Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 325–332

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

An FT-EPR investigation of the anomalous CIDEP in photoreactions of chromone and chromone-2-carboxylic acid with alcohol induced by hydrochloric acid

Keishi Ohara[a,*], Debora M. Martino[b,1], Hans van Willigen[b]

[a] *Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790-8577, Japan*
[b] *Department of Chemistry, University of Massachusetts at Boston, Boston, MA 02125, USA*

Received 8 September 2005; received in revised form 10 November 2005; accepted 15 December 2005

Abstract

The anomalous net absorptive CIDEP spectra observed in the photoinduced hydrogen abstraction reaction of chromone (CR) and chromone-2-carboxylic acid (CRCA) from 2-propanol with addition of hydrochloric acid (HCl) were investigated with FT-EPR. In neat 2-propanol, the spectra of the ketyl and 2-hydroxypropan-2-yl (2-HP) radicals display E*/A (low-field side emission and high-field side absorption, the asterisk denoting excess net polarization) or E/A type polarization, which is explained by the ST_0 mixing radical pair mechanism and minor contributions of the triplet mechanism (TM). The addition of HCl to these systems gives the net absorptive CIDEP spectra, while the triplet states of CR and CRCA should have emissive polarizations. The analysis of the time developments of the EPR signals indicates that the radical generation rate increases with the increase of the HCl concentration, while the signal intensity of radicals does not increase. The net absorptive polarization might be explained by non-reactive quenching of the triplet by the spin-sublevel dependent back charge-transfer process in the intermediate exciplex.

Keywords: FT-EPR; CIDEP; Hydrochloric acid; Photolysis; Chromone

---

1. Introduction

The photochemistry of a series of aromatic carbonyl compounds has been an attractive theme and has been studied with a variety of spectroscopic techniques such as transient absorption spectroscopy, emission spectroscopy, and magnetic resonance. For example, the spectroscopic and photochemical properties of xanthone (Xn, Fig. 1) have been a topic of considerable interest because the close proximity of the $^3\pi\pi^*$ and $^3n\pi^*$ states gives rise to unique features of triplet Xn ($^3Xn^*$), such as the strong solvent polarity effect on the character of the lowest triplet state and the unusual phenomenon of dual phosphorescence [1–7]. The phenomenon of chemically induced dynamic electron polarization (CIDEP) observed in the photochemical reaction systems by means of the time-resolved EPR (TREPR) have been one of the subjects in photochemical studies, and often provides valuable information not only on spin and reaction dynamics, but also on precursor excited states. For the most part, CIDEP producing mechanisms are now well understood [8–11].

Recently, unusual CIDEP behaviors were reported on Xn and chromone-2-carboxylic acid (CRCA, Fig. 1) induced by the addition of hydrochloric acid (HCl) to their photoreaction systems in alcohols [12–15]. Most of the CIDEP spectra obtained in the photochemical reactions on Xn and CRCA show net emissive or E*/A (low-field side emission and high-field side absorption, the asterisk denoting excess net polarization) polarization. This polarization pattern can be accounted for in terms of a combination of two CIDEP mechanisms. (1) The triplet mechanism (TM), stemming from sublevel dependent intersystem crossing (isc) in the triplet state ($^3Xn^*$ or $^3CRCA^*$), giving rise to emissive polarization. (2) The ST_0 mixing (ST_0M) of the radical pair mechanism (RPM) which is responsible for the E/A contribution to the polarization. On the other hand, addition of hydrochloric acid to the photoreaction system of Xn (or CRCA) in alcohols

---

[*] Corresponding author. Tel.: +81 89 927 9596; fax: +81 89 927 9590.
E-mail address: ohara@chem.sci.ehime-u.ac.jp (K. Ohara).
[1] Present address: The Physics Department, FBCB, UNL, 3000 Santa Fe, Argentina.

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.12.014

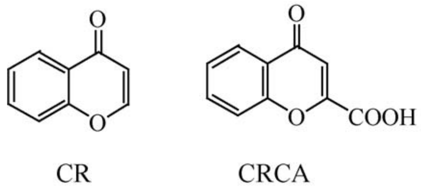


Fig. 1. Molecular structures of chromone (CR), chromone-2-carboxilic acid (CRCA), and xanthone (Xn).

could give rise to TREPR spectra of the ketyl radical of Xn (or CRCA) and alcohol radicals exhibiting net absorptive polarization [12–15]. It is noteworthy that benzophenone and flavone which resemble Xn and CRCA in structure and chemical properties do not show this unusual change in CIDEP upon addition of HCl. This HCl addition effect on CIDEP spectra is probably observed on the photoreactions of the aromatic carbonyl compounds of which the lowest triplet state T_1 is $^3\pi\pi^*$ and is lying closely to the second triplet state T_2 with $^3n\pi^*$ character [16,17]. Moreover, the CW TREPR result on the CRCA system suggests that the CRCA ketyl and the CRCA alkyl type radicals are generated through the independent processes [14]. In the presence of HCl, the net polarization of the CRCA ketyl radical is absorptive, whereas that of the CRCA alkyl radical is emissive. The results might suggest that the hydrogen abstraction on the carbonyl group of ^{3}CRCA* gives the ketyl type radical (the $^3n\pi^*$ character reaction) and that on the carbon double bond gives the alkyl type radical (the $^3\pi\pi^*$ character reaction). Further time domain investigations are needed to clarify the mechanism by which HCl affects the reaction and the spin polarization.

