 μs after the laser pulse at −88 °C.

whereas only the separated radical is shown to exist at 8 μs from the 1D spectra. The $\omega_a+\omega_b$ component (ω_1) was clearly separated from the ω_a and ω_b components in the spectrum at 0.5 μs and was definitely assigned as that of the SCRP.

Time Developments of the CIDEP Spectra[16,17,20)]

The time profile of the CIDEP signal of the 2-hydroxypropan-2-yl radical produced by the photolysis of acetone in 2-propanol obtained by the CW-method is shown in Fig. 7.[16)] The analysis is made by solving the following modified Bloch equation for the magnetization ($\boldsymbol{M}(t)$) and obtaining the time-dependence of its y component, $M_y(t)$.

$$\dot{\boldsymbol{M}}(t)=\boldsymbol{L}\boldsymbol{M}(t)+\boldsymbol{F}_{\mathrm{eq}}(t)+\frac{\dot{n}(t)}{n(t)}\boldsymbol{M}(t), \tag{9}$$

where $\boldsymbol{L}$ is a matrix,

$$\boldsymbol{L}=\begin{pmatrix} -1/T_2 & \Delta\omega & 0 \\ -\Delta\omega & -1/T_2 & \omega_1 \\ 0 & -\omega_1 & -1/T_1 \end{pmatrix}, \tag{10}$$

and

$$\boldsymbol{F}_{\mathrm{eq}}(t)=\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} n(t)\frac{P_{\mathrm{eq}}}{T_1}. \tag{11}$$

$n(t)$ is the radical concentration, and ω_1 the angular frequency of the microwave field, $\Delta\omega$ the linewidth, T_1 the spin-lattice relaxation time, and T_2 the spin–spin relaxation time. The second term in Eq. 9 represents the time dependence of the equilibrium magnetization. The last term represents the decay of the radical. The intensity of the EPR signal is proportional to $M_y(t)$, which is generally dependent on T_1, T_2, and ω_1. When $T_1 \gg T_2$ and in the limit of low microwave power, the signal is predicted to decay with $1/T_1$. The time dependence of the $M_I=-1$ peak shown in Fig. 7 was simulated with $T_1=2.7$ μs and $P_0/P_{\mathrm{eq}}=15$, where P_0 is the value of the initial polarization. The agreement is reasonably good, though a small deviation probably due to the F-pair is found at $t=10$—20 μs. The estimated value of T_1 is also in good agreement with the value determined by FT-EPR. However, in general the time development is complicated in the CW experiments because the spin system is constantly interacting with the microwave. The time resolution of the CW measurement is also not sufficient. Therefore, in studying the spin and reaction dynamics it is desirable to follow the time development

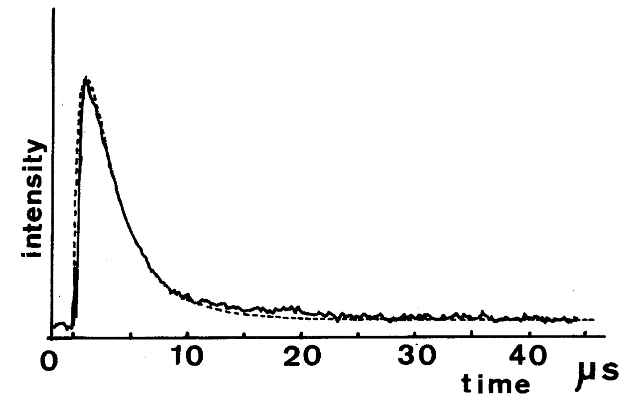

Fig. 7. Time profile of the $M_I=-1$ peak of the CIDEP signal of the 2-hydroxypropan-2-yl radical in 2-propanol at room temperature. The dashed curve is the one simulated from the solution of the modified Block equation.

of the magnetization more directly by FT-EPR.

