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Anomalous Triplet Mechanism Spin Polarization Induced by the Addition of Hydrochloric Acid in the Photochemical System of Xanthone in Alcohol

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The hydrochloric-acid-addition effect on the photochemical reaction of xanthone in alcohol is studied by a time-resolved ESR technique. The CIDEP spectra of the transient radicals peculiarly reveal an enhanced absorption by the addition of hydrochloric acid, while the ordinary triplet mechanism of xanthone is known to be emissive. The spin-polarization inversion phenomenon is explained by the triplet mechanism induced by the excitation of a ground-state weak charge-transfer complex of xanthone and HCl.

Introduction

The CIDEP (chemically induced dynamic electron polarization) study[1] is now very popular and provides a wide variety of new aspects of photochemistry and radiation chemistry along with CIDNP (chemically induced dynamic nuclear polarization) study. The spin polarization not only helps the sensitivity of ESR detection even without its field modulation but also carries the information about the excited state of the precursor molecule and/or the consecutive reaction steps. Most of the reported data have been explained by well-established theories of the radical pair mechanism (RPM) and the triplet mechanism (TM) so far.[2−4] However, the applications of a time-resolved ESR (trESR) to a variety of systems are occasionally revealing strange CIDEP phenomena. For example, emission(low field)/absorption(high field) shaped hyperfine (hf) lines observed in a micellar system[5] are explained by the appearance of the exchange interaction of a transient radical pair known as a spin-correlated radical pair (SCRP).[6,7] The emissive polarization induced by the interaction of an excited triplet molecule and a doublet radical is now known as the radical-triplet pair mechanism (RTPM).[8,9] The report of the absorptive polarization from the system of photosensitized electron-transfer reaction suggests the contribution of molecular-encounter-induced spin−orbit interaction in the CIDEP signal.[10] The discovery of a new phenomenon in CIDEP promises the potential development of a very new conceptual view of chemical reactions.

Concerning the TM, the spin polarization is governed by the intersystem crossing (ISC) of the excited state of the precursor molecule, and it is conserved during the successive fast reactions. This is always true as long as the reaction is straightforward. In the present paper, a new discovery of an anomalous spin-polarization change by the addition of hydrochloric acid to the photochemical system of xanthone in alcohol is presented. A brief discussion and a tentative conclusion are also given.

Experimental Section

A conventional X-band ESR spectrometer was used for time-resolved measurements with a minor modification. A boxcar integrator or a transient wave memory (Iwatsu DM901) with a microcomputer (NEC PC9801VX) was used for the data acquisition and processing. A nitrogen gas laser (NDC JS-1000, $\lambda = 337$ nm) or an excimer laser (Lumonics EX-510, XeF, $\lambda = 351$ nm) was used for the excitation of the sample.

Commercially available G.R. grade xanthone (Xn) was recrystallized from ethanol. G.R. grade ethanol, 2-propanol, isobutyl alcohol (2-methyl-1-propanol), *tert*-butyl alcohol, cyclohexanol (*c*-hexanol), and 2,6-di-*tert*-butylphenol (DTBP) were used without further purification. Super special grade hydrochloric acid (37 wt %) was used as received. All the chemicals were supplied by Wako Pure Chemical Industries. The concentration of Xn was about 1×10^{-2} M (mol dm^{-3}), and that of HCl was changed from 1×10^{-2} to 1 M. The concentration of DTBP was controlled from 0.01 to 0.11 M. The solutions were previously deoxygenated by bubbling with pure nitrogen gas and flowed through a flat quartz cell fixed inside the ESR cavity. The detailed experimental procedure appeared in our previous papers.[11,12] In the present report, the results obtained in isobutyl alcohol are mainly presented.