Fourier transform EPR (FT-EPR) offers both higher sensitivity and better spectral resolution than the CW TREPR technique [10,13,18–20]. For these reasons, FT-EPR gives the opportunity to obtain new information about spin and reaction dynamics at the early stages of photochemical reactions. Since the time evolution measured by FT-EPR is free from microwave field perturbation, an analysis of the rise and decay of the EPR signals can reveal the intrinsic properties of the transient species more clearly. In the present work, we have used FT-EPR in a study of the time development of transient EPR signals of the radicals produced by photolysis of chromone and CRCA (Fig. 1) in 2-propanol with various amounts of HCl. From the time domain data obtained by FT-EPR measurements, the mechanism generating the spin polarization in these photochemical reactions are discussed.

2. Experimental

FT-EPR measurements were performed at room temperature with a lab-built spectrometer described before [13,18–20]. A XeCl excimer laser (Lambda Physik EMG 103 MSC, 308 nm, 12 Hz, for chromone) or a Nd–YAG laser (Quanta-Ray GCR-14S, THG 355 nm, 10 Hz, for CRCA) was used for photoexcitation. Quadrature detected free induction decay (FID) signals were accumulated using the CYCLOPS phase-cycling procedure. The number of acquisitions per spectrum ranged from 256 to 1200. FT-EPR power spectra were obtained by Fourier transformation of the FIDs. The time evolution of EPR signals was measured by changing the delay time between laser excitation and microwave pulse. The data acquisition and processing methods were the same as those reported previously [13,18–20]. The time resolution of the present experiments was estimated to be $(2–3) \times 10^{-8}$ s, this value is mainly determined by the microwave and laser pulse widths and jitter in the timing of the pulses. Because the bandwidths of the spectra of the transient radicals far exceed the spectrometer bandwidth, complete spectra were assembled from FIDs recorded with four to six distinct field settings. The FT-EPR spectra shown here were converted to magnetic field representation (left side is low field, i.e. high frequency) for easy comparison with CW TREPR spectra.

Chromone and CRCA were commercially available special grade reagents (Aldrich) and used without further purification. A G.R. grade 2-propanol (Aldrich) was also used as received. Concentrated hydrochloric acid was used as received from EM Science (36.5% HCl, S.S.G.). The sample solutions were deoxygenated by purging with nitrogen gas before and during experiments, and pumped through a quartz cell held in the EPR cavity. The concentrations of chromone and CRCA were kept at 1.0×10^{-2} M and the concentration of HCl ranged from 0 to 0.16 M. Other experimental conditions were kept the same for comparison.

3. Results and discussion

3.1. Chromone

The FT-EPR spectrum observed on the photolysis of chromone (CR) in 2-propanol at the delay time of 0.24 μs is shown in Fig. 2a. The sharp and strong lines marked by arrows in Fig. 2a are due to the 2-hydroxypropan-2-yl (2-HP) radical, and the multiline signal in the center of the spectrum is assigned to the CR ketyl (CR-K) radical. This spectrum is almost similar to the CW TREPR spectrum reported previously [21,22]. These radicals were produced by the hydrogen abstraction reaction of the triplet state of CR (^{3}CR*) from the solvent 2-propanol as shown in Scheme 1. The signals for the CR alkyl type (CR-A) radical in the present FT-EPR spectrum is too small to discuss on it. The spectrum shows a symmetrical E/A polarization explained in terms of the ST_0M RPM. Fig. 3a shows the time developments of the $M_I = \pm 1$ hyperfine (hf) lines of the 2-HP radical in this neat 2-propanol system, indicating that these $M_I = \pm 1$ hf lines have almost the same signal intensity and time constants for rise and decay.

As shown in Fig. 2b and c, the addition of hydrochloric acid to this photolysis system gradually changed the EPR spectrum from E/A to E/A*. This increase of the net absorptive polarization with the increase of HCl concentration may be due to the increase of the contribution of the TM polarization as a result of acceleration of the radical-generating reaction. However, the TM polarization in ^{3}CR* was reported to be emissive [21,22]. Thus, the absorptive polarization observed in the present CR system is not due to the normal TM. This CIDEP behavior induced with the HCl addition is analogous to those reported on the Xn and CRCA systems, and the production mechanism

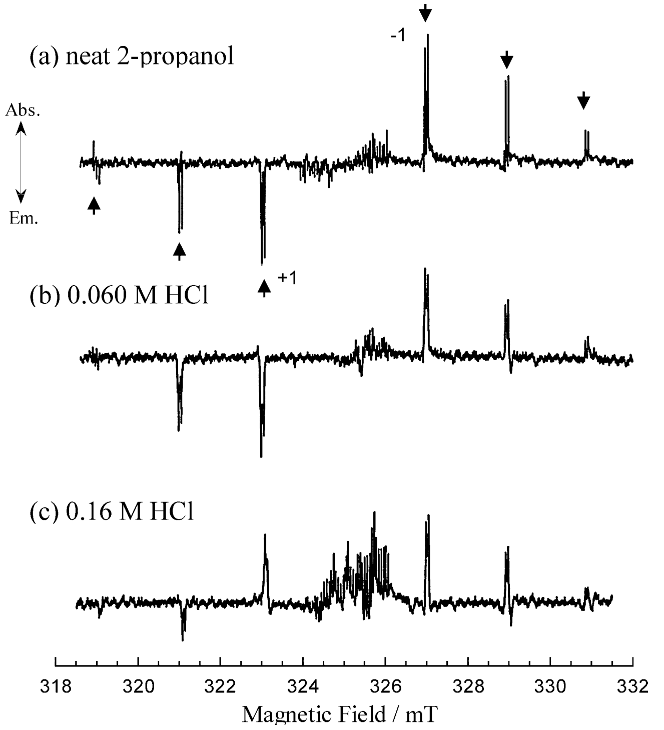
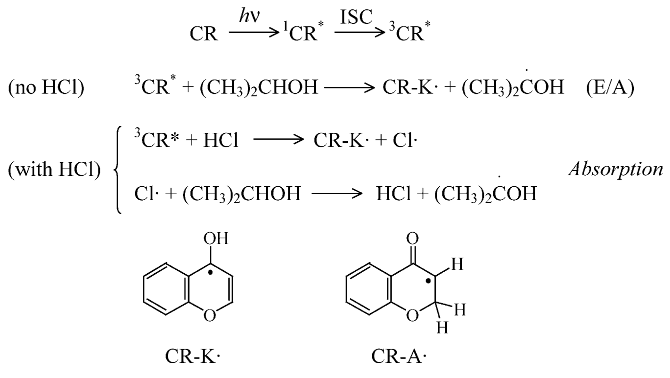