The time development of the polarization of the 2-hydroxypropan-2-yl radical in 2-propanol was studied in detail by Levstein and van Willigen using FT-EPR.[20,21] In the case of the polarization due to ST_0M, the peaks with the nuclear spin states $M_I=\pm1$, ±2, ±3 appear as pairs of lines with equal intensities but opposite signs on the high field and low field sides of the center of the spectrum, respectively. Then, assuming that the contribution due to ST_-M is negligible, the difference of the peaks corresponding to $M_I=M$ and $-M$, $\Delta S_M=S(M)-S(-M)$, represents the magnitude of the ST_0M polarization, because ΔS_M for TM or an equilibrium polarization is equal to zero. The time dependence of ΔS_M of the 2-hydroxypropan-2-yl radical can be expressed well by the following equation:

$$\Delta S_M = \frac{A_M k_f}{k_{T1} - k_f}\left(e^{-k_f t} - e^{-k_{T1} t}\right). \tag{12}$$

The rate constants k_f and k_{T1} were determined to be $1.1\times10^7\ s^{-1}$ and $3.4\times10^5\ s^{-1}$ for 2-hydroxypropan-2-yl and $5.5\times10^6\ s^{-1}$ and $1.1\times10^5\ s^{-1}$ for 2-hydroxypropan-2-yl-d_7, respectively at room temperature. Here the rate constant for the rise, k_f, is mainly determined by the hydrogen abstraction rate and k_{T1} represents the decay rate constant of the CIDEP signal due to the spin-lattice relaxation ($T_1=2.9$ μs for 2-hydroxypropan-2-yl).

The sum of the peaks, $\sum S_M=S(M)+S(-M)$, gives the total absorptive signal. It was found that the growth of $\sum S_M$ is similar to that of $\Delta S_M(k_f=6\times10^6\ s^{-1}$ for 2-hydroxypropan-2-yl-d_7). The ΔS_M signal growth and decay could be accounted for by the transfer of Boltzmann spin polarization in the acetone triplets to the ketyl radicals. This generates a spin polarization in the radical that is 4/3 times larger than the polarization of the radical itself at thermal equilibrium. On the basis of this observation it was concluded that the TM contribution is not important.

The time profile of the CIDEP signal of the 2-hydrxypropan-2-yl radical produced in the photolysis of acetone in TEA shows an interesting phenomenon.[11] As shown in Fig. 8, the time profile obtained in the CW experiment shows the inversion of the polarization. For example, the peak corresponding to $M_I=-1$ state shows an emission initially, but it is inverted at $t=1.5$ μs. This inversion was interpreted qualitatively in terms of the polarizations due to the singlet geminate radical pair and triplet free pair (F-pair). However, the time developments of the signals in the first 0.5 μs could not be followed precisely in the CW-experiments, and FT-experiments had to be performed to confirm the proposed mechanism and to follow the dynamics.

Figure 9 gives the result of an FT-EPR study. Here the sum ($\sum S_M$) and the difference (ΔS_M) of the $M_I=+1$ and -1 lines are given. $\sum S_M$ gives the total absorptive component of the polarization. ΔS_M gives the emission–absorption antisymmetric polarization with respect to the center of the spectrum. Ohara et al.[17] made the following analysis of these quantities. First it is necessary to know the time dependences of the radical concentration and of the polarizations due to various mechanisms. They are given as follows.

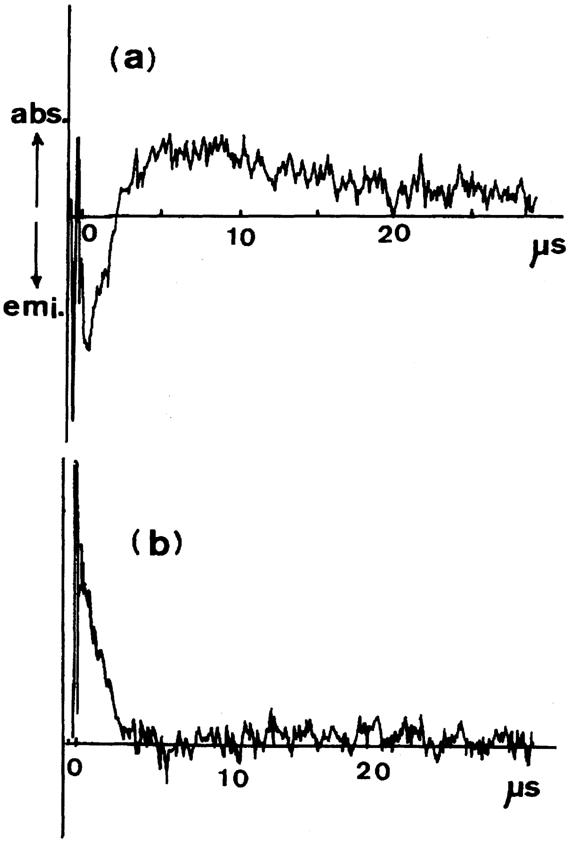

Fig. 8. Time evolutions of the CIDEP signals of the (a) −1 and (b) +1 peaks of the 2-hydroxypropan-2-yl radical in triethylamine at room temperature.