Results

Figure 1a shows a typical CIDEP spectrum observed 0.5 and 0.7 μs after the laser excitation of Xn in isobutyl alcohol at room temperature. This spectrum is explained by the superposition of two signals that are assigned to the isobutyl alcohol radical ($^{\bullet}$ROH = $^{\bullet}C_3H_7OH$)[13] and the Xn ketyl radical ($^{\bullet}$XnH),[14] having the spectral pattern of *E*/*A** (the low field side is emissive and the high field absorptive, where the asterisk indicates the enhanced character). The stick diagrams in this figure are typical RPM spectra drawn by using the reported hf coupling constants (hfc) of these species.[13,14] These *E*/*A** patterns are tentatively explained by the triplet-precursor geminate-pair RPM of $S-T_0$ mixing and the excess absorptive component, but the latter component is not rationalized by the net effect by Δg or by the simple TM.[1] The reaction of the excited triplet state of Xn with thermal equilibrium[15] may explain the absorptive polarization, but the phase of the polarization easily changes with the experimental conditions such as the solvent used.

A drastic change of the spectral pattern by the addition of HCl to the isobutyl alcohol solution was observed, and this effect was enhanced by increasing the concentration of HCl. The

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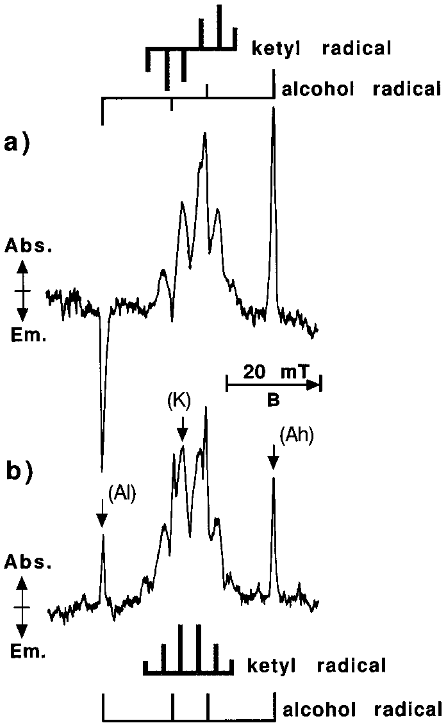

Figure 1. (a) CIDEP spectrum observed in the photolysis of Xn (1.1×10^{-2} M) in isobutyl alcohol at room temperature. The stick spectra of the ketyl and alcohol radicals with RPM polarization are presented. (b) CIDEP spectrum after the addition of hydrochloric acid (5.8 vol %; HCl 0.70 M) to the solution above. The stick spectra with absorptive TM polarization are presented. Here, (**K**) and (**Al** and **Ah**) indicate the peak positions of the ketyl and alcohol radicals used for the data analysis, respectively (see text). The dark thick lines of the stick spectra of the ketyl radical show the representative hf structure.

typical spectrum is shown in Figure 1b. Apparently, all the hf lines of •ROH and •XnH show enhanced absorption, but the lower field lines of •ROH are slightly weaker than the higher ones. These spectral patterns may be explained by the absorptive TM and the triplet-precursor geminate-pair RPM under these conditions. The enhanced absorption by TM in this particular case is very peculiar, because ordinary TM polarization by Xn is known to be emissive in alcohol media.[11,16,17] The lowest excited triplet state of Xn in several media is also known to have emissive character.[18,19]

When ethanol and 2-propanol were used as the solvent, similar *E*/*A** patterns of •ROH and •XnH were observed. When *c*-hexanol was used as the solvent, a slightly emissive *E*/*A* pattern (*E**/*A*) was observed, as shown in Figure 2a. The appearance of the weak excess absorption or emission component in the alcoholic solution of Xn without any other additives is an attractive phenomenon,[20] but the cause of the spin polarization has not been clarified yet. By the addition of HCl, similar results of enhanced absorption were obtained in all these solutions. The spectrum observed in *c*-hexanol solution by the addition of HCl is given in Figure 2b.

When *tert*-butyl alcohol was used as the solvent, no alcohol and Xn ketyl radicals were observable without HCl, probably due to the low reactivity of this alcohol as a hydrogen donor. By the addition of HCl, an absorptive signal of •XnH appeared, but no •ROH was detected. This indicates that the photoreduction of Xn takes place by the addition of hydrochloric acid and •XnH gets an absorptive polarization. No appearance of the counter radical may be due to the fast quenching reaction or the fast spin relaxation of the Cl atom or the Cl atom reaction related intermediate radical, but it has not been clarified at this stage yet.