Fig. 2. FT-EPR spectra of free radicals formed by photolysis of chromone (1.0×10^{-2} M) observed at a delay time of 240 ns after the laser pulse, (a) in neat 2-propanol, (b) in 2-propanol with 6.0×10^{-2} M HCl, and (c) in 2-propanol with 0.16 M HCl.

of the absorptive polarization should be closely related to each other [12-14]. These facts suggest that the CR-K radical was produced through the reaction of $^3CR^*$ with HCl (or Cl^-), and the generated Cl radical reacted rapidly with 2-propanol solvent and produced the 2-HP radical (Scheme 1) [13,14,23]. The HCl effect on this CR system is smaller than that on the Xn system because the spectral change to absorption in the Xn system could be observed by lower HCl concentration than 0.05 M. For further investigation on the CIDEP generation mechanism of this system, a kinetic analysis of the time domain FT-EPR data was performed. The data treatment method was followed by the previous reports [13,19].

Fig. 3b and c show the time developments of the $M_I = \pm 1$ hf lines of the 2-HP radical observed in the photolysis system of CR with 6.0×10^{-2} M and 0.16 M HCl. Depicted are the



Scheme 1.

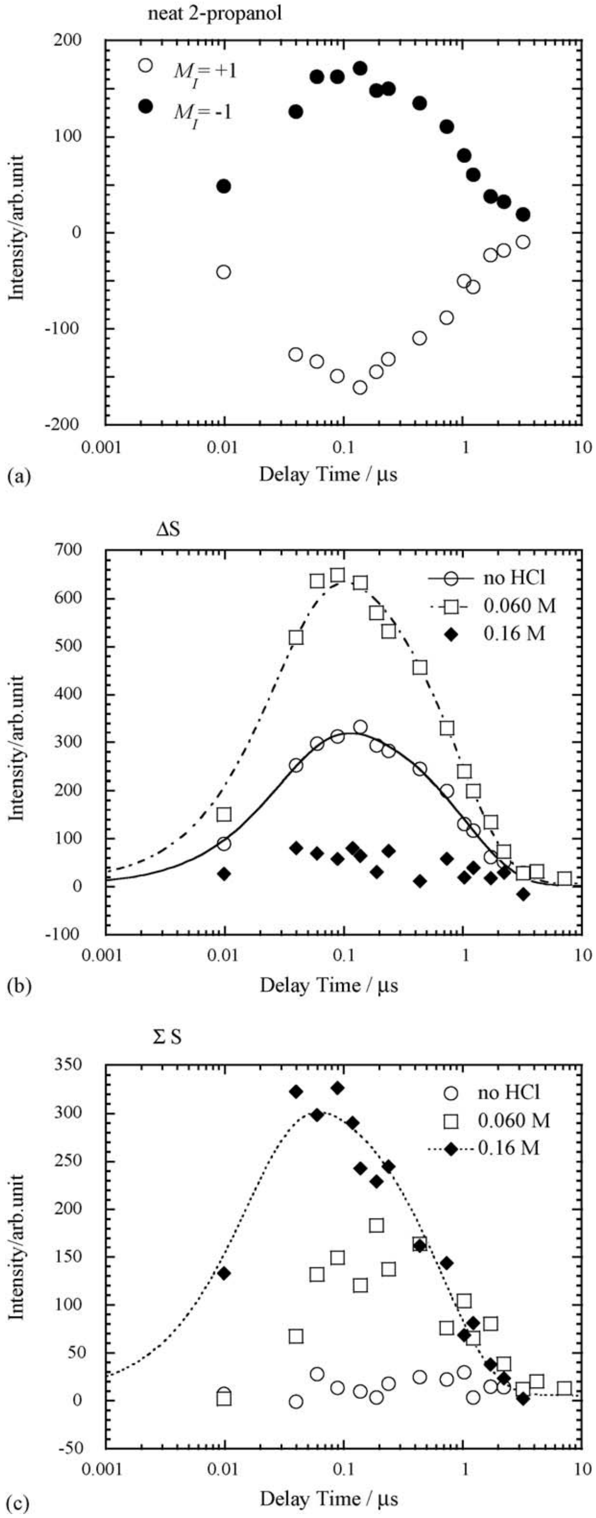


Fig. 3. (a) Time developments of the $M_\mathrm{I} = \pm 1$ hf lines of the 2-HP radical observed on the photolysis of CR in neat 2-propanol. Time developments of (b) the difference of the intensities of the −1 and +1 hf lines (ΔS) and (c) the sum of the intensities of the $M_\mathrm{I} = \pm 1$ hf lines ($\sum S$) in the spectrum of the 2-HP radical for various HCl concentrations.