1) Radical Concentration

$$N_R = \frac{N_0}{(k_{2r}N_0 t + 1)}. \tag{13}$$

Here k_{2r} is the rate constant of the second-order radical decay. It is assumed that the rates of radical formation are fast compared to the instrumental response time so that the initial concentration is set equal to N_0.

2) Geminate Pair RPM

$$\begin{aligned} P_{RPM} = {} & P^0_{RPM}[\exp(-t/T_1^R) - \exp(-k_f t)] \\ & + P_{RPM}[1 - \exp(-t/T_1^R)]. \end{aligned} \tag{14}$$

Here, P^0_{RPM} and P_{RPM} are the initial polarization and the polarization at thermal equilibrium of the geminate-pair RPM, respectively. T_1^R is the spin-lattice relaxation time of the radical. k_f is the growth rate constant of the signal.

3) F-Pair RPM

$$\begin{aligned} P_{FRPM} = {} & a k_F (N_0)^2 \cdot T_1^R \\ & \times \left\{\frac{1}{(k_{2r}N_0 t + 1)^2} - \exp(-t/T_1^R)\right\}. \end{aligned} \tag{15}$$

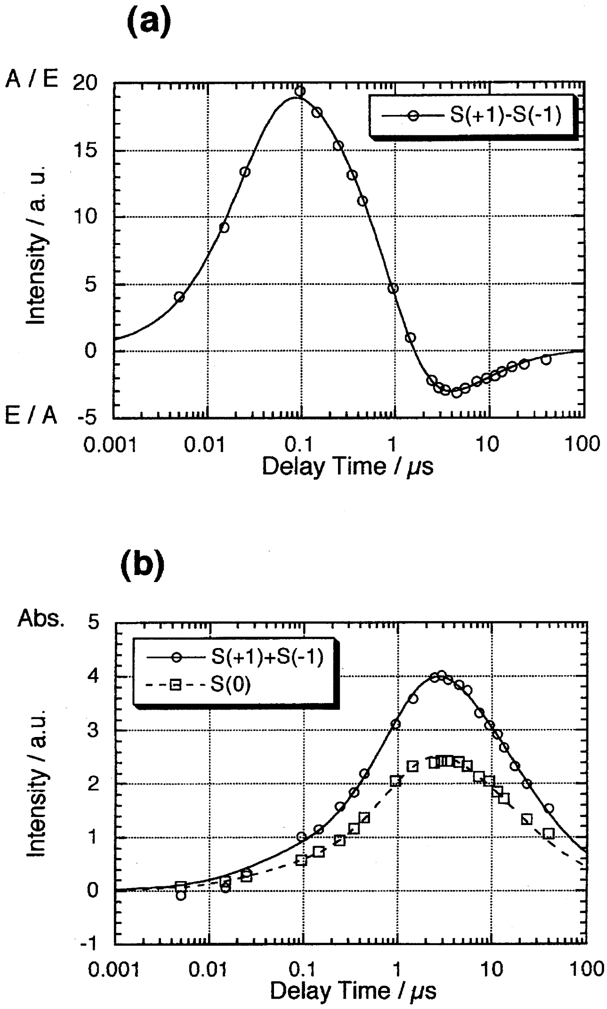

Fig. 9. (a) Time evolution of ΔS_M of the CIDEP spectrum of the 2-hydroxypropan-2-yl radical in triethylamine. The solid line represents the result of a least-squares fit of the data points to Eq. 17. (b) Time evolutions of $\sum S_M$ (○) and the center hyperfine line (□). The lines represent the results of the least-squares fits to the data points to Eq. 18.

Here, k_F is the second order rate constant of the F-pair RPM.

4) TM

$$P_{\mathrm{TM}}=P_{\mathrm{TM}}^0\{\exp(-t/T_1^{\mathrm{R}})-\exp[-({}^3k_{\mathrm{HA}}+1/T_1^{\mathrm{T}})t]\}$$
$$+P_{\mathrm{TM}}[1-\exp(-t/T_1^{\mathrm{R}})]. \qquad (16)$$

Here, P_{TM}^0 and P_{TM} are the initial polarization and the polarization at thermal equilibrium, respectively. T_1^{T} is the spin-lattice relaxation time of acetone triplet state. k_{HA} is the rate constant of the hydrogen abstraction reaction.