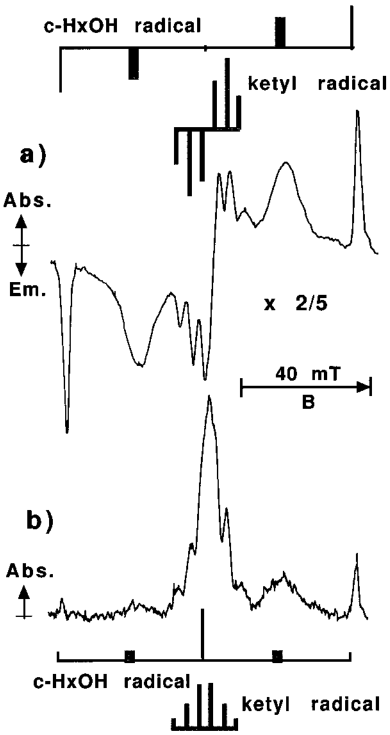

Figure 2. (a) CIDEP spectrum observed in the photolysis of Xn (1.0×10^{-2} M) in *c*-hexanol at room temperature. The stick spectra of the ketyl and *c*-hexanol radicals with RPM polarization are presented. (b) CIDEP spectrum after the addition of hydrochloric acid (4.1 vol %; HCl 0.50 M) to the solution above. The stick spectra of the ketyl and *c*-hexanol radicals with absorptive TM polarization are presented. The dark thick lines of the stick spectra of the *c*-hexanol radical show the broadened lines by the ring motion of the radical.

Xn is known to show a dual phosphorescence phenomenon,[21−26] and its excited states are very sensitive to the environment. To investigate whether HCl affects the electronic excited states of Xn to invert the spin polarization or not, DTBP, which is known to be a good reducing agent in photochemical systems, is added along with HCl. As shown in Figure 3a,b, the effect of the reducing agent is very dramatic, and the 2,6-di-*tert*-butylphenoxyl radical (DTBP radical) and the ketyl radical show an emissive pattern due to the apparent TM. The absorptive pattern of •ROH still remains in the spectrum, but is slightly quenched by increasing the concentration of DTBP. The solution of Xn and DTBP without HCl showed apparent strong emissive TM (with *E*/*A* by RPM) pattern of •DTBPH and •XnH. The addition of HCl weakened the emissive component, but this effect was not very significant and the spectrum of the alcohol radical appeared. These results indicate that the overall polarization of the excited triplet states of Xn must be emissive when ordinary TM is carried out, and the addition of DTBP quenches the absorptive signal of •ROH formed in connection with HCl. The dependence of the signal intensities of respective radical species upon the concentration of DTBP is given in Figure 4.

Discussion

In the system of aromatic nitro-compounds, the photoreduction is known to be accelerated by the addition of HCl and is believed that Cl^- plays an important catalytic role.[27,28] This situation is similar to the present case. However, the addition of lithium chloride aqueous solution to the present system instead of HCl to examine the contribution of Cl^- did not affect the spectral pattern. Since the addition of sulfuric acid and nitric acid instead of HCl, believed to form H^+, does not enhance the