time developments of the net emissive component ($\sum S$, sum of the intensities of the $M_{\mathrm{I}} = \pm 1$ hyperfine lines) and the RPM (E/A) signal contribution (ΔS, difference of the intensities of the +1 and −1 lines). The ΔS component should include the geminate-pair $\mathrm{ST_0M}$ RPM and F-pair RPM polarizations. When the F-pair polarization created by radical termination reactions is ignored, the time development of the RPM spin polarization is represented by the following equation [13,19]:

$$P_{\mathrm{RPM}} = P^{0}_{\mathrm{RPM}}\{\exp(-k_{\mathrm{d}}t) - \exp(-k_{\mathrm{f}}t)\} \tag{1}$$

Here, P^{0}_{RPM} is the initial polarization generated by the geminate RPM, k_{f} and k_{d} are the growth and decay rates of the RPM signal, and it was assumed that $k_{\mathrm{f}} \gg k_{\mathrm{d}}$. When the radical lifetime is long compared with the spin–lattice relaxation time (T_1^{R}) of the radical, we should obtain $k_{\mathrm{d}} = 1/T_1^{\mathrm{R}}$. The hydrogen abstraction rate constant (k_{HA}) can be obtained as $k_{\mathrm{HA}} = k_{\mathrm{f}}$ when the k_{f} value is less than the inverse of the spectrometer response time. On the other hand, the time development of the TM polarization is represented by [13,19],

$$P_{\mathrm{TM}} = P^{0}_{\mathrm{TM}}\left\{\exp\left(\frac{-t}{T_1^{\mathrm{R}}}\right) - \exp\left[-\left({}^{3}k_{\mathrm{HA}} + \frac{1}{T_1^{\mathrm{T}}}\right)t\right]\right\} + P_{\mathrm{eq}}\left\{1 - \exp\left(\frac{-t}{T_1^{\mathrm{R}}}\right)\right\} \tag{2}$$

Here, P^{0}_{TM} and P_{eq} are the initial polarization generated by TM and the thermal equilibrium polarization, respectively. T_1^{T} is the spin–lattice relaxation time of the precursor triplet state, and it is assumed that $k_{\mathrm{HA}} + 1/T_1^{\mathrm{T}} \gg 1/T_1^{\mathrm{R}}$. In many systems, the time development of the net polarization ($\sum S$) can be reasonably simulated by Eq. (2).

The measured time developments of the signals were simulated by Eqs. (1) and (2). The lines in Fig. 3b and c depict the least squares fits of the ΔS and $\sum S$ data points to Eqs. (1) and (2). The obtained rate constants of signal growth and decay are listed in Table 1. The obtained k_{f} values of the ΔS data are $3.2 \times 10^{7}\,\mathrm{s^{-1}}$ in neat 2-propanol, $3.4 \times 10^{7}\,\mathrm{s^{-1}}$ in 2-propanol with 6.0×10^{-2} M HCl, and $6.2 \times 10^{7}\,\mathrm{s^{-1}}$ in 2-propanol with 0.16 M HCl. The value of $k_{\mathrm{f}} = 6.2 \times 10^{7}\,\mathrm{s^{-1}}$ for the 0.16 M HCl system might be controlled by the response time of the spectrometer, however, this value is unreliable because the number of data points in the early time region is not enough to determine the acceptable rise rate. The k_{d} values of the ΔS data in neat 2-propanol, in 2-propanol with 6.0×10^{-2} M HCl, and in 2-propanol with 0.16 M HCl are 0.93, 1.1, and $1.4 \times 10^{6}\,\mathrm{s^{-1}}$, respectively. These values are larger than the spin–lattice relaxation rate constant ($1/T_1^{\mathrm{R}} = 0.53 \times 10^{6}\,\mathrm{s^{-1}}$) of the 2-HP radical reported [13,20], suggesting that the chemical quenching of the 2-HP radical occurred in this system [24]. The 2-HP radical probably gives rise to an addition reaction to the non-aromatic double bond of CR. The value $P_{\mathrm{eq}} = 0$ was obtained from the least squares fits of $\sum S$ data to Eq. (2), probably because of this chemical quenching. The rise rate of $\sum S$ in 2-propanol with 0.16 M HCl was estimated to be $6.2 \times 10^{7}\,\mathrm{s^{-1}}$, which might be also unreliable and controlled by the response time of the spectrometer. The delayed rise of small amount of net absorptive signal observed in neat 2-propanol system was considered to be due to the thermal population produced by the relaxation of the spin system.

Table 1
Rate constants of formation and decay of FT-EPR signals of the 2-HP and the CRCA-A radicals

	k_{f} ($\sum S$) ($10^{6}\,\mathrm{s^{-1}}$)	k_{f} (ΔS) ($10^{6}\,\mathrm{s^{-1}}$)	k_{d} ($10^{6}\,\mathrm{s^{-1}}$)
2-HP radical in CR system			
2-Propanol	–	32	0.93
2-Propanol and HCl 6.0×10^{-2} M	–	34	1.1
2-Propanol and HCl 0.16 M	62	62	1.4
2-HP radical in CRCA system			
2-Propanol	–	28	1.21
2-Propanol and HCl 1.2×10^{-2} M	–	31	1.12
2-Propanol and HCl 6.0×10^{-2} M	–	35	1.37
2-Propanol and HCl 0.16 M	–	52	1.50
CRCA-A radical in CRCA system			
2-Propanol	–	14	0.56
2-Propanol and HCl 1.2×10^{-2} M	–	20	0.56
2-Propanol and HCl 6.0×10^{-2} M	–	25	0.56
2-Propanol and HCl 0.16 M	–	26	0.56

See text for details on the data analysis.