ΔS_M and $\sum S_M$ are given by the combinations of the above equations. ΔS_M reflects the contribution from two mechanisms: RPM due to singlet geminate pairs (A/E) and RPM due to triplet F-pairs. Then the time development of ΔS_M should be given by

$$\Delta S_M=\frac{A\{\exp(-t/T_1^R)-\exp(-k_{\mathrm{f}}t)\}}{(k_{2\mathrm{r}}N_0t+1)}$$
$$+B\left\{\frac{1}{(k_{2\mathrm{r}}N_0t+1)^2}-\exp(-t/T_1^{\mathrm{R}})\right\}. \qquad (17)$$

The obtained data were reproduced quite well by this equation, as shown in Fig. 9. The analysis gave $k_{\mathrm{f}}=4.0\times10^7\ \mathrm{s}^{-1}$ and $T_1^{\mathrm{R}}=0.89$ μs. This k_{f} is considered to be determined by the time resolution of the apparatus. T_1^{R} is much shorter than in 2-propanol. The decay of the initial polarization and the inversion of the polarization pattern are accounted for very well by the inclusion of the F-pair RPM.

$\sum S_M$ represents a net absorptive signal. Since its rise is slow, the contribution of the TM can be neglected. The rise and decay of $\sum S_M$ are well explained by the following equation which assumes that signal growth and decay are due to relaxation of the spin system to thermal equilibrium and second-order chemical decay.

$$\sum S_M=\frac{A\{1-\exp(-t/T_1^R)\}}{(k_{2\mathrm{r}}N_0t+1)}. \qquad (18)$$

In a benzene solution of acetone and TEA (1 M), the time developments of ΔS_M and $\sum S_M$ are also analyzed in a similar way. They are explained in terms of the triplet geminate pair RPM, F-pair RPM, and TM including the second order radical decay and relaxation. Here, as the result of the CW-experiment shows, the radicals are produced predominantly from the triplet states. The rises of ΔS_M and $\sum S_M$ are fast, indicating that they are determined by the time resolution of the experiment. The fast rise of $\sum S_M$ is likely to be determined by TM, but this contribution was found to be relatively small. In summary, it was concluded that the contribution due to F-pair RPM is appreciable and that decay analysis without including this contribution could lead to a considerable error.

Theoretical Analysis of the Polarization[16,22—24]

Although qualitative features of the CIDEP spectra are usually explained fairly well by the mechanisms discussed in the preceding section, quantitative analysis of the CIDEP spectra has been scarcely made. Since the CIDEP spectrum of acetone is simple and has a good S/N ratio, it is suited for a detailed analysis.

Attempts to calculate the absolute magnitude of CIDEP polarization theoretically have been made by Pedersen and Freed using the stochastic Liouville equation (SLE).[30] We followed their method to calculate the magnitude of the polarization of the acetone/2-propanol system. Here, we summarize the method. The starting point is to use the SLE to describe the spin dynamics of a pair composed of radicals a and b under a combined effect of the spin interaction and relative diffusion,

$$\frac{\partial\rho(r,t)}{\partial t}=-i[H(r),\rho(r,t)]+D\Gamma_r\rho(r,t), \qquad (19)$$

where $\rho(r,t)$ is the density matrix of the radical pair at time t and inter-radical separation r. The spin Hamiltonian is given by

$$H(r)=\beta(g_\mathrm{a}S_\mathrm{a}+g_\mathrm{b}S_\mathrm{b})B_0+\sum_n A_{\mathrm{a}n}I_{\mathrm{a}n}S_\mathrm{a} + \sum_m A_{\mathrm{b}m}I_{\mathrm{b}m}S_\mathrm{b}-J(r)[2S_\mathrm{a}S_\mathrm{b}+1/2]. \qquad (20)$$

$J(r)$ is the exchange interaction between the two radicals and is assumed to depend on r. We employ the usual form of $J(r)$

$$J(r)=J_0\exp\left[-\lambda(r-d)\right], \qquad (21)$$

where d is the distance of the closest approach. $D\Gamma_r$ is a diffusion operator with a mutual diffusion coefficient D. Γ_r is expressed as

$$\Gamma_\mathrm{r}=1/r^2\left(\frac{\partial}{\partial r}\right)r^2\left(\frac{\partial}{\partial r}\right). \qquad (22)$$

The time-dependent polarization of radical a, $P_\mathrm{a}(t)$, is given by

$$P_\mathrm{a}(t)=-2T_r\{\int_0^\infty r^2\rho(r,t)\mathrm{d}rS_\mathrm{az}\}. \qquad (23)$$