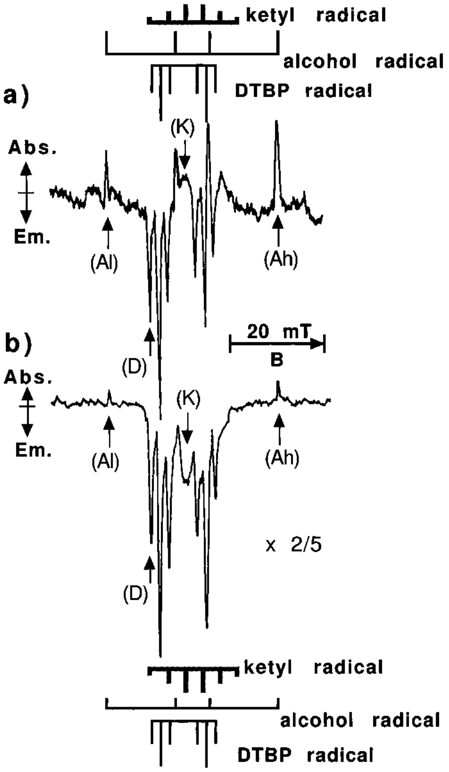

Figure 3. (a) CIDEP spectrum observed by the addition of DTBP (1.1×10^{-2} M) to the solution of Xn (1.1×10^{-2} M) and hydrochloric acid (5.8 vol %; HCl 0.70 M) in isobutyl alcohol at room temperature. This experiment was performed in the same series of those presented in Figure 1. The stick spectra of the ketyl and alcohol radicals with absorptive TM polarization and the DTBP radical with emissive TM are presented. (b) CIDEP spectrum observed by the addition of DTBP (3.4×10^{-2} M) to the solution. The stick spectra of the ketyl and DTBP radicals with emissive TM polarization and the alcohol radical with absorptive TM polarization are presented. Here, (**K**), (**D**), and (**Al** and **Ah**) indicate the peak positions of the ketyl, DTBP, and alcohol radicals used for the calculations, respectively (see text).

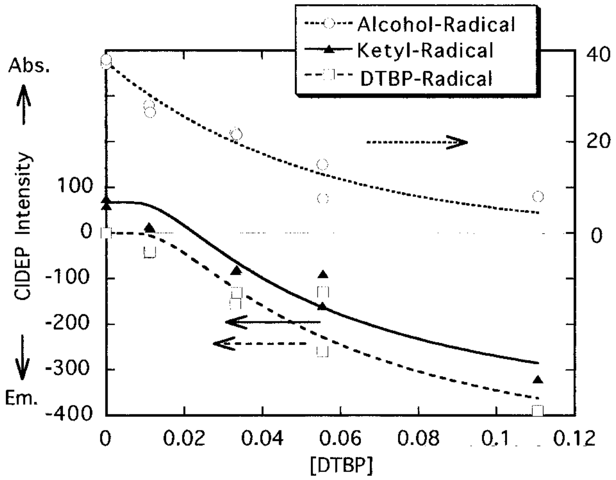

Figure 4. Plots of the CIDEP intensities of the ketyl, DTBP, and alcohol radicals versus the concentration of DTBP obtained in the solution of Xn (1.1×10^{-2} M) in isobutyl alcohol with HCl (5.8 vol %; 0.70 M) at room temperature. The intensity of the alcohol radical is obtained by the calculation of (**Al** + **Ah**)/2. The lines presented here are obtained by the best fitting of the simple calculations of the intensity of the respective signals (see text).

absorptive spin polarization, the effect of H^+ without Cl^- on the polarization inversion is excluded. The presence of both H^+ and Cl^- or the presence of HCl molecules must be necessary to induce the peculiar absorptive TM polarization in these particular systems.

The effects of the DTBP addition shown in Figure 4 are analyzed semiquantitatively in the following ways. (1) The quenching of the signal of $^\bullet$ROH is thought to be due to the reaction of $^\bullet$ROH with DTBP. The pseudo-first-order reaction by the hydrogen-transfer reaction from DTBP to the alcohol radical is assumed.

$$\mathrm{DTBP} + {}^\bullet\mathrm{ROH}\ (k_1) \rightarrow {}^\bullet\mathrm{DTBP} + \mathrm{ROH} \tag{1}$$

