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A CIDEP Study on the Photosensitized Reaction of Maleimide with Xanthone: Addition Effect of Hydrochloric Acid

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The photosensitized reaction of maleimide (MI) with xanthone (Xn) in 2-propanol was investigated by the time-resolved EPR method. The emissive CIDEP spectrum observed in neat 2-propanol is predominantly assigned to two kinds of MI alkyl-type radicals. On the other hand, the absorptive spectrum of the MI anion radical has been newly observed in 2-propanol including hydrochloric acid. The addition effect of hydrochloric acid indicates the existence of two mechanisms for the photosensitization of MI by Xn. One is a typical triplet–triplet energy transfer followed by hydrogen abstraction by the triplet state of MI from the solvent. The other is an electron-transfer process to MI from the Xn ketyl radical produced primarily by a fast reaction of the triplet Xn with HCl. The spin-polarization transfer mechanism based on these photosensitization processes can successfully explain the present CIDEP results. The effect of water and the sensitizer dependence on the above reaction were also investigated.

Maleimide (MI) and maleic anhydride (MA) are simple olefins, and very useful molecules in organic syntheses for introducing various substituents.[1—3] Addition reactions, cyclodimerizations, and Diels–Alder reactions are well-known as their photochemical reactions. They are also known as electron acceptors in photoinduced electron-transfer reactions. Photosensitization is one of the useful and popular methods for photoinduced processes, and are generally applied to organic syntheses and photophysical approaches.[4—6]

The photosensitization mechanism is very important for controlling the reactions because the photosensitization is often used in complicated systems involving many reactants and substances. Therefore, investigating the mechanism of the photosensitized reaction for MI and MA under various conditions is of great interest.

Chemically induced dynamic electron polarization (CIDEP) phenomena often provide important information not only on the observable radicals, but also on their precursor species.[7—22] Various phenomena have been successfully explained by the CIDEP producing mechanisms, such as the radical-pair mechanism (RPM), the triplet mechanism (TM), and the radical-triplet pair mechanism (RTPM).[7—18] Spin-polarization transfer is sometimes useful for investigating photochemical reactions, including secondary processes.[19—22] A detailed investigation of spin-polarization transfer is considered to be possible to analyze various complicated reactions, such as photosensitized ones. A CIDEP study on the photosensitized reaction of MA by xanthone (Xn) in alcohols has already been repoted.[22] The CIDEP results clearly indicate triplet–triplet (T–T) energy transfer from the excited triplet state of Xn (^{3}Xn*) to the ground state MA followed by hydrogen abstraction of the triplet state of MA from solvent alcohol. Moreover, the subsequent secondary process, which is spin-adduct formation by the addition of the solvent radical to MA, has been successfully explained by the spin-polarization transfer mechanism.

In the present work, a CIDEP investigation on the photosensitized reaction of MI by Xn was carried out by time-resolved EPR. The effect of the addition of hydrochloric acid and the time evolution of the CIDEP spectrum observed in this photosensitized reaction give clear evidence of a novel sensitization process. The effect of water and the sensitizer dependence on the reaction were also investigated.

Experimental

Time-resolved EPR measurements were carried out with a modified JEOL FE-2X X-band EPR spectrometer without field modulation at room temperature.[23] The CIDEP spectra at several delay times of between 0.7 to 5 μs were recorded by accumulating dc EPR signals with a boxcar-integrator (Stanford Research System SR-250), whose gate width was kept at 0.2 μs. A Nd-YAG laser (Continuum Surelight-I, THG 355 nm, 10 Hz) was used for photoexcitation. Since the laser light cannot excite MI and MA, only a photosensitizer was excited in all of the experiments. The microwave power was kept at 1 mW.