We only need the limiting value of $P_\mathrm{a}(\mathrm{t})$ as $t\rightarrow\infty$. The time development of the density matrix of any two-level system can represented by a Bloch type equation. The SLE is conveniently rearranged into a simple form of secular ρ_0, and vector $\boldsymbol{\rho}$ as,

$$\rho_0=r(\rho_\mathrm{SS}+\rho_{\mathrm{T_0T_0}}),$$
$$\boldsymbol{\rho}=r\begin{pmatrix}\rho_{\mathrm{ST_0}}+\rho_{\mathrm{T_0S}}\\ -i(\rho_{\mathrm{ST_0}}-\rho_{\mathrm{T_0S}})\\ \rho_\mathrm{SS}-\rho_{\mathrm{T_0T_0}}\end{pmatrix}=\begin{pmatrix}\rho_x\\ \rho_y\\ \rho_z\end{pmatrix}. \qquad (24)$$

These quantities obey the following relations.

$$\frac{\partial\rho_0}{\partial t}=D\cdot\frac{\partial^2}{\partial r^2}\rho_0,$$
$$\frac{\partial\boldsymbol{\rho}}{\partial t}=D\frac{\partial^2\boldsymbol{\rho}}{\partial r^2}+\Omega\times\boldsymbol{\rho}, \qquad (25)$$

where

$$\Omega=\begin{pmatrix}0 & -2J(r) & 0\\ -2J(r) & 0 & 2Q\\ 0 & 2Q & 0\end{pmatrix}. \qquad (26)$$

It is noted that the x component of $\boldsymbol{\rho}$, ρ_x, corresponds to the electron spin polarization. Employing a finite-difference technique in r, we can solve Eq. 25 to obtain ρ_x.

We calculated the polarization due to RPM, $P_{\mathrm{ST_0M}}(M_\mathrm{I})$, for the 2-hydroxypropan-2-yl radical.[16] We first used the Stokes–Einstein equation and the known value of viscosity to estimate the mutual diffusion constant D with a hydrodynamic of 3.5 Å. The calculation was made by changing J_0 from 10^9 s^{-1} to 10^{15} s^{-1} and r_ex from 4 to 16 Å. Several calculated results are shown in Fig. 10. The calculated values of $P_{\mathrm{ST_0M}}(-1)/P_\mathrm{eq}(-1)$ depend on the choices of the parameters, r_ex and J_0, but they are too small compared with the observed values, no matter how we change these parameters.

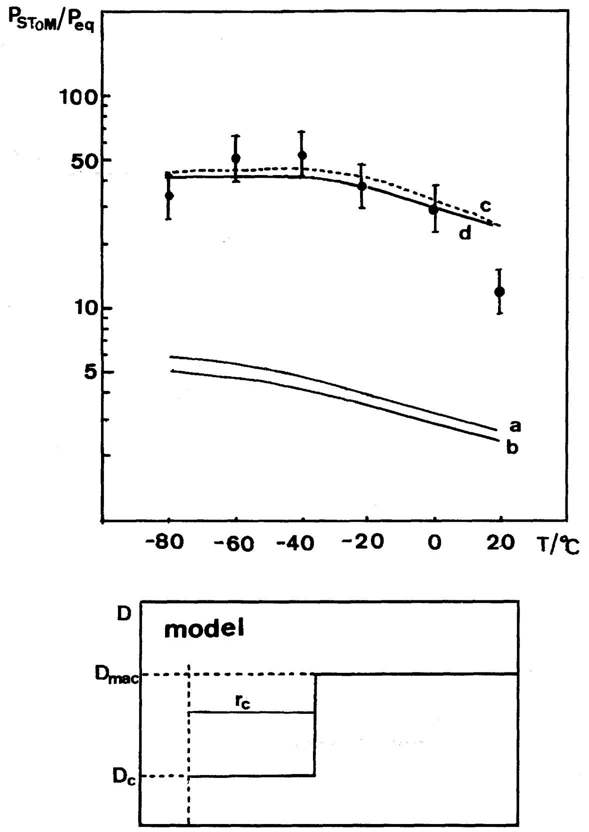

Fig. 10. Temperature dependence of the absolute magnitude of the polarization due to $\mathrm{ST_0M}$ for the 2-hydroxypropan-2-yl radical in 2-propanol. The simulation curves are obtained with the following diffusion models and the parameters; (a) $J_0=10^{13}$ s^{-1} and $r_\mathrm{ex}=8$ Å, (b) $J_0=10^{15}$ s^{-1} and $r_\mathrm{ex}=8$ Å and normal diffusion process, (c) $J_0=10^{13}$ s^{-1} and $r_\mathrm{ex}=8$ Å and the cage model shown in the figure with $D_\mathrm{c}=D_\mathrm{mac}/8$ and $r_\mathrm{c}=12.4$ Å, (d) $J_0=10^{13}$ s^{-1} and $r_\mathrm{ex}=8$ Å and another cage model with two potential wells.