Therefore, the signal intensity of the alcohol radical, I_{alc}, at the observation time t_1, is expressed as

$$I_{\mathrm{alc}}(t_1) = I_{\mathrm{alc}}(0)\exp\{-k_1 t_1[\mathrm{DTBP}]\} \tag{2}$$

where k_1 is the rate constant of this reaction. The best fitting curve using this equation and $t_1 = 0.6$ μs is given by a dotted line in the figure and the approximate rate constant, k_1, of 3.2 $\times$ 10^7 M^{-1} s^{-1}, is derived. (2) Concerning the reaction of ^{3}Xn* and DTBP, the following hydrogen abstraction reaction takes place:

$$^3\mathrm{Xn}^* + \mathrm{DTBP}\ (k_3) \rightarrow {}^\bullet\mathrm{XnH} + {}^\bullet\mathrm{DTBP} \tag{3}$$

In the analysis, some assumptions are employed. The absorptive signal of the ketyl radical (**K** in the Figure 1b) is solely the result of HCl addition, and the addition of DTBP independently provides the emissive signal of the TM polarization that can be simply added to the signal of the absorptive one. Since the latter is a typical TM polarization, the signal intensities of the ketyl and DTBP radicals are determined by the competition of the spin relaxation rate of the excited triplet state of Xn and the hydrogen abstraction reaction rate (k_3). To estimate the TM polarization of the ketyl and DTBP radicals, the empirical equation that was used in the other systems was employed.[29,30] The signal intensity is expressed by the sum of the observed absorptive TM (A in the equation, and this value is zero for the DTBP radical) that appears from the HCl addition and the emissive TM from DTBP addition:

$$I_{\mathrm{TM}} \propto A + C\exp\left\{-\frac{1}{T_1 k_3[\mathrm{DTBP}]}\right\} \tag{4}$$

where C denotes the maximum TM polarization amplitude. The slight contribution of the RPM is disregarded in the data processing for the ketyl and DTBP radicals, and the yield of the reaction is assumed to be the same in the concentration range of DTBP. By assuming the spin−lattice relaxation time of the excited triplet state of Xn (T_1) in isobutyl alcohol is close to that in 2-propanol, 6×10^{-9} s,[29] the obtained best fitting provides a rough estimation of the rate constant ($k_3 \approx 3 \times 10^9$ M^{-1} s^{-1} from the data of both the ketyl and DTBP radicals) for this hydrogen abstraction reaction. The solid and broken lines in the figure show the fittings of the data of the ketyl and DTBP radicals, respectively. These rate constants seem to be reasonable values, but we are not intending to evaluate these rate constants because the absolute intensity of the CIDEP signal is not always credible enough. We only claim that this model of the existence of two different reaction processes, the HCl-related and ordinary hydrogen abstractions, well explains the spectral change by the addition of DTBP.

The UV absorption spectra of Xn in ethanol were examined in the presence and absence of hydrochloric acid. A slight red shift of the absorption band was observed by the addition of HCl. This suggests the possibility of the protonation of Xn by the acid or the formation of a charge-transfer (C-T) complex between Xn and HCl in their ground state. The addition of

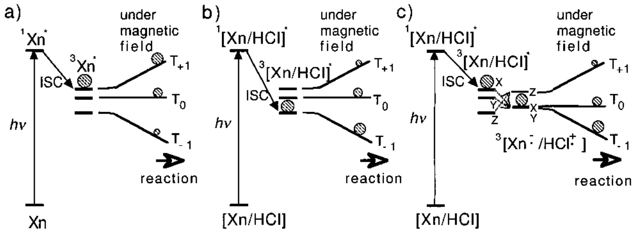

Figure 5. Schematic diagrams of different triplet mechanisms: (a) the ordinary TM of xanthone, (b) the TM of the strongly interacting C-T complex, and (c) the TM of the transient contact radical-ion pair that is formed by the fast charge separation (see text).

H_2SO_4 to the solution of Xn in ethanol also provided a slight shift of the absorption band. These experiments imply that the red shift of the absorption band is mainly attributed to the protonation of Xn in alcohol. The same shift of the absorption band by the addition of acids was also observed in case of isobutyl alcohol solution. Under the experimental conditions of the trESR measurement, the roughly estimated absorbance of the red-shifted absorption band is not very strong (less than 10% of that of Xn), according to these data. At this stage, the contribution of the excitation of the red-shifted band to the spin polarization is not clarified, but the excitation of highly protonated Xn does not enhance the absorptive spin polarization as the result of the addition of the other acids shows. Therefore, the possibility of a strongly interacting ground-state C-T complex formation is unlikely. The existence of a weak C-T complex of Xn and HCl that has a similar absorption spectrum to that of Xn is postulated to rationalize all the experimental data presented here.