Maleimide (Nacalai tesque), maleic anhydride (Wako Pure Chemical), and chromone-2-carboxylic acid (CRCA) (Aldrich Chemical) were commercially available reagents and were used as received. Xanthone and benzophenone (BP) were purified by recrystallization from ethanol repeatedly. An ultra-fine grade of hydrochloric acid (35 wt% water solution; Nacalai), special-grades of 2-propanolic hydrochloric acids (0.1 and 0.5 mol dm^{-3} of HCl;

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Katayama Chemical), and a special-grade of 2-propanpol (Wako) were used as received. The concentrations of sensitizers (Xn, BP, CRCA) and maleimide were kept at 1.0×10^{-2} M (M = mol dm^{-3}) and 0.10 M, respectively. The sample solutions were deoxygenated by bubbling with nitrogen gas before and during the experiments, and flowed through a quartz flat cell (optical path: 0.3 mm) in an ESR cavity.

Results and Discussion

(1) The Photosensitized Reaction of MI in 2-Propanol. Figure 1 shows the time evolution of the CIDEP spectrum observed for the photosensitized reaction of MI by Xn in 2-propanol. The spectrum is predominantly assigned to two kinds of MI alkyl type radicals (radical I, g = 2.0035, $A_{\mathrm{H}\alpha}$ = 2.05 mT, $A_{\mathrm{H}\beta}$ (2 equivalent protons) = 3.06 mT, A_{N} = 0.04 mT, and A_{NH} = 0.15 mT; radical II, g = 2.0035, $A_{\mathrm{H}\alpha}$ = 2.03 mT, $A_{\mathrm{H}\beta}$ = 3.01 mT, A_{N} = 0.04 mT, and A_{NH} = 0.15 mT). Each EPR line of radical II is broadened compared with that of radical I, probably due to the unresolved hyperfine splitting by the substituent protons. Around the center of the spectrum, there are small signals due to another radical, which is considered to be the MI anion-type radical (radical III) (Chart 1). The spectrum shows strong total emission and the intensities of the lower field lines are stronger than those of the higher ones. This spectral pattern is explained by the superposition of a net emission probably due to the TM and weak contribution of an *E*/*A* (the low field side is emissive and the high field side is absorptive) polarization due to the RPM. The present result is quite similar to that for MA reported previously,[22] indicating that the reaction mechanism and the CIDEP producing process of the present MI system are also similar to those for MA. Therefore, the radical-generation process in the present photosensitized reaction may be represented by the following scheme (Scheme 1):

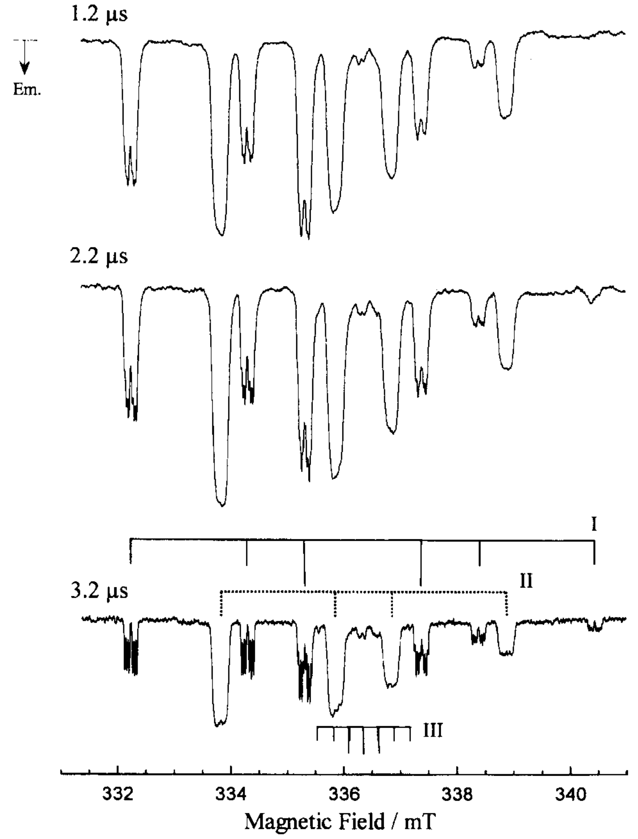


Fig. 1. The time evolution of the CIDEP spectrum on the photosensitized reaction of MI by Xn in 2-propanol. Stick diagrams show the EPR lines of the radicals I, II, and III.