We next considered modification of the diffusion model. Since the radical pairs exist as stable entities at low temperatures, we may assume that microscopic solvent structures like clusters develop to hold radical pairs and the diffusion of the radicals in the pair is a much slower process than expected from the macroscopic diffusion constant. We examined the models which presupposed the existence of the solvent structure. In the first model, the diffusion process of the radicals in the pair is suppressed within a sphere of a diameter of r_c, as depicted in Fig. 10. Here D_c is the diffusion constant of the radical in the sphere and D_mac is the macroscopic diffusion constant. In another model, two potential wells were assumed in the regions where $J(r)\gg Q$ and $J(r)\ll Q$. The potential wells represent an attractive interaction between the radicals in the pair. As shown in Fig. 10, these models can reproduce the observed large values of polarization. For example, reasonably good results were obtained for $P_{\mathrm{ST_0M}}(-1)/P_\mathrm{eq}(-1)$ when $D_\mathrm{mac}/5>D_\mathrm{c}>$

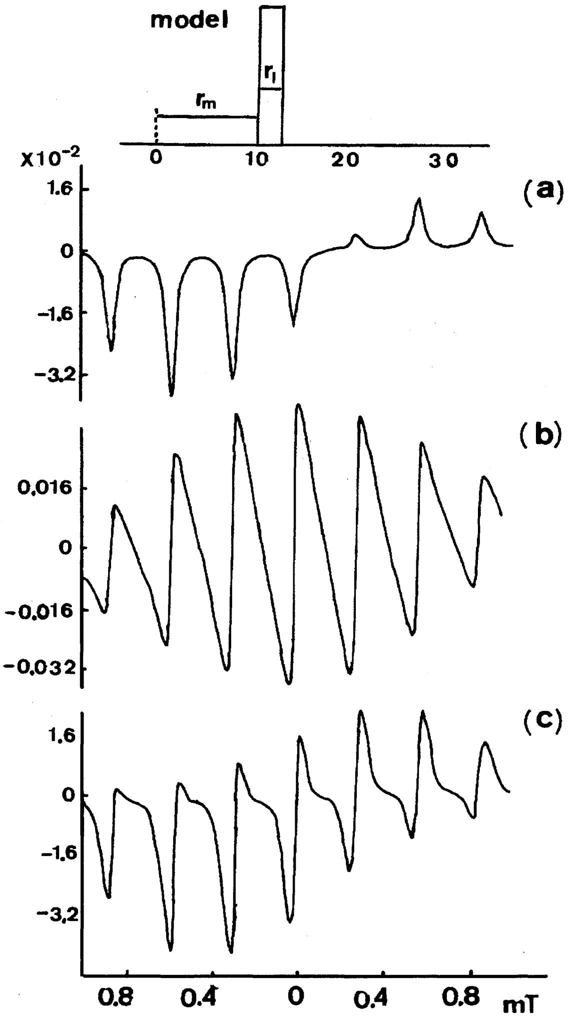

Fig. 11. The simulated spectra for (a) the separated radical and (b) the radical pair of 2-hydroxypropan-2-yl-d_7 obtained by using the normal diffusion process at −86 °C. (c) The simulated spectrum by the model shown in the figure with N=30%, r_m=11 Å, and r_l=1 Å.

$D_{mac}/15$ for the model depicted in Fig. 10. Similarly the calculated values reproduced the observed values of $P_{ST_0M}(-1)/P_{ST_0M}(-2)$ with these models. Although these models are crude, the success in reproducing the observed values of $P_{ST_0M}(-1)/P_{eq}(-1)$ seems to indicate the validity of the basic assumption of the models.