The trESR spectrum of the excited triplet state of Xn has already been reported in frozen media at 77 K.[18,19] The trESR spectrum of the excited triplet state detected in a frozen mixed solvent of 2-propanol and hydrochloric acid was almost identical with that observed in 2-propanol with a small amount of water at 77 K. This implies that the zero-field splitting value of the lowest excited triplet state of Xn and the anisotropic intersystem crossing (ISC) to that particular state are not affected by the addition of HCl. Therefore, the emissive TM observed by the addition of DTBP is the contribution of the locally excited triplet state of Xn in polar media (see Figure 5a). No appearance of the trESR spectrum of the excited triplet state of the C-T complex may be due to either the fast spin relaxation of this state or the fast back reaction of the excied C-T complex at 77 K. All these data show that the change of the electronic excited state of Xn by the addition of HCl that affects the TM spin polarization is unlikely, and only the formation and excitation of the C-T complex elucidate the experimental results.

The postulated reaction scheme of the excitation of the weak C-T complex is given as follows:

$$[\mathrm{Xn/HCl}] + h\nu \rightarrow {}^1[\mathrm{Xn/HCl}]^* \tag{5}$$

$$^1[\mathrm{Xn/HCl}]^* \rightarrow {}^3[\mathrm{Xn/HCl}]^* \tag{6}$$

$$^3[\mathrm{Xn/HCl}]^* + \mathrm{ROH} \rightarrow {}^\bullet\mathrm{XnH(TM)} + {}^\bullet\mathrm{ROH(TM)} + \mathrm{HCl} \tag{7}$$

where asterisks and parentheses (TM) denote the respective excited states and the polarization origin, respectively. This TM polarization must be absorptive and dominates the spin polarization of other origins.

Consequently, the appearance of the CIDEP spectrum having inverted spin polarization may be responsible for the excitation of the ground-state weak C-T complex that is in equilibrium with the isolated solute molecules in the solution. (1) One of the postulations of the induction of the absorptive polarization is the formation of a strongly interacting excited C-T complex. The ISC within the complex induced by the overall spin−orbit interaction makes the population of the lower spin sublevels high, as shown in Figure 5b. The successive reaction finally forms absorptive signals of $^\bullet$XnH and $^\bullet$ROH. (2) Another postulation is the formation of the transient contact radical-ion pair where two charges are separated perpendicular to the molecular plane of xanthone by way of the excited C-T complex as follows:

$$^3[\mathrm{Xn/HCl}]^* \rightarrow {}^3[\mathrm{Xn}^{\bullet -}/\mathrm{HCl}^{\bullet +}] \tag{8}$$

The highest spin-sublevel of the excited triplet state of the complex is expected to be initially populated by the ISC due to the predominant local orbital character of Xn where the sublevel of the direction of the C═O group is the most active. In the radical-ion pair, the spin sublevel of which the direction of the principal axes is parallel to the axis of two charges becomes the upper one.[31] If reaction 8 takes place before the quantizing of the triplet spin system to the direction of the external magnetic field, the spin population in the molecular frame is conserved during this very fast process. Consequently, one of the lower spin sublevels of which the direction is parallel to that of the C═O group of Xn in the radical-ion pair is populated as shown in Figure 5c. Therefore, the absorptive TM may be anticipated under the external magnetic field. This type of the spin conservation in the molecular frame during fast processes has been reported in the system of several chemical reactions,[32−34] triplet−triplet energy transfer[35,36] and the triplet−triplet internal conversion.[37]