The rate constant of the hydrogen abstraction reaction of ${}^{3}\mathrm{CR}^{*}$ in neat 2-propanol ($3.2 \times 10^{7}\,\mathrm{s^{-1}}$) obtained from the rise of the ΔS data is one order larger than that reported for Xn ($3.2 \times 10^{6}\,\mathrm{s^{-1}}$) [13]. On the other hand, from the dependence of k_{f} on the HCl concentration, the second-order reaction rate constant for CR with HCl was roughly estimated to be $2.0 \times 10^{8}\,\mathrm{M^{-1}\,s^{-1}}$. This value is one order smaller than that reported for Xn with HCl ($2.7 \times 10^{9}\,\mathrm{M^{-1}\,s^{-1}}$) [13].

3.2. Chromone-2-carboxylic acid (CRCA)

The FT-EPR spectrum observed on the photolysis of CRCA in 2-propanol at the delay time of 0.24 μs is shown in Fig. 4a. This spectrum is consistent with the CW TREPR spectrum reported previously [14,21,22], and explained by an overlap of the three radicals. The sharp and strong lines are due to the 2-HP radical, the multiline signal in the center of the spectrum is mainly due to the CRCA ketyl (CRCA-K) radical, and two set of the multiline signal marked by asterisks is to the CRCA alkyl (CRCA-A) radical. The E/A/E/A type distortion of the lines of the CRCA-K radical in the center of the spectrum might be due to the contribution of the spin-correlated radical pair [8–11]. These radicals were produced by the hydrogen abstraction reaction of the triplet state of CRCA (${}^{3}\mathrm{CRCA}^{*}$) from the solvent 2-propanol, as shown in Scheme 2 (a) and (b). ${}^{3}\mathrm{CRCA}^{*}$ reacted on its two active reaction sites; one is the carbonyl group and the other is the non-aromatic carbon double bond. The spectrum shows an

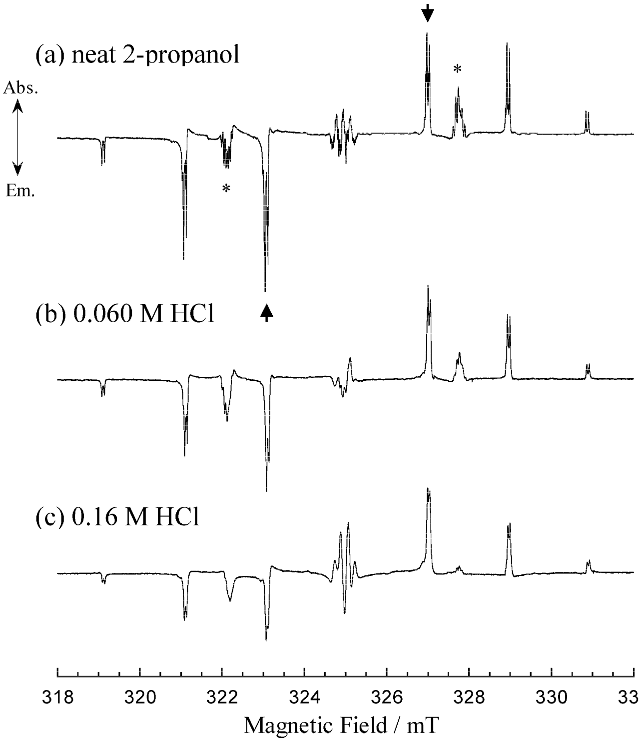
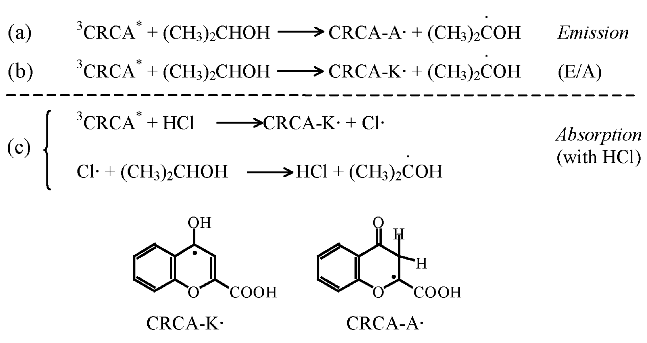


Fig. 4. FT-EPR spectra of free radicals formed by photolysis of CRCA (1.0×10^{-2} M) observed at a delay time of 240 ns after the laser pulse, (a) in neat 2-propanol, (b) in 2-propanol with 6.0×10^{-2} M HCl, and (c) in 2-propanol with 0.16 M HCl.

E*/A polarization pattern that can be accounted for in terms of a dominant E/A contribution generated by ST_0M RPM and a minor net emissive component that may be due to TM CIDEP.