The spectra obtained at very low temperatures are reproduced by a superposition of the spectra due to SCRP and separated radicals. It was shown, however, that neither the normal diffusion nor the modified diffusion model described above could reproduce the observed pair spectra. These diffusion models predict only very weak intensities for the pair. The model assuming that the radicals comprising the pair are concentrated in a narrow region as in a micelle such as shown in Fig. 11 was able to reproduce the observed spectra reasonably well. In this model, N percent of all the radicals remain in pairs in a sphere shell of diameter of r_m and a thickness of r_l. The best simulated spectrum for the deuterated radical was obtained when N=30%, r_m=11 Å, and r_l=1 Å, as shown in Fig. 11. This model is of course very crude and a smooth distribution around r_m should be considered to be more realistic. As stated in an earlier section, a broad background signal appears in the spectrum in early times, which may be due to the radical pairs with smaller separations and larger $J(r)$. Furthermore, the observed spectra should be the results of the time average of the structurally fluctuating pairs. Nevertheless, it is considered that at low temperatures the radical pair stays in a relatively rigid solvent structure with a rather well-defined configuration for a few microseconds. In this regard comparison between the result in 2-propanol and that in triethylamine is suggestive. Though both solvents become highly viscous at low temperatures and the CIDEP spectrum of the separated 2-hydroxypropan-2-yl-d_7 radical is dominated by emissive signals due to ST$_-$M, no spectrum of SCRP was observed in triethylamine, indicating that the radical pairs are short-lived even at very low temperatures. Thus it seems likely that formation of the microscopic solvent structure in alcohols is essential in stabilizing the radical pair.

Although chemists now have easy access to fast computers for numerical calculations of SLE, it is always good to have analytical solutions in order to get insight into the essential points of the problem. In a series of papers, Shushin developed an effective and accurate method for an analytical solution of SLE and gave a simple expression for CIDEP intensities.[22)] Here we discuss his results in connection with ours. First, he analyzed the antiphase spectrum of SCRP of the 2-hydrxypropan-2-yl radical in 2-propanol. He concluded that there must be a strong inter-radical attractive interaction leading to the formation of a long-lived cage to account for the observed spectrum.[23)] He predicted that the shape of the CIDEP spectrum (relative intensities of hyperfine lines) depends strongly on the diffusion model employed such as a) short-lived cage, b) free rapid diffusion, c) slow free diffusion, and d) a long-lived cage. His result indicates that the intensities of the hyperfine components of the CIDEP spectra of the 2-hydroxypropan-2-yl and 2-hydroxypropan-2-yl-d_7 radicals are considerably different depending on the type of the diffusive motion; a careful analysis would provide information on the details of the radical motion and the interaction in radicals. Unfortunately, no detailed comparison has been made between his prediction and the observation, though our previous data on $P_{ST_0M}(-1)/P_{ST_0M}(-2)$ at very low temperatures seems to be compatible with the long-lived cage model.[44)]

Shushin also calculated the intensities of the CIDEP spectra of SCRP using a free diffusion model of the radical.[24)] The result showed that the predicted intensity at −45 °C is two orders of magnitude smaller than the observed one, suggesting that the free diffusion model description is not applicable. This is in agreement with the conclusion reached in our work.

Some Applications[18,19]

CIDEP studies of acetone and the 2-hydroxypropan-2-yl radical may have a number of applications in solving some interesting chemical problems. Here we briefly discuss two cases. The first one is the mechanism of the hydrogen abstraction reaction[18] and the second one is the quenching reaction of the 2-hydroxypropan-2-yl radical.[19]

The mechanism of the hydrogen abstraction reaction is an important subject. A particularly intriguing question is whether or not the tunneling mechanism plays an important role in the reaction. There are many well-known examples in the solid phase reactions where the hydrogen abstraction reactions proceed via tunneling.[45,46] However, the mechanism in this solution reaction is not clear-cut. Scaiano[47] and Topp[48] discussed the hydrogen abstraction rate on the basis of the classical thermal activation process, whereas Formoshinho[49] suggested a tunneling mechanism for this reaction. His calculation predicted the ratio of the abstraction rate constants ($k_\mathrm{H}/k_\mathrm{D}$) for the protonated and deuterated molecules to be about 4. We have applied the CIDEP to determine $k_\mathrm{H}/k_\mathrm{D}$ at various temperatures.[18] We found that the value of $k_\mathrm{H}/k_\mathrm{D}$ is 3.5—4 over a wide temperature range. This observation is not consistent with the prediction of the classical activation process, since it predicts a much larger temperature effect. In the CW experiment, however, we were unable to determine the rate constants directly. With FT-EPR having superior time resolution it would be possible to determine the hydrogen abstraction rate accurately over a wide range of temperature. The ratio determined from the rise times of the transient EPR signals in the FT measurements was about 2 at room temperature,[20] which is somewhat smaller than that estimated from the CW-TREPR. Clearly further detailed investigation is needed to determine the reaction mechanism precisely.