The conclusive mechanism of the spin-polarization inversion is not clarified from the data provided here, but the complex formation in the ground state is thought to be the main cause. In the present system, final radicals $^\bullet$XnH and $^\bullet$ROH having absorptive TM polarization may be produced by the consecutive proton and/or hydrogen-transfer reactions:

$$^3[\mathrm{Xn/HCl}]^* \text{ or } {}^3[\mathrm{Xn}^{\bullet -}/\mathrm{HCl}^{\bullet +}] \rightarrow {}^\bullet\mathrm{XnH} + {}^\bullet\mathrm{Cl} \tag{9}$$

$$^\bullet\mathrm{Cl} + \mathrm{ROH} \rightarrow {}^\bullet\mathrm{ROH} + \mathrm{HCl} \tag{10}$$

The reactions 8, 9, and 10 may constitute reaction 7.

On the other hand, the reaction of the excited triplet state of the isolated Xn in alcohol is as follows:

$$\mathrm{Xn} + h\nu \rightarrow {}^1\mathrm{Xn}^* \tag{11}$$

$$^1\mathrm{Xn}^* \rightarrow {}^3\mathrm{Xn}^* \tag{12}$$

$$^3\mathrm{Xn}^* + \mathrm{ROH} \rightarrow {}^\bullet\mathrm{XnH(RPM)} + {}^\bullet\mathrm{ROH(RPM)} \tag{13}$$

The reaction of the excited triplet state of Xn with free HCl may take place, but this reaction must involve alcohol:

$$^3\mathrm{Xn}^* + \mathrm{HCl} + \mathrm{ROH} \rightarrow {}^\bullet\mathrm{XnH} + {}^\bullet\mathrm{ROH} + \mathrm{HCl} \tag{14}$$

This reaction may provide emissive TM polarization when the concentration of HCl is high. However, the contribution of reaction 14 to the overall CIDEP may not be significant because much stronger absorptive TM signals dominate the emissive one, because the concentration of the equilibrated ground-state complex may become high under high concentration condition of HCl.

Okutsu et al. reported the effect of quenchers on the spin-polarization inversion of intermediate radicals produced in the photolysis of benzil.[38] In their paper, the excitation of the ground-state C-T complex of organic compounds is proposed to be the cause of the dual spin polarization. Their observation is similar to the case observed in the present system.

The possibility of the contribution of molecular-encounter-induced spin−orbit interaction[10] to the spin polarization is unlikely in the present case, because the quantitative analysis of the polarization change by the addition of DTBP shows that the two CIDEP processes are not competing, and the complete cancellation of the initial strong emissive TM polarization by the mechanism may be difficult in the present conditions. Another possibility of the polarization inversion is due to the excited state of Xn influenced by the addition of HCl. However, it may also be excluded, because the triplet spectrum of trESR of this state has not been detected as mentioned before, and the result of the addition of DTBP in the solution with HCl does not support this possibility either. The appearance of the excess absorptive or emissive polarization observed in alcohol solutions without HCl may have something to do with the problem of the electronic states of Xn. For instance, the change of the reactivity of the higher excited triplet state ($n\pi^*$) of Xn and/or the spin sublevel inversion of one of the excited triplet states by the spin−orbit interaction of another excited triplet state located nearby may invert the spin polarization of the intermediate radical species in different circumstances. The contamination by a small amount of water in the alcohol solution is not very important, because it does not affect the CIDEP spectral pattern. Finally, it is noteworthy to state that benzophenone having a rather nonplanar structure and the lowest excited triplet state of $n\pi^*$ did not show any special effect of the addition of HCl upon the CIDEP. This indicates that the appearance of this peculiar spin polarization is a very characteristic phenomenon of Xn.

In conclusion, the addition of hydrochloric acid to the photoreduction system of Xn in alcohol changes the CIDEP spectra of ketyl and alcohol radicals from RPM to the enhanced absorptive TM. When DTBP, which is known as a good reducing agent, is added to the system, the radicals formed by the photoreduction show emissive TM polarization along with the signal of the alcohol radical with absorptive TM. The effect of HCl was postulated by the excitation of a weakly charge-transferred ground-state complex that provides the absorptive TM. The possibility of the HCl effect on the electronic states of Xn is not likely.

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