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Time-Resolved ESR Studies on Photosensitized Reaction of Maleic Anhydride in Alcohols: CIDEP Memory Transfer in Spin-Adduct Formation

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A triplet photosensitization reaction of maleic anhydride with alcohols and the subsequent secondary reaction were studied by a time-resolved ESR method. The hydrogen abstraction reaction of the C=C bond site of maleic anhydride in the excited triplet state was examined and discussed as the primary step. The adduct radical formed in the secondary reaction between maleic anhydride and alcohol radicals showed a characteristic E/A-shaped hyperfine line(s). This phenomenon can be explained by the CIDEP "memory transfer" of the multiplet (E/A) spin polarization of the alcohol radicals to the adduct radical. The spin-lattice relaxation times of the excited triplet state of xanthone as the sensitizer in 2-propanol and cyclohexanol were also estimated.

Maleic anhydride (MA), one of the simplest carbonyl compounds, was intensively studied by Schenck et al. three decades ago.(1,2) A cyclodimerization reaction and addition to aromatic compounds by photosensitized MA were found. A photosensitized addition of the solvent to MA was also observed, in which the formation of solvent radicals was postulated.(3) One decade ago, Chen et al. showed ESR evidence for the formation of an anion radical as well as two kinds of neutral carbon-centered radicals in 2-propanol and tetrahydrofuran via its excited triplet state.(4) One of the neutral radicals is produced by hydrogen-atom abstraction from the solvent molecule at the C=C bond site. Another is the adduct of the solvent radical to MA in the ground state; that is, MA works as a good spin-trapping reagent in solutions.

In the present paper, the reduction of the triplet photosensitized maleic anhydride was investigated by using a time-resolved ESR (trESR) method in alcoholic media. The spin-polarization transfers (1) from the excited triplet state of the sensitizer to maleic anhydride, and (2) from the primary radical to the secondary radical were intensively studied. The first aim of this paper is to examine how photosensitization (triplet–triplet energy transfer) works in this particular system in alcoholic media, and to determine the spin-lattice relaxation time of the excited triplet state of the sensitizer. The second is to clarify whether the hydrogen abstraction reaction from the alcohol molecule is directly by the C=C bond, or a step-wise process, such as hydrogen abstraction by the carbonyl group followed by intramolecular hydrogen migration. The third aim, which is the main part of the present report, is to detect and discuss the transfer of CIDEP (Chemically Induced Dynamic Electron Polarization) through a secondary reaction, namely, a spin-trapping process by MA in the ground state.

Spin-polarization transfer in photolysis and radiolysis may become very important subjects to be investigated, since it provides new information concerning the chemical behavior and nuclear spin state of the reaction intermediates. The primary radicals produced by the photoreaction get CIDEP by the triplet mechanism (TM) and/or the radical pair mechanism (RPM).(5–7) When photosensitization (triplet–triplet energy transfer) takes place, the TM polarization carries information concerning the excited triplet state of the precursor. When successive reactions of these spin-polarized radicals are much faster than the spin-lattice relaxation, secondary radicals should be spin-polarized by the reaction. In most cases, the CIDEP spectrum of the secondary radicals shows an overall electron spin polarization transferred from the primary radicals (net emission or enhanced absorption due to the TM or S–T_{-1} mixing and so on). This is because the multiplet effect of the spin polarization induced by S–T_0 mixing does not mean the existence of overall electron spin polarization; this RPM polarization is diminished or obscured (depending upon the reaction system) in the secondary radicals. In addition, an extra CIDEP, such as RPM by F-pair and/or the radical-triplet pair mechanism,(8) may also smear the delicate change in spin polarization during subsequent reactions. Though the polarization-transfer phenomenon in the reaction dynamics is important, studies in this field have been scarce. Recently, McLauchlan and Simpson, as well as Akiyama, Depew, and Wan independently and successfully demonstrated the transfer of the electron spin polarization of RPM to secondary radicals in the reaction of phosphorus radical and simple olefins.(9,10) When the nuclear spin state causes a large hyperfine splitting in the primary radicals, which also causes hyperfine splitting in the secondary radicals, the RPM spin polarization of the precursor radicals can be memorized in the hyperfine lines of the secondary radicals. If this condition is fulfilled, we can obtain information concerning the sign of the hfc as well as the reactivity of the primary radicals, even if it cannot be detected directly. The reported polarization transfer is limited to secondary reactions of the phosphorus radicals which have large hfc constants. The photosensitized reaction system of MA, which produces typical spin-adduct radicals,(11) is useful for studying such spin-polarization transfer processes, since the TM and RPM contributions to the spin polarization are controllable by varying several reaction conditions.[12]