The 2-hydroxypropan-2-yl radical is a common product of the hydrogen abstraction reactions involving carbonyls, quinones and azaaromatics.[50] However, the decay rate constant of the 2-hydroxypropan-2-yl radical in 2-propanol estimated from the time profiles of the transient signals are quite different depending on the reacting molecule and its concentration. This is due to the secondary quenching reaction of the 2-hydoxypropan-2-yl radical by these molecules. By analyzing the decay of the signal the quenching rate constant for pyrazine was determined to be $6\times10^6\ \mathrm{M^{-1}\,s^{-1}}$ ($\mathrm{M=mol\,dm^{-3}}$). The values are much larger for *p*-benzoquinone and quinoxaline, being on the order of $10^8\ \mathrm{M^{-1}\,s^{-1}}$.

Remaining Problems and Future Outlook

The examples discussed in the preceding sections amply show the power of the CIDEP in providing detailed information about the initial processes of photochemical reactions in solution and that the CIDEP of acetone has played an important role. Nevertheless, there still remain a number of unsolved problems. We here list some of these problems. They are by no means exhaustive and perhaps biased by our own personal views. With recent developments in experimental techniques, particularly in pulsed EPR, fast computers to solve SLE, and progress in theoretical approaches in treating solution phenomena, it would now be fruitful to pursue these problems further.

1) Careful comparison between the experimental values and theoretically predicted ones on the relative intensities of the hyperfine lines in various solvents and at different temperatures would be useful to find appropriate diffusion models of the radicals under different conditions. Further investigations on the ST_M including accurate estimates of the ratio of $P_{\mathrm{ST_0M}}/P_{\mathrm{ST_{-}M}}$ over a wide range of temperature are needed to understand the motions and interactions in interacting radicals.

2) CIDEP measurements at different microwave frequencies would be interesting in connection with the magnetic field effects on reactions. Detailed analyses of the CIDEP spectra at low microwave frequencies are needed to obtain additional information concerning the motions and interactions in radicals and radical pairs.

3) Complete agreement has not been reached yet as to the exact mechanism which produces the net absorptive component of the spectrum of 2-hydroxypropan-2-yl in 2-propanol. Careful investigations on the factors which may affect the magnitude and time profile of the absorptive component, such as the concentrations of 2-propanol and triethylamine in mixed solvents and the intensity of the excitation light. High frequency experiments at W-band (95 GHz) with better time resolution may also be useful in clarifying the origin of the absorptive component.

4) More detailed FT-EPR studies on the time profiles of the CIDEP signals of both radicals and radical pairs over a wide range of temperature would be useful in order to understand the details of various dynamic processes, for example, the formation and dissociation dynamics of the radical pair and the mechanism of the hydrogen abstraction reaction.

5) Development of a consistent theory including a continuous polarization transfer from SCRP to RPM polarization of separated radicals is needed. An attempt by Norris and co-workers[51] using a vector model of the polarization appears attractive in this regard.

6) Observation of coherent phenomena such as quantum beats in the EPR signals of the SCRP would provide information about the exchange interaction in the radical pair and its static and dynamic properties.

In conclusion, we feel that a combination of accurate experimental studies and detailed theoretical analyses will provide very valuable and unique information concerning the motions and interactions in radical pairs in solution that cannot be obtained by other means.

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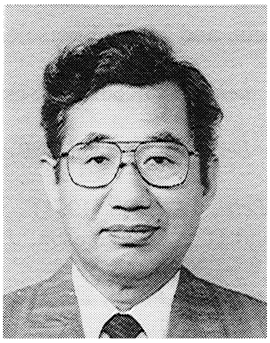

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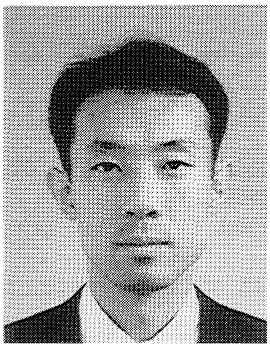

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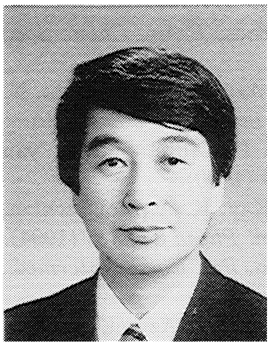

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