As shown in Fig. 4b and c, the addition of hydrochloric acid to this system gradually changed the EPR spectrum from E*/A to E/A*. This increase of the net absorptive polarization with the increase of HCl concentration cannot be explained by the increase of the contribution of the absorptive TM polarization because ^{3}CRCA* should have the emissive TM polarization as reported before [21,22]. The A/E/A pattern around the center of Fig. 4c can be explained by the overlap of the absorptive hf lines of the CRCA-K radical and the emissive center hf line of the CRCA-A radical. As shown in Fig. 4, the increase of HCl concentration increases the net A polarization in the hf lines of the 2-HP and the CRCA-K radicals, while the spectrum of the CRCA-A radical keeps the E*/A pattern. These results suggest that the CRCA-K and the CRCA-A radicals are generated through the different ways.



Scheme 2.

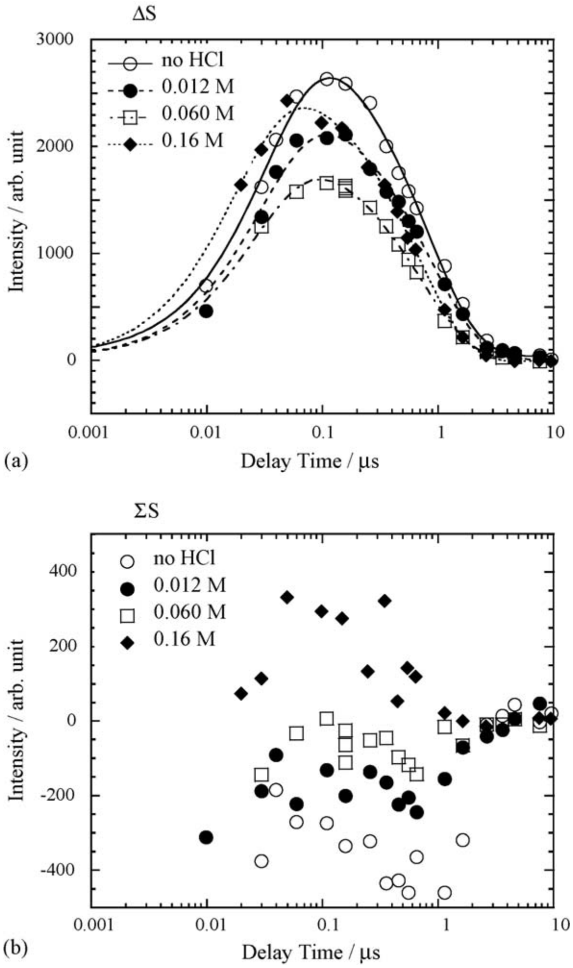


Fig. 5. Time developments of the difference of the intensities of the −1 and +1 hf lines (ΔS) and the sum of the intensities of the $M_I = \pm 1$ hf lines ($\sum S$) in the spectrum of the 2-HP radical observed on the photolysis of CRCA in 2-propanol with various HCl concentrations.

Fig. 5 shows the time developments of the $M_I = \pm 1$ hf lines of the 2-HP radical in the FT-EPR spectrum of the CRCA system for various HCl concentrations. As shown in Fig. 5a, the rise rate of the ΔS component gradually increased with the increase of HCl concentration. The $\sum S$ component in Fig. 5b clearly shows that the net polarization changes from emission to absorption with the increase of HCl concentration. The rise and decay rates given by least-squares fits of the ΔS data to Eq. (1) are listed in Table 1. The rise rate in 0.16 M HCl system (5.2×10^7 s^{-1}) is probably instrument controlled. The signal decay rates of the ΔS data are also larger than the reported $1/T_1^R$ value of the 2-HP radical, suggesting that the chemical quenching of the 2-HP radical, such as an addition reaction to the non-aromatic double bond of CRCA, also occurred. The second-order reaction rate constant for ^{3}CRCA* with HCl roughly estimated from the dependence of k_f on the HCl concentration is 1.5×10^8 M^{-1} s^{-1}, which is the same order as that for ^{3}CR*.

Fig. 6 shows the time developments of the hf lines of the CRCA-A radical marked by asterisks in Fig. 4. As shown in

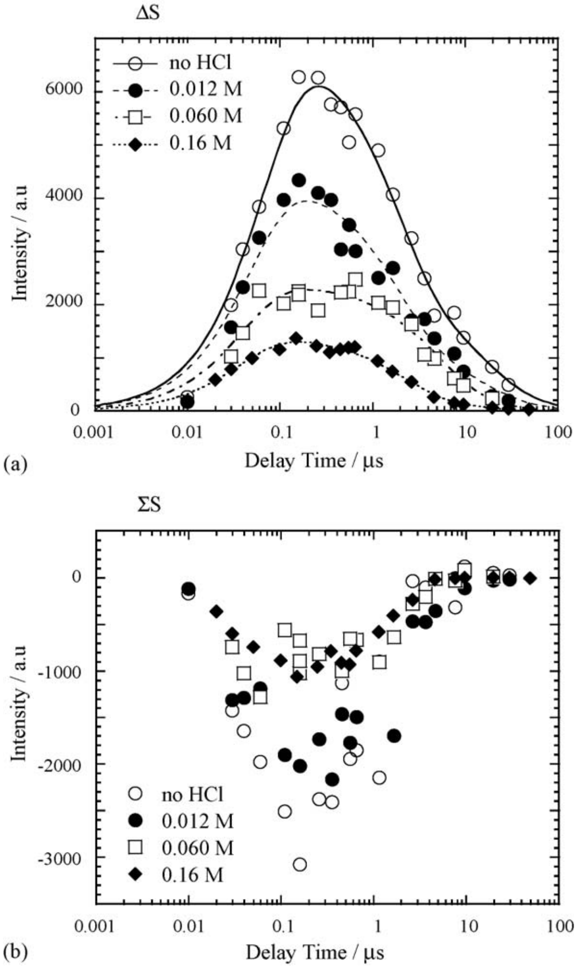


Fig. 6. Time developments of the difference of the intensities of the high and low field lines (ΔS) and the sum of the intensities of the high and low field lines ($\sum S$) in the spectrum of the CRCA-A radical observed on the photolysis of CRCA in 2-propanol with various HCl concentrations.

Fig. 6a, with the increase of the HCl concentration, the intensity of ΔS component gradually decreased, and the rise rate of the ΔS component slightly increased. The $\sum S$ component shown in Fig. 6b keeps emissive character, and slightly decreased in intensity with the increase of the HCl concentration. The rise and decay rates given by least-squares fits of the ΔS data to Eq. (1) are also listed in Table 1. The decay of the ΔS data of the CRCA-A radical was explained by the spin–lattice relaxation ($1/T_1^{\mathrm{R}} = 5.6 \times 10^5\,\mathrm{s}^{-1}$) and the second-order decay of the small contribution of F-pair polarization [13]. In every HCl concentration, the rise rate constant for the CRCA-A radical is different from that obtained for the 2-HP radical. The amount of the increase in the rise rate constant for the CRCA-A radical with HCl concentration is smaller than that for the 2-HP radical. Although the HCl addition accelerated the quenching of ^{3}CRCA*, the EPR signal intensity of radicals did not increase much, probably suggesting the existence of non-reactive quenching process by HCl for ^{3}CRCA* [13].

The present results on CRCA suggest that the CRCA-K and the CRCA-A radicals are generated by the independent processes. The possible reaction mechanism was shown in Scheme 2. The hydrogen abstraction on the carbon double bond of ^{3}CRCA* produces the CRCA-A and the 2-HP radicals as shown in Scheme 2(a). This reaction (the $^3\pi\pi^*$ character reaction) occurs whether HCl exists in the system or not, and gives the radicals the excess emissive polarization (E*/A). On the other hand, the hydrogen abstraction on the carbonyl group of ^{3}CRCA* in the absence of HCl produces directly the CRCA-K and the 2-HP radicals as shown in Scheme 2(b). The produced polarization on the radicals is a symmetrical E/A type originated from the ST$_0$M RPM. With the existence of HCl, the reaction between ^{3}CRCA* and HCl shown in Scheme 2(c) (the ^{3}nπ^* character reaction) occurs and dominates the reaction of Scheme 2(b). This reaction finally produces the CRCA-K and the 2-HP radicals, however, the polarization on the radicals is absorptive.

3.3. Reaction and absorptive polarization generating mechanisms

Xn, CR, and CRCA are known to a group of aromatic carbonyl compounds of which the lowest triplet state T$_1$ is $^3\pi\pi^*$ and is lying closely to the second triplet state T$_2$ with ^{3}nπ^* character. The anomalous behavior on CIDEP spectra of these compounds induced by HCl addition probably relates to such a property of their triplet states. Common features of the anomalous CIDEP in these Xn, CR, CRCA systems are as follows. (1) The absorptive polarization was induced in the ketyl and alcohol radicals, while the lowest triplet state should have emissive character. (2) The radical yields (overall EPR signal intensities) did not increase much (or reduces) although the fast quenching of the triplet by HCl occurred. From these facts, the generation mechanism of the absorptive polarization is discussed.

From the results of the CRCA system, the CRCA-K and CRCA-A radicals seems to be produced from different states, such as T$_1$ and T$_2$. The population between T$_1$ and T$_2$ is considered to be unequilibrated just after the photoexcitation and to relax into the thermal equilibration by the internal conversion (IC). If the simultaneous reactions from T$_1$ and T$_2$ in the unequilibrated population occur, the different radicals which have the opposite net polarization each other can be generated. However, it needs sufficient lifetime ($\geq 10^{-9}$ s) of T$_2$ for the reaction, although the IC process between T$_1$ and T$_2$ is generally considered to be much faster. It was suggested that the T$_2$ state can be populated by Boltzmann distribution when the energy gap between T$_1$ and T$_2$ is quite small, and that the equilibrium population gives the possibility of the simultaneous reactions from T$_1$ and T$_2$ [25]. It was suggested that the absorptive polarization can be induced in the T$_2$ state by coupling with the closely-lying T$_1$ state [26]. However, in polar solvents such as 2-propanol, the energy gap between two triplet states is considered to be so large that the equilibrated population of T$_2$ should be negligibly small [16].

Recently, some systems were reported in which unusual net absorptive polarization was observed in the CIDEP spectra on the photoinduced electron transfer reactions [27,28]. For example, the photooxidation of benzoquinones by eosin Y induced the net absorptive polarization on the spectra of the benzoquinone anion radicals, while the triplet state of eosin Y should have emissive polarization. This net absorptive CIDEP was interpreted in terms of the sublevel-selective back electron transfer from the contact radical pairs or triplet exciplexes to the singlet manifolds. The spin–orbit coupling of the radical ion pair (RIP) enhances these spin-sublevel selective isc. This phenomenon resembles to the absorptive CIDEP observed in the present CR and CRCA systems, although the radicals observed in the present systems were not ion radicals.

The ketyl and 2-HP radicals observed in the CR and CRCA systems seems to be produced by the hydrogen abstraction reaction of the triplet from solvent 2-propanol. However, for the reaction between the triplet ($^3CR^*$ or $^3CRCA^*$) and HCl, the RIP or the triplet exciplex which has charge-transfer character can be considered. Apparently, the presence of HCl or both H^+ and Cl^- is required to produce the net absorptive polarization because it was found that the addition of LiCl to these systems does not affect the spin polarization. Therefore, the intermediate triplet exciplex between CR (CRCA) and HCl for this system should be considered ($^3[CR\text{-}HCl]^*$ or $^3[CR\text{-}H^+\text{-}Cl^-]^*$) [13]. The net absorptive polarization in the free radicals can have its origin in the non-reactive quenching of the triplet state as the back charge-transfer through a triplet–singlet isc process that is expected to be highly sublevel dependent. If quenching from the upper spin sublevels is faster than quenching from the lowest level, then the reaction involving triplet exciplex will produce radicals with absorptive spin polarization. The escape process for the charge-transferred exciplex or the RIP may transiently produce the CRCA (or CR) anion radical and the Cl (or HCl^+) radical. In the acidic condition of these systems, the anion radical should capture a proton rapidly, and the ketyl radical is generated. Since the Cl radical rapidly abstracts a proton from 2-propanol solvent, the 2-HP radical is generated. These radical should conserve the absorptive spin polarization from their precursors. As a result, the absorptive polarization was induced in the ketyl and the 2-HP radicals which seem to be produced by the hydrogen abstraction reaction. For the existence of the competing non-reactive process as the back charge transfer, the quantum yield of the hydrogen abstraction reaction is relatively low despite of the increase of the reaction rate. It is noted that this mechanism is essentially similar to the spin–orbit coupling mechanism in the electron transfer described above [27]. The difference between Xn and CRCA (CR) in the rate constants of the reactions with HCl is considered to come from the efficiency of the charge transfer and the back charge-transfer in the exciplex (RIP) controlled with some factors (for example, D value: the zero-field splitting constant) as suggested in the spin–orbit coupling mechanism [27]. However, it is not clear why these absorptive CIDEP induced by HCl could be observed for CR, CRCA, and Xn systems and could not for other systems of their related molecules, such as flavone. There should be a reason relating to their triplet state properties for enhancing this spin-selective process.

On the other hand, the CRCA-A radical showed an E^*/A polarization explained by the ordinary TM and the ST_0M RPM whether HCl was included or not. The reason for this might be that the CRCA-A radical was produced through the normal hydrogen abstraction reaction of $^3CRCA^*$ from 2-propanol. The relative increase of the net emissive contribution in the spectrum of the CRCA-A radical with the HCl concentration was caused by the decrease of the ST_0M RPM polarization in later time region for the fast quenching of $^3CRCA^*$ with HCl in the early stage. The formation reaction of the CRCA-A radical should be competing with the other process which produced CRCA-K radical.

4. Conclusions

The anomalous net absorptive CIDEP spectra observed in the photoinduced hydrogen abstraction reaction of CR and CRCA from 2-propanol with addition of HCl were investigated with FT-EPR. In neat 2-propanol, the spectra of the ketyl and 2-HP radicals display E^*/A or E/A type polarization, which is explained by the ST_0M RPM and minor contributions of TM. The addition of HCl to these systems gives the net absorptive CIDEP spectra, while the triplet states of CR and CRCA should have emissive polarizations. The analysis of the time developments of the EPR signals indicates that the radical generation rate increases with the increase of the HCl concentration, while the signal intensity of the radicals does not increase. The net absorptive polarization might be explained by non-reactive quenching of the triplet by the spin-sublevel dependent back charge-transfer process in the intermediate exciplex. This mechanism is essentially similar to the reported spin–orbit coupling mechanism in the electron transfer reaction.

Acknowledgments

K.O. is grateful to Professor N. Hirota. This work was partly supported by Grants-in-Aid for Encouragement of Young Scientists (11740328) and for the Scientific Research C (16550016) from the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References

[1] H.J. Pownall, J.R. Huber, J. Am. Chem. Soc. 93 (1971) 6429.
[2] A. Chakrabarti, N. Hirota, J. Phys. Chem. 80 (1976) 2966.
[3] J.J. Cavaleri, K. Prater, R.M. Bowman, Chem. Phys. Lett. 259 (1996) 495.
[4] J.C. Scaiano, J. Am. Chem. Soc. 102 (1980) 7747.
[5] H. Murai, M. Minami, Y. I'Haya, J. Phys. Chem. 92 (1988) 2120.
[6] H.J. Pownall, W.M. Mantulin, Mol. Phys. 31 (1976) 1393.
[7] R.E. Conors, P.S. Walsh, Chem. Phys. Lett. 52 (1977) 436.
[8] K.A. McLauchlan, J.H. Hore, in: A.J. Hoff (Ed.), Advanced EPR: Application in Biology and Biochemistry, Elsevier, Amsterdam, 1989.
[9] K.A. McLauchlan, in: L. Kevan, M.K. Bowman (Eds.), Modern Pulsed and Continuous-Wave Electron Spin Resonance, John Wiley & Sons, New York, 1990 (Chapter 7).
[10] H. van Willigen, P.R. Levstein, M.H. Ebersole, Chem. Rev. 93 (1993) 173.
[11] S. Nagakura, H. Hayashi, T. Azumi (Eds.), Dynamic Spin Chemistry, Kodansha, Tokyo, 