Experimental

Commercially available xanthone (9-xanthenone, Xn) was used as the photosensitizer after repeated recrystallization from acetone. MA (G.R. grade) and special-grade 2-propanol and cyclohexanol provided by Wako Pure Chemical Industries, Co. Ltd., were used as received. Partially deuterated ethanol (C_2H_5OD 99 atom%d) was supplied by Aldrich Chemical Company Inc. The concentration of Xn was 0.010 mol dm^{-3}. The concentration of MA was controlled as described in a later section. The solutions were deoxygenated by bubbling with pure nitrogen gas prior to flowing the solutions.

A nitrogen gas laser (λ=337.1 nm) was used for the photoexcitation. The time-resolved ESR spectra were measured by a modified X-band ESR spectrometer (time resolution of ca. 60 ns) without field modulation. The typical spectra shown in the present paper were recorded by a boxcar integrator with a gate opening time of from 0.5 to 0.7 μs after the laser pulse. A combined system of a transient wave memory (Iwatsu Co. Ltd., DM901) and a micro-computer (NEC PC9801VX) was also used to obtain more detailed information concerning the time evolution of the spectra. The experiments were carried out at temperatures between 0 and 30 °C. The detailed experimental procedures were similar to those reported before.[13,14]

Results and Discussion

This section comprises five subsections: (I) CIDEP results in 2-propanol, (II) CIDEP results in cyclohexanol, (III) photosensitization as a triplet–triplet energy transfer, (IV) mechanism of the hydrogen abstraction reaction by photoexcited maleic anhydride and (V) explanation of the anomalous E/A hf line shape.

(I) In 2-propanol. Figure 1 shows a typical spectrum obtained by a time-resolved ESR measurement of the photosensitized reaction of MA at high concentration (0.12 mol dm^{-3}) in 2-propanol at room temperature. This emissive spectrum indicates the presence of several radical species. These are assigned to the radical formed by the addition of a hydrogen atom to the double bond of MA (radical I, a_α=2.07 and a_β=3.50 mT) and the radical formed by the addition of much larger radical species, such as the solvent one to the double bond of MA (radical II, a_α=2.03 and a_β=3.33 mT).[4] Although a weak peak observed at the center of the entire spectra may be assigned to the trace of the anion radical of MA (radical III),[1] the assignment is not sure in the present experiment. The structures of these radicals, as well as their ESR stick diagrams, are also shown in the figure. No other radical species could be detected.

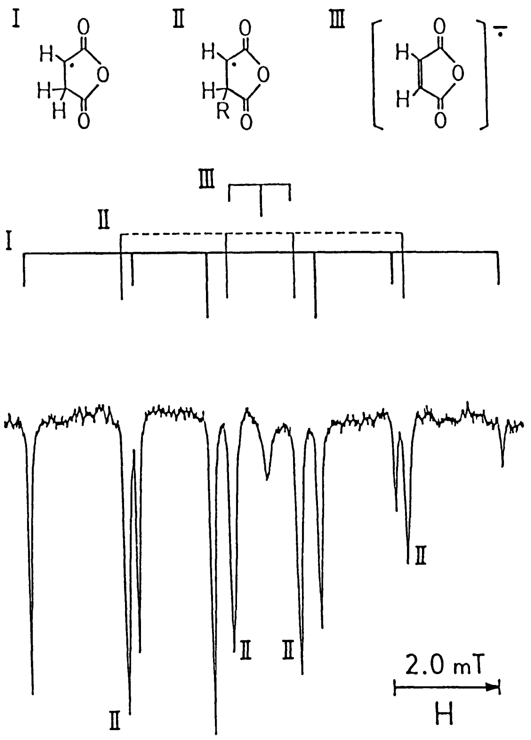


Fig. 1. Time-resolved ESR spectrum and assignment of the radical species observed in the photosensitization reaction of maleic anhydride in 2-propanol (0.12 mol dm^{-3}) at room temperature.