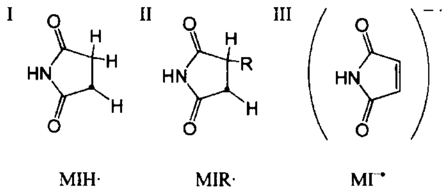


Chart 1.

The photoexcitation of Xn followed by the inhomogeneous intersystem crossing (ISC) produces ^{3}Xn*, which has emissive spin polarization in its triplet sublevels.[24,25] The subsequent T–T energy transfer from ^{3}Xn* to the ground state MI generates the triplet state of maleimide (^{3}MI*) effectively. When this energy transfer occurs fast enough compared with the relaxation of the spin polarization in ^{3}Xn*, the emissive spin polarization is also transferred to ^{3}MI*. This situation is realized under the present experimental condition because the process is expected to be nearly diffusion controlled and the MI concentration is set high enough. The spin-polarized ^{3}MI* abstracts a hydrogen from the solvent alcohol (RH) quite rapidly, probably at nearly the diffusion-controlled rate. Then, the radical I (MIH·) and the solvent radical (R·) are produced with emissive polarization, since the spin polarization of the precursor triplet is conserved in the produced radicals, as known in the TM. The subsequent rapid addition of R· to the ground state MI produces radical II (MIR·). In this secondary process, the spin polarization of the primary radical (R·) is transferred to the secondary radical (MIR·). Consequently, the emissive polarization of the observed radicals originates from the TM polarization of ^{3}Xn*. The *E*/*A* polarization in MIR·, which is not significant compared with that of MIH· may be generated by a geminate-like interaction with MIH·, as described in the previous report.[22] The formation of radical III (MI$^{-\bullet}$) is considered to be a minor process. The time evolution of the CIDEP spectrum can be explained in terms of the growth and the relaxation of the spin polarization in these radicals. The present result shows that the main reaction of ^{3}MI* is hydrogen abstraction caused by the electrophilic property of the carbon double bond in MI. The lowest triplet state of MI

$$\mathrm{Xn} \xrightarrow{h\nu} {}^1\mathrm{Xn}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{Xn}^*$$

$${}^3\mathrm{Xn}^* + \mathrm{MI} \longrightarrow \mathrm{Xn} + {}^3\mathrm{MI}^*$$

$${}^3\mathrm{MI}^* + \mathrm{RH} \longrightarrow \mathrm{MIH}\cdot + \mathrm{R}\cdot$$

$$\mathrm{R}\cdot + \mathrm{MI} \xrightarrow{addition} \mathrm{MIR}\cdot$$

Scheme 1.

has a $^3\pi\pi^*$ character, and it reacts as an excited olefin at the unsaturated carbon double bond.

Similar results were obtained when BP or CRCA was used as a sensitizer in place of Xn. The T–T energy transfer successfully occurs, since the triplet energies of these sensitizers are larger than that of MI, and the TM polarization is emission for Xn, BP, and CRCA. Furthermore, the concentration of MI is high enough to quench the triplet sensitizer sufficiently before the other reactions take place. Then, the sensitizer scarcely participates in the radical production as reactants. Consequently, only the emissive ^{3}MI* participates in the radical generation process, and the CIDEP results are independent of the sensitizer.

(2) The Effect of Addition of Hydrochloric Acid. Figure 2 shows the time evolution of the CIDEP spectrum on the photosensitized reaction of MI in 2-propanol including hydrochloric acid. The concentration of HCl is 0.60 M. In comparison with Fig. 1, the clear HCl effect on the CIDEP is observed. On the other hand, the addition of water instead of hydrochloric acid gives spectra similar to Fig. 1. In Fig. 2, the spectra at earlier delay times ($\leq$1.2 μs) show a particular *E*/*A*/*E* (low field emission/center absorption/high field emission) pattern. It can be explained by the superposition of some species which have different spin polarization; namely, some have emissive characters and the others have absorptive characters. In the spectra at early delay times ($\leq$1.2 μs), the *emissive* lines in the low- and high-field sides are assigned to radicals I and II, and the *absorptive* ones around the center are due to the Xn ketyl radical (XnH•) (see Scheme 3). XnH• is not observed in Fig. 1 because fast quenching by the T–T energy transfer is quite dominant. Absorptive XnH• formation with the addition of HCl has already been reported.[26,27] The reaction of ^{3}Xn* with HCl produces XnH•, since the reaction rate is large enough to overcome the triplet quenching by MI. As discussed in previous reports,[26,27] the production of absorptive spin polarization cannot be explained by ordinary TM, and further investigations will be necessary.

The time evolution around the center of the spectrum is drastic and of great interest. At a delay time of 2.2 μs, some sharp lines overlapped with XnH• newly appear. Moreover, at a delay time of 3.2 μs, seven sharp absorptive lines are mainly observed around the center, whereas XnH• has disappeared. The new lines can be assigned to the MI anion-type radical ($\mathrm{MI}^{-\bullet}$, $g = 2.0036$, $A_\mathrm{H}(2) = 0.533$ mT, $A_\mathrm{N} = 0.266$ mT, $A_\mathrm{NH} = 0.028$ mT). The hyperfine coupling constant of the imide (NH) proton of $\mathrm{MI}^{-\bullet}$ reduces compared with the value for radical III ($A_\mathrm{NH} \approx 0.098$ mT) obtained from Fig. 1, probably because the exchange of the NH proton occurs under the acidic and water-rich condition. The time evolutions of radicals I and II can be explained by the growth and the relaxation of the spin polarization. The lines of radicals I and II show emission with weak *E*/*A* distortion in the early time region. It is explained by the superposition of a net emission due to the TM and an *E*/*A* polarization due to the RPM. The *E*/*A* contribution of these lines increases with time because the *F*-pair RPM newly generates *E*/*A* polarization continuously,[28] while the initial polarization (emission with weak *E*/*A* distortion) decays due to relaxation. On the other hand, the formation and the absorptive polarization of $\mathrm{MI}^{-\bullet}$ cannot be explained by the ordinary photosensitized reaction based on the T–T energy transfer described in the preceding section. The net polarization due to the TM should be emissive, as described above. The slow development of the $\mathrm{MI}^{-\bullet}$ suggests secondary formation from the other precursor radical. The absorptive spin polarization of $\mathrm{MI}^{-\bullet}$ can also be explained in terms of the spin-polarization transfer with the secondary reaction. In the spin-polarization transfer, the net polarization of the precursor radical is conserved in the secondary radical, whereas the *E*/*A* polarization is scarcely conserved. In the present case, the precursor radical of $\mathrm{MI}^{-\bullet}$ should have net absorptive polarization. Further, in this system, there is no other possible process which can produce a net absorptive polarization except for the reaction of ^{3}Xn* with HCl.[22,24—27] Therefore, the precursor of $\mathrm{MI}^{-\bullet}$ has to be XnH•. In the presence of HCl, the absorptive XnH• is produced primarily and predominantly by the quite fast reaction of ^{3}Xn*. Secondarily, the fast electron-transfer reaction from XnH• to MI is expected to produce the absorptive $\mathrm{MI}^{-\bullet}$ by the spin-polarization transfer. Therefore, the feature of the time evolution of the CIDEP spectrum can be explained by following scheme (Scheme 2):

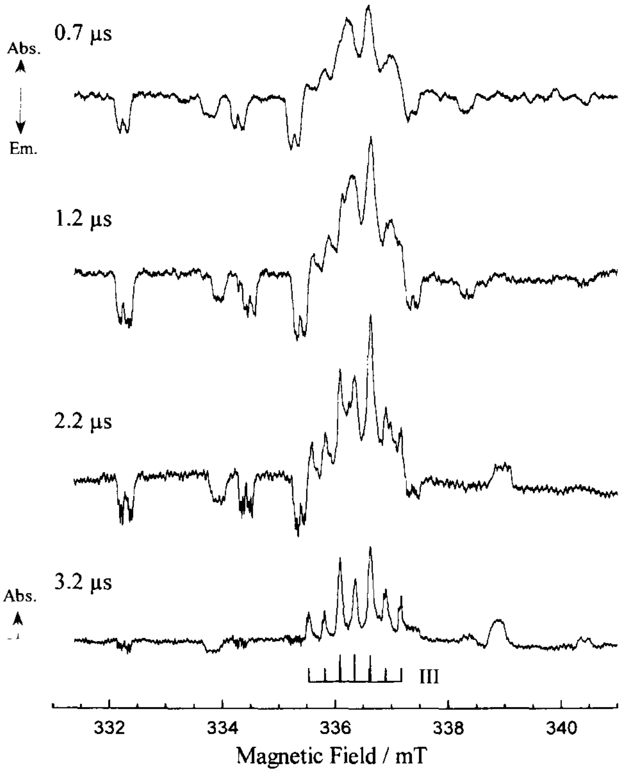


Fig. 2. The time evolution of the CIDEP spectrum on the photosensitized reaction of MI by Xn in 2-propanol including hydrochloric acid (0.60 M HCl). Stick diagram shows the EPR lines of $\mathrm{MI}^{-\bullet}$.

As described above, $\mathrm{MI}^{-\bullet}$ develops with diminishing XnH•. The reaction rate of the MI anion radical formation can be roughly estimated to be 10^6—10^7 $\mathrm{M^{-1}\,s^{-1}}$ from the

$$\mathrm{Xn} \xrightarrow{h\nu} {}^{1}\mathrm{Xn}^{*} \xrightarrow{\mathrm{ISC}} {}^{3}\mathrm{Xn}^{*},$$

$${}^{3}\mathrm{Xn}^{*} + \mathrm{RH} \xrightarrow{\mathrm{HCl}} \mathrm{XnH}\cdot(\mathrm{net}\,A) + \mathrm{R}\cdot(\mathrm{net}\,A),$$

$$\left(\mathrm{R}\cdot(\mathrm{net}\,A) + \mathrm{MI} \xrightarrow{\textit{addition}} \mathrm{MIR}\cdot(\mathrm{net}\,A)\right),$$

$$\mathrm{XnH}\cdot + \mathrm{MI} \xrightarrow{e^{-}\ \textit{transfer}} \mathrm{Xn} + \mathrm{MI}^{-\bullet}\ (\mathrm{net}\,A) + \mathrm{H}^{+}.$$

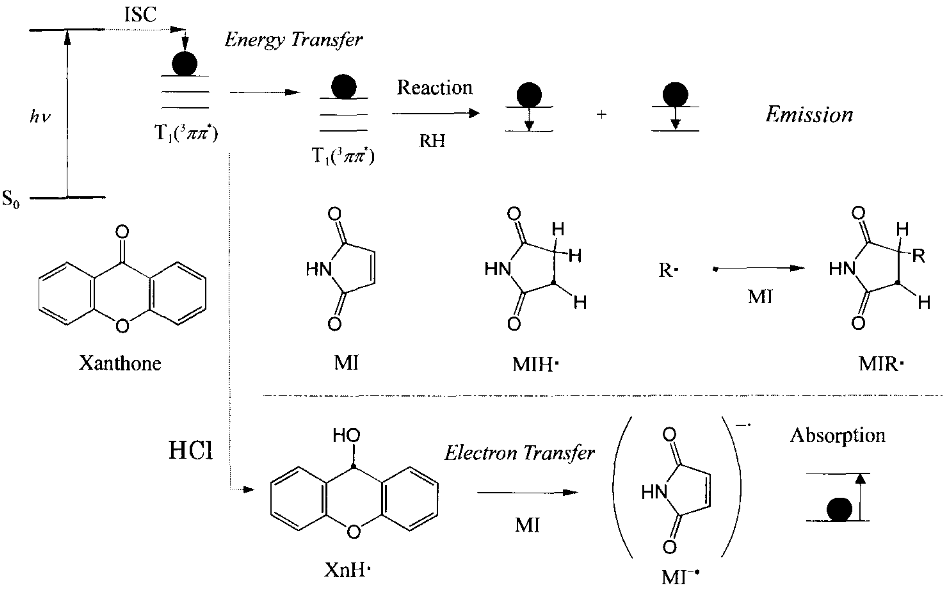
Scheme 2.

time evolution of the spectrum. It is rather slow compared with other processes observed in the present system. On the other hand, radicals I and II in Fig. 2 show emission similar to that in Fig. 1, suggesting that the photosensitized reaction and CIDEP process which started from the T–T energy transfer from ${}^{3}\mathrm{Xn}^{*}$ to MI are independent of HCl, and that the T–T energy transfer occurs competitively with the fast reaction of ${}^{3}\mathrm{Xn}$ with HCl. The quenching rate constant of ${}^{3}\mathrm{Xn}^{*}$ with HCl is reported to be $2.7\times10^{9}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[27] Therefore, in the present condition (HCl 0.60 M), the reaction rate of ${}^{3}\mathrm{Xn}^{*}$ is estimated to be $1.6\times10^{9}\ \mathrm{s}^{-1}$, which is around 4-times as large as the estimated T–T energy-transfer rate for MI (0.10 M) in 2-propanol. The relative intensity of the radical II to the radical I in Fig. 2 is weaker compared with that in Fig. 1. In the system including hydrochloric acid, radical II is produced from both the emissive R· generated by the photosensitized reaction of MI, and the absorptive R· generated by the reaction of ${}^{3}\mathrm{Xn}^{*}$. Hence, the cancellation of the net A and E polarization results in the relatively weak intensity of radical II.

Scheme 3 shows the CIDEP mechanisms on the present photosensitized reactions. In the presence of HCl, it is reasonable to consider that two photosensitization processes progress independently and competitively. One is T–T energy transfer followed by the hydrogen abstraction of ${}^{3}\mathrm{MI}^{*}$. The other is secondary electron transfer to MI from XnH· produced by the rapid reaction of ${}^{3}\mathrm{Xn}^{*}$ and HCl. The spin polarization produced in the former process is emissive, whereas that in the latter absorptive. The present result suggests the existence of two independent precursor states for Xn, which give the emissive and absorptive polarizations. This situation is quite similar to that for CRCA.[29] The HCl-induced anomalous CIDEP phenomena on Xn might be explained by the simultaneous processes from the emissive and the absorptive precursor states.

(3) The Effect of Water. Figure 3 shows the time evolution of the CIDEP spectrum on the photosensitized reaction of MI in 0.50 M 2-propanolic hydrochloric acid (water free). In the early time regions (≤ 1.2 μs), the spectra are very similar to those in Fig. 2, and are also assigned to the *absorptive* XnH· and the *emissive* MI alkyl type radicals (MIH· and MIR·). However, the time evolution of the spectra can be explained only by the relaxation of each radical, differing from that in Fig. 2. In the spectrum at a delay time of 3.2 μs, $\mathrm{MI}^{-\bullet}$ cannot be observed, whereas it is clearly observed in Fig. 2. The difference in the experimental conditions between Figs. 2 and 3 is the water content in the sample solutions. The result suggests that water is necessary for the formation of the $\mathrm{MI}^{-\bullet}$. The reason for the necessity of water on $\mathrm{MI}^{-\bullet}$ formation can be explained as follows: $\mathrm{MI}^{-\bullet}$ is highly stabilized under a water-containing condition, probably because of hydration and the fast proton exchange of NH. XnH· is also hydrated, but not so much stabilized. Consequently, the redox reaction between XnH· and MI is more favorable.

(4) Sensitizer Dependence. Since the triplet energies of Xn, BP, and CRCA are larger than that of MI, T–T energy transfer successfully occurs by using them as photosensitizers. The CIDEP spectra obtained in the photosensitization of MI without hydrochloric acid are independent of the sensitizer, and are almost the same as that in Fig. 1. On the other hand, if hydrochloric acid is included in solutions, the



Scheme 3.

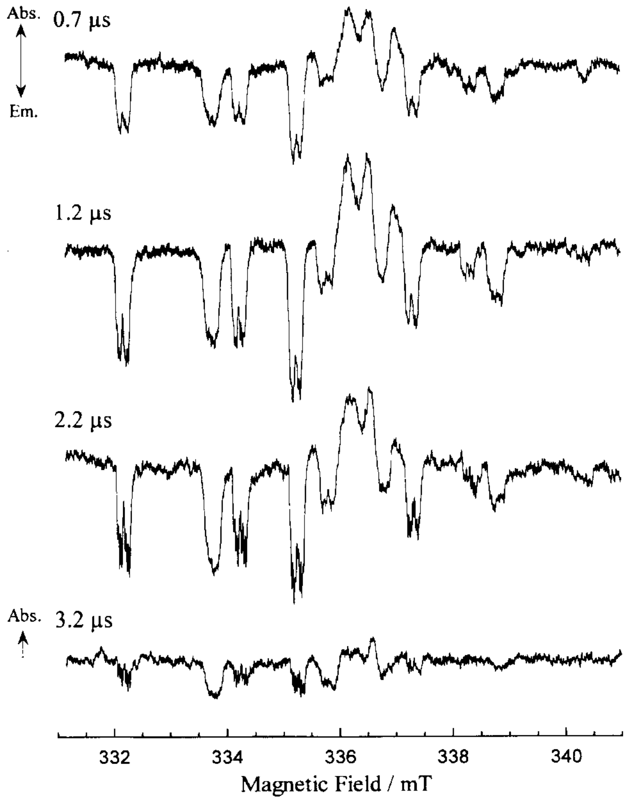


Fig. 3. The time evolution of the CIDEP spectrum on the photosensitized reaction of MI by Xn in 0.50 M 2-propanolic hydrochloric acid (water free).

CIDEP spectra are expected to be strongly dependent on the sensitizer, since MI$^{-\bullet}$ is generated by electron transfer from the sensitizer radical. Figure 4 shows the sensitizer dependence of the CIDEP spectrum for the photosensitized reaction of MI in 2-propanol including hydrochloric acid at a delay time of 3.0 μs. The result obtained for BP (Fig. 4a) indicates that the presence of HCl never affects both the CIDEP and the sensitized reaction. As reported previously,[26,27] no process related to HCl occurs, because the CIDEP on the photolysis of BP, itself, is independent of HCl. On the other hand, CRCA shows a clear HCl effect on the CIDEP.[29] In the photolysis of CRCA without HCl, both the ketyl and the alkyl type radicals of CRCA are produced with emissive polarization. However, under the presence of HCl, the CRCA ketyl radical is mainly produced with absorptive polarization (Chart 2). CRCA is expected to show a HCl effect, similar to Xn, on the photosensitization of MI. The CIDEP in the photosensitized reaction of MI with CRCA in 2-propanol (without HCl, not shown) is similar to that in Fig. 1. The HCl dependence of the CIDEP for the photosensitized reaction of MI with CRCA is shown in Figs. 4b and 4c. In both spectra, the MI anion radical is not observed. The absorptive sharp four lines around the center of the spectra are assigned to the CRCA ketyl radical ($g = 2.0039$, $A_H(3) = 0.166$ mT), which can be observed in the photolysis of CRCA with HCl. The emissive signals are assigned to the MI alkyl type radicals. These results clearly indicate that the formation of MI$^{-\bullet}$ is dependent on the sensitizer. The electron transfer from XnH• to MI occurs favorably and produces MI$^{-\bullet}$. In contrast, the CRCA ketyl radical cannot give an electron to MI. The reason for this is considered to be related to the difference in stability between the CRCA ketyl and XnH•.

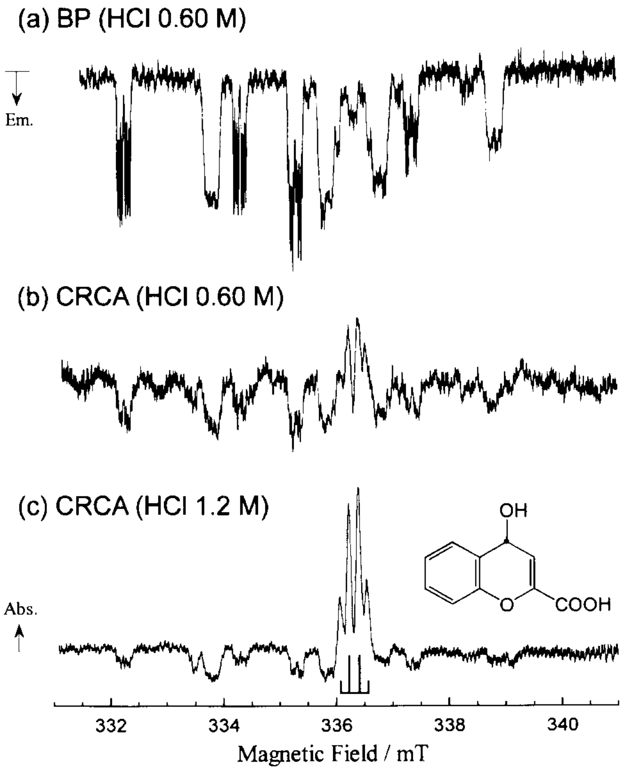


Fig. 4. The sensitizer dependence of the CIDEP spectra for the photosensitized reaction of MI by Xn in 2-propanol including hydrochloric acid. (a) BP with 0.60 M HCl, (b) CRCA with 0.60 M HCl, and (c) CRCA with 1.2 M HCl. The delay time is kept at 3.0 μs. Stick diagram shows the EPR lines of the CRCA ketyl radical.

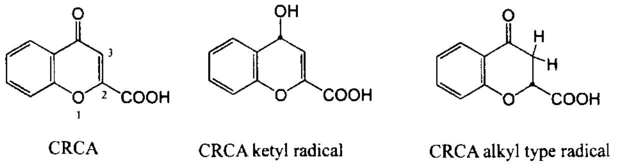


Chart 2.

(5) Maleic Anhydride (MA). Figure 5 shows the CIDEP spectrum on the photosensitized reaction of MA (saturated; the concentration was more than 0.2 M) by Xn in 2-propanol with 1 M hydrochloric acid. The strong absorptive three EPR lines are assigned to the MA anion radical ($A_H(2) = 0.64$ mT).[30] In the strong acidic condition, the hydrolysis of MA proceeds so fast that the detailed investigation on the photosensitization is quite difficult. The photosensitization of MA in 2-propanolic hydrochloric acid (water free) gives a similar result to that of MI. Therefore, the results for MA and MI can be explained by the same mechanisms as described above. The formation rate of the MA anion radical is estimated to be faster than that of MI.

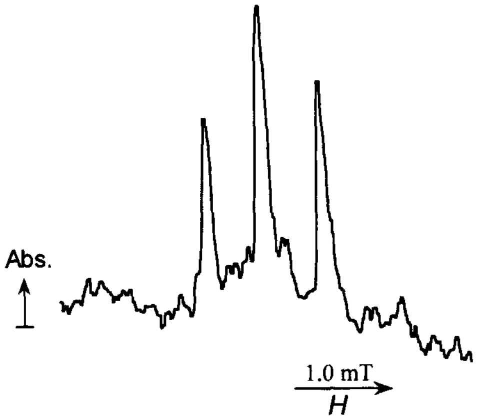


Fig. 5. The CIDEP spectrum on the photosensitized reaction of MA by Xn in 2-propanol including hydrochloric acid (1 M HCl). The delay time is 0.5 μs.

Conclusion

The CIDEP on the photosensitized reaction of MI by Xn in 2-propanol was investigated. The HCl addition effect on the CIDEP indicates the existence of two mechanisms for the photosensitization of MI by Xn. One is a typical T–T energy transfer to MI followed by hydrogen abstraction by ^{3}MI* from solvent. The other is an electron-transfer process to MI from XnH• produced by the reaction of ^{3}Xn* with HCl. The spin-polarization transfer mechanism can successfully explain the present CIDEP results based on these photosensitization processes.

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