As shown in Fig. 1, the emissive intensity of the lower field hf lines is stronger than that of the higher ones in both radicals I and II. These unbalanced emissive spectral patterns can be explained by the superposition of emissive TM and the geminate pair RPM. The former polarization is transferred from the excited triplet state of Xn;[15,16] the latter mechanism provides the emissive character in lower field and the absorptive one in higher field (E/A pattern). Since no apparent signal was detected in the absence of Xn, MA cannot be directly excited by laser light. In the absence of MA, no total emissive (TM) signal was detected,[17] suggesting that the direct reaction of xanthone with alcohol is much slower than an energy transfer to MA. These results lead to the conclusion that the excited triplet state of MA rapidly abstracts a hydrogen atom from the solvent alcohol at the C=C double bond to form radical I and an alcohol radical. Radical II is considered to be formed rapidly by an addition reaction of the alcohol radical to MA; the initial spin polarization of the precursor radical is still preserved. The overall main reaction schemes are summarized below:

$$\mathrm{Xn} + h\nu \longrightarrow {}^1\mathrm{Xn}^* \longrightarrow {}^3\mathrm{Xn}^* \tag{1}$$

$$ {}^3\mathrm{Xn}^* + \mathrm{MA} \longrightarrow \mathrm{Xn} + {}^3\mathrm{MA}^* \tag{2}$$

$$ {}^3\mathrm{MA}^* + \mathrm{RH} \longrightarrow {}^3[\cdot\mathrm{MAH} + \cdot\mathrm{R}] \tag{3}$$

$$ {}^3[\cdot\mathrm{MAH} + \cdot\mathrm{R}] \Longleftrightarrow {}^1[\cdot\mathrm{MAH} + \cdot\mathrm{R}] \qquad \text{S–T}_0 \text{ mixing} \tag{4}$$

$$ {}^{1,3}[\cdot\mathrm{MAH} + \cdot\mathrm{R}] \longrightarrow \cdot\mathrm{MAH} + \cdot\mathrm{R} \tag{5}$$

$$ \cdot\mathrm{R} + \mathrm{MA} \longrightarrow \cdot\mathrm{MAR} \tag{6}$$

Here, RH, ·R, ·MAH, and ·MAR are the alcohol, alcohol radical, radical I, and radical II, respectively. The asterisks denote the respective excited states.

The E/A-type distortion on the spectrum of radical

II, which is not significant compared with that of radical I, may be induced by *a geminate-like interaction* with radical I, since the addition reaction of the alcohol radical to MA is thought to be extremely fast.

$$ {}^{1,3}[\cdot\mathrm{MAH}+\cdot\mathrm{R}]+\mathrm{MA}\longrightarrow {}^{1,3}[\cdot\mathrm{MAH}+\cdot\mathrm{MAR}] \qquad (7) $$

The rate can be roughly estimated to be near to the diffusion-controlled value by an analysis of the data concerning the alcohol radical and radical II in cyclohexanol systems (described later).

The CIDEP spectra observed by diluting the concentration of MA (0.019 mol dm^{-3}, 16% of that used in Fig. 1) and observed by lowering the temperature of the diluted solution are shown in Figs. 2a and 2b, respectively. By diluting MA, the spectral pattern was altered drastically. The lower lines are emissive and the higher ones absorptive. The difference in the spectral pattern between Figs. 1 and 2a can be explained by the difference in the relative amount of the contributions of TM and RPM. Since the dilution of MA directly makes the energy-transfer rate slow, the spin-lattice relaxation in the excited triplet state works to quench TM polarization. By lowering the temperature, a much better signal intensity and a slightly different pattern are obtained. The contribution of TM and RPM is slightly altered in radical I and radical II, as is shown in Fig. 2b.

Through low-concentration experiments a very anomalous phenomenon was observed at the highest field hf line of radical II. Under these conditions, both contributions by emissive TM and the absortive portion of RPM can be expected to offset the signal intensity at the high-resonant fields indicated by asterisks in Figs. 2a and 2b. The hf line has an E/A-like shape and is no longer either simple emission or absorption. There are several possible cases which cause this kind of phenomenon, showing an E/A-shaped hf line, as follows: 1) superposition of the neighboring hf line of radical I, 2) deformation by the microwave power effect on the time evolution of the spin polarized spectrum,[18,19] 3) direct observation of the radical pair surviving in this observation time region,[20,21] and 4) transfer of the polarized nuclear spin of the precursor radicals which is induced by the geminate pair RPM.[9,10] Cases 1) and 2) are easily excluded by a careful examination of all of the hf lines and the experimental conditions. Since possibilities 3) and 4) are most plausible, in order to make the problem simple and clear, viscosity-controlled experiments were carried out (as described below).

(II) In Cyclohexanol. Figure 3 shows the time-resolved ESR spectra observed for the photosensitized reaction of MA in cyclohexanol as a viscous solvent at room temperature. The concentrations of MA were 0.079 and 0.029 mol dm^{-3} in Figs. 3a and b, respectively. The observed radical species and the spectral feature were almost the same as the results for a 2-propanol

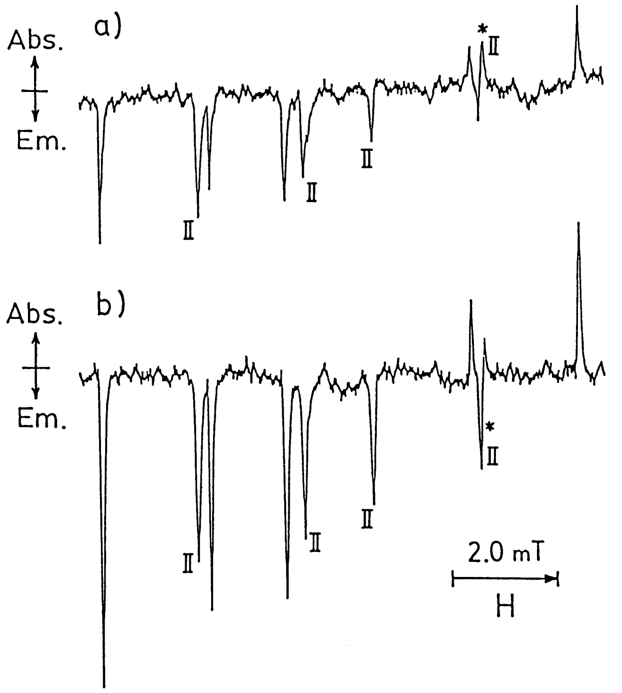


Fig. 2. Time-resolved ESR spectra observed in the photosensitization reaction of maleic anhydride in 2-propanol (0.019 mol dm^{-3}) at (a) 28 °C and (b) 6 °C.

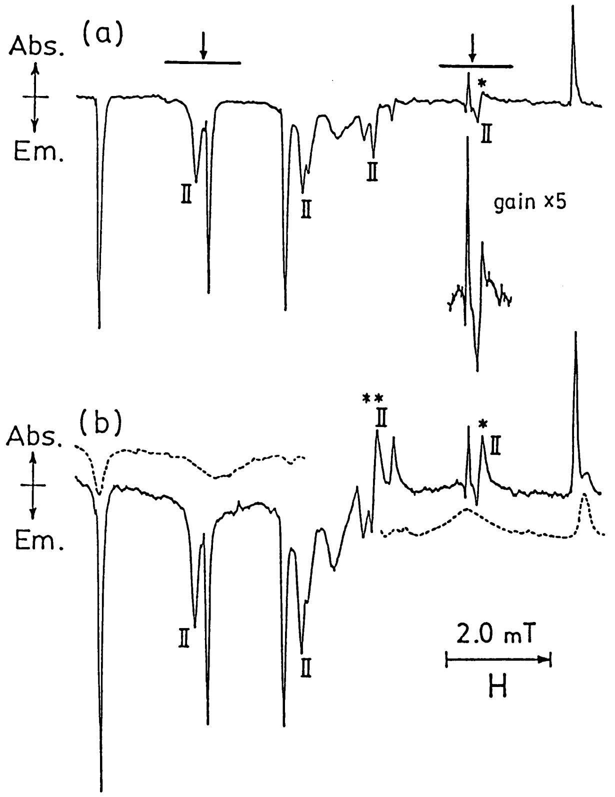


Fig. 3. Time-resolved ESR spectra observed in the photosensitization reaction of maleic anhydride in cyclohexanol ((a) 0.079 mol dm^{-3} and (b) 0.029 mol dm^{-3}) at room temperature. The spectrum of the alcohol radical observed without maleic anhydride is given by the broken curve.

solution, except that the cyclohexanol radical was observed at low concentrations of MA (indicated by broken spectrum in Fig. 3b). Although the contribution of the RPM E/A pattern was more significant than that in 2-propanol systems, there still existed the emissive component in this viscous medium.

The peculiar point in this system is that the TM contribution is less likely when the concentration of MA and the viscosity of cyclohexanol is concerned (discussed later). The anomalous hf line shape appeared again on the highest hf line of radical II (asterisks in Fig. 3). The cyclohexanol radical shown in Fig. 3b disappeared within 1 μs. The viscosity of cyclohexanol is known to be very high (η=68 cp at 22 °C, 1 cp=10^{-3} Pa s);[22] the diffusion-controlled rate constant estimated from this value is 1.5×10^8 mol^{-1} dm^3 s^{-1}.[22,23] The disappearance rate of the alcohol radical is consistent with that estimated by assuming a diffusion-controlled reaction with MA. This result and the absence of the spectrum of the alcohol radical at high concentrations of MA (Fig. 3a), and also in 2-propanol (Figs. 1 and 2), suggest that the alcohol radical having the E/A pattern reacts with the ground-state MA to produce radical II at a rate close to the diffusion-controlled one. An explanation of the E/A-shaped hf line will appear in subsection V.

(III) T-T Energy Transfer. Since a triplet–triplet energy transfer is known to be almost diffusion controlled, the mean lifetime of the excited triplet state of Xn is approximated by the reciprocal of the product of the diffusion-controlled rate constant and the concentration of MA, which works as an energy and polarization accepter, $(k_{\mathrm{diff}}[\mathrm{MA}])^{-1}$. The ratio of the intensities of the emissive component and the E/A pattern of radical I (I_{TM} for the emissive component and I_{RPM} for the E/A one, see Fig. 4) may be expressed approximately[24] according to the following empirical equation:

$$\frac{I_{\mathrm{TM}}}{I_{\mathrm{RPM}}}=\left(\frac{I_{\mathrm{TM}}}{I_{\mathrm{RPM}}}\right)_0 \exp\left\{-\frac{1}{T_1\, k_{\mathrm{diff}}[\mathrm{MA}]}\right\}. \qquad (8)$$

In this equation, following three assumptions are made: 1) the intensity of the E/A pattern induced by S–T_0 mixing of RPM is independent of the emissive TM component, and is only proportional to the geminately formed radical concentration; 2) the spin-lattice relaxation of the spin polarization in the excited state of Xn competes with the triplet–triplet energy-transfer reaction; and 3) the emissive spin polarization of the geminately-formed radicals is transferred from the excited triplet state of Xn and is conserved during the chemical events. Plots of $-\ln(I_{\mathrm{TM}}/I_{\mathrm{RPM}})$ versus $(k_{\mathrm{diff}}[\mathrm{MA}])^{-1}$ for radical I obtained in a solution of 2-propanol are shown in Fig. 4; the straight line indicates that the transfer of spin polarization is controlled by diffusion, as is expected. The slope of the straight line provides a value for reciprocal T_1 ($T_1=5.6\times10^{-9}$ s). This T_1 value of Xn is typical for the spin-lattice relaxation time of the excited triplet state in usual solutions,[6] like 2-propanol.

In order to examine the contribution of TM in a solution of cyclohexanol, plots of $-\ln(I_{\mathrm{TM}}/I_{\mathrm{RPM}})$ versus $(k_{\mathrm{diff}}[\mathrm{MA}])^{-1}$ for radical I were also made; they, however, did not show a linear relation, as is demonstrated in Fig. 5. The ratio became almost constant below a concentration of 6×10^{-2} mol dm^{-3}. It is concluded that the spin-lattice relaxation of the excited triplet state

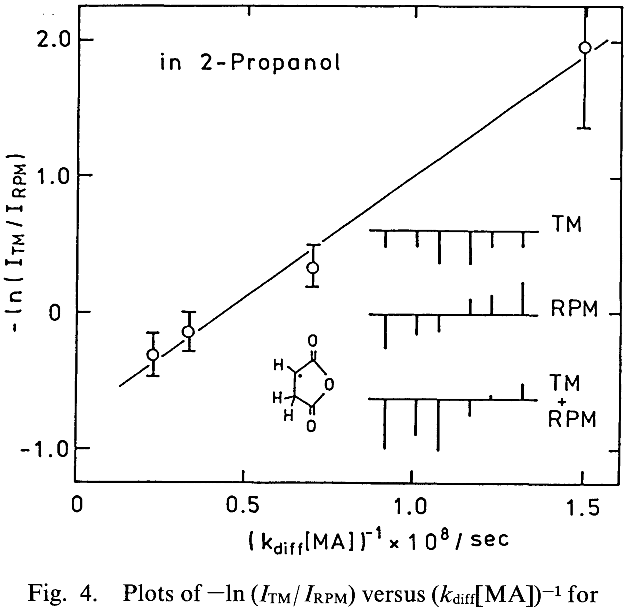


Fig. 4. Plots of $-\ln(I_{\mathrm{TM}}/I_{\mathrm{RPM}})$ versus $(k_{\mathrm{diff}}[\mathrm{MA}])^{-1}$ for radical I obtained in a 2-propanol solution, where a k_{diff} of 4.5×10^9 mol^{-1} dm^3 s^{-1} is employed.[22] The inset shows conceptual diagrams of both the TM and RPM components and the composed (corresponds to the observed) one.

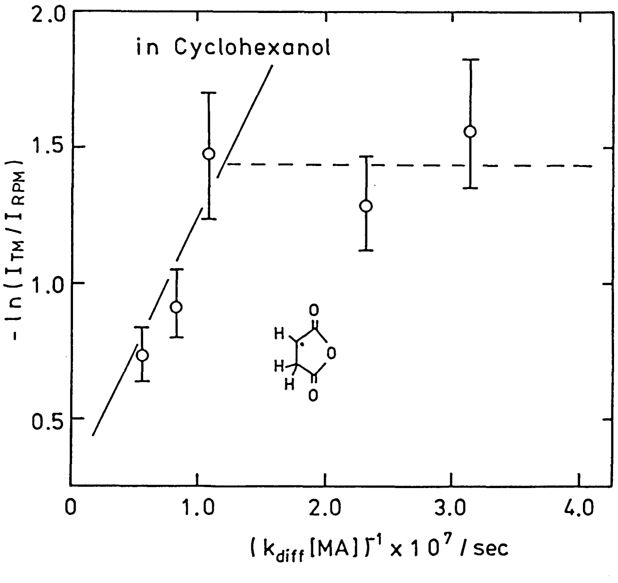
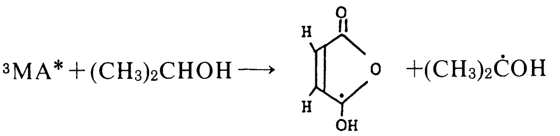


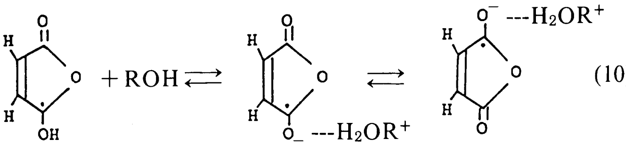
Fig. 5. Plots of $-\ln(I_{\mathrm{TM}}/I_{\mathrm{RPM}})$ versus $(k_{\mathrm{diff}}[\mathrm{MA}])^{-1}$ for radical I obtained in a cyclohexanol solution, where a k_{diff} of 1.5×10^8 mol^{-1} dm^3 s^{-1} is employed.[22] The slope of the solid straight line is drawn by assuming that T_1 of the triplet state of Xn is 1.0×10^{-7} s.

of Xn in cyclohexanol is much slower than that in 2-propanol (the slowest limit of T_1 is ca. 10^{-7} s), and that there exists another polarization mechanism which provides an emissive component that is especially remarkable at lower concentrations of MA in cyclohexanol. The first conclusion is consistently explained by the contribution of the diffusional motion of the excited state to the spin-lattice relaxation time, since the condition of a slow-motion limit[25] is fulfilled under a high viscosity of cyclohexanol. The other polarization mechanism observed here may be rationalized by introducing the contribution of S–T_{-1} mixing, which requires large hf constants and a long correlation time for the interacting radical pair.[26] These conditions may be satisfied in the present system where radical I has protons of relatively large hf constants, and cyclohexanol makes the viscosity very high.

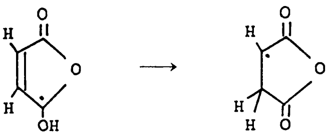
(IV) Hydrogen Abstraction Mechanism. Chen et al. suggested an indirect hydrogen addition to the C=C double bond in 2-propanol.[4] This means by way of the ketyl-type intermediate which is in equilibrium with MA anion radical, as follows:



(9)

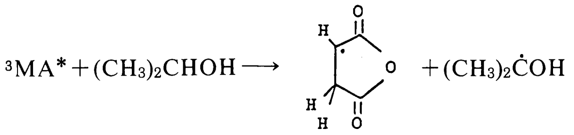


(10)



(11)

Under the conditions of the present experiment, equation (10) is not important, since only a trace amount of the anion radical, which is tentatively assigned here, is detected. If hydrogen migration takes place after obtaining RPM S–T_0 mixing between the ketyl-type radical and the alcohol radical, very anomalous spin polarization, such as E/A alternation of each hf line, must appear in the spectrum of radical I, since migration can change the sign of the hfc of one of the protons on the ketyl-type precursor. Since no such clear evidence of this phenomenon was obtained in the spectrum of radical I, we can say that the hydrogen abstraction reaction takes place directly by a C=C double bond, or via a ketyl-type radical formation followed by fast hydrogen migration. In the latter case, the migration must be much faster than ca. 10^{-8} s, which is the estimated value for S–T_0 mixing.[7] Recent trESR studies of aromatic carbonyl compounds which have a triplet ππ* as their reactive excited states showed the formation of cyclohexadienyl type radicals instead of ketyl radicals.[27] In the case of the photoreaction of MA, the unsaturated C=C portion may become active and abstract the hydrogen atom from a solvent molecule.



(12)

Concerning the study on the primary reaction mechanism of hydrogen abstraction from alcohols, partially deutrated ethanol was used as the solvent. Although the observed spectra were assigned to radicals I and II, no spectrum of the deuterium-adducted radical was detected: that is, no D atom of the OD group was transferred to MA. This implies that hydrogen abstraction takes place directly from the methylene group of ethanol and that it is not step-wise, such as a charge transfer followed by a proton transfer, which has been reported in a system of Xn in partially deuterated ethanol.[28] This experiment also showed that the equilibrium rate (Eq. 10) is very slow, even when ketyl radical formation is the primary step of this hydrogen-abstraction reaction.

(V) Anomalous E/A Shaped hf Line. In order to study the anomalous E/A-shaped hf line, the detailed time evolution of the hf line and the corresponding lowest hf line (marked by arrows in Fig. 3a) were examined in a solution of cyclohexanol. The result is shown in Fig. 6. In this figure, each sharp hf line in both the low- and high-field portions is due to radical I; these lines show a serious microwave power dependence,

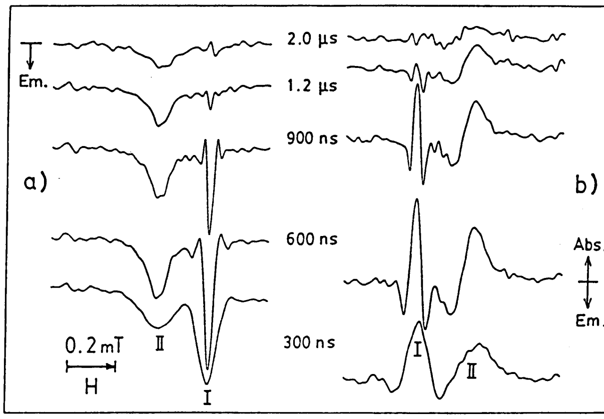
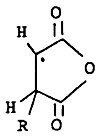


Fig. 6. Time evolution of the lower (a) and higher (b) portions of the spectrum shown by arrows in Fig. 3a. The higher broad hf line of radical II shows the E/A shape.

as is shown in the figure.[18] The hf lines due to radical II are broad, and this signal does not show any serious microwave-power dependence under the experimental conditions. The high-field portion of this figure clearly indicates that the E/A shape remains for a long time (>2.0 μs) until the intensity almost disappears. This long lifetime of the E/A-shaped hf line implies that this is not caused by a transient radical pair, since the radical pair cannot survive a very long time, even in a highly viscous solvent of cyclohexanol. The most plausible explanation for this phenomenon is a conservation of the nuclear spin polarization of the precursor radicals. In Fig. 3b, one more hf line near the spectral center also shows an E/A-shaped hf line (marked by double asterisks). The other hf lines of radical II should show a line-shape distortion due to a superposition of this E/A shape. In fact, the low-field hf line of radical II in Fig. 6 is not symmetric. However, this type of distortion is obscured by the intense single-phase (emissive or absorptive) signal in most cases.

·R + MA ⟶



(13)

The geminate pair RPM (from the triplet precursor) of radical I and the alcohol radical may induce an E/A-type polarization (Eqs. 4 and 5). Both 2-propanol and cyclohexanol radicals have several β-protons with a positive hfc value. Since the sign of the hfc of protons for these groups which added to MA must be positive, the matched hfc signs of these added groups provide an E/A-shaped hf line in radical II. A schematic diagram of this phenomenon employing a simple-model reaction is given in Fig. 7. This phenomenon is only observable in the following cases: 1) the precursor radicals have large hfc values; 2) the hf splittings of the particular added groups appear in the secondary radicals (even in the case of inhomogeneous line broadening due to the small hfc, like in the present case); 3) the secondary reaction is sufficiently fast to conserve the initial polarization; and 4) the contribution of the net effect on each hf line is sufficiently small, or is cancelled at the resonant field (e.g. offsetting of total emission by TM and enhanced absorption of higher field portion by RPM). This kind of phenomenon must be generally observable, when experiments are designed carefully, and may provide important information concerning the very early time region of the reaction, where the time resolution of the time-resolved ESR cannot be obtained.

In conclusion, the photosensitized reaction of maleic anhydride with alcohols was studied by time-resolved ESR. By an analysis of the spectra, the spin-lattice relaxation time of the excited triplet state of xanthone (photosensitizer) in 2-propanol was estimated to be 5.6×10^{-9} s. In cyclohexanol under a low concentration of MA, the contribution of S–T_{-1} mixing is postulated, rather than the TM. We propose that this reaction takes place at the C=C bond site of the excited triplet state of MA.

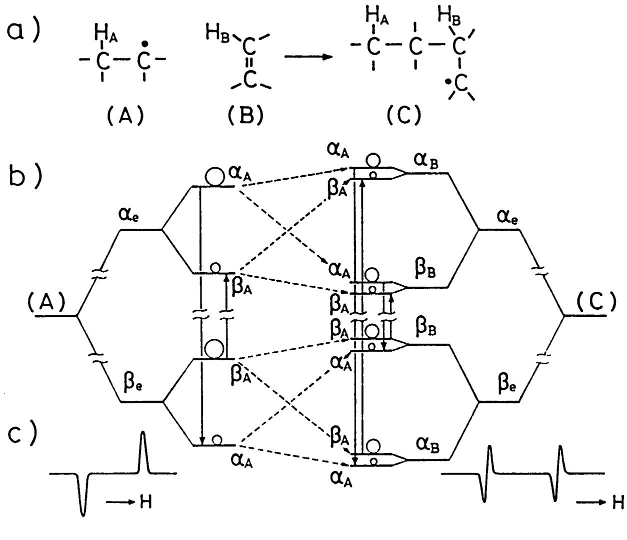


Fig. 7. Schematic diagrams of a CIDEP memory transfer. a) Reaction scheme of a simple model system having minimum protons. b) The transfer of nuclear spins from radical A to C (shown by arrows with broken lines) by the reaction where α_e and β_e denote the electron spins, and α_N and β_N denote the nuclear spins of H_N (N=A and B). c) Expected CIDEP spectra of A and C.

An anomalous CIDEP spectrum observed on the hf line of the secondary radical can be explained as follows: The E/A-shaped hf line is due to a transfer of the spin polarization from the primary radical to the secondary radical. This proves that the sign of the hfc of both alcohol radicals and the added group of the secondary radical are the same. It was also shown that the spin adduct formation of MA with the alcohol radical is quite fast (near diffusion controlled), and that the secondary radical experiences a geminate-like S–T_0 mixing with the primarily produced hydrogen adduct radical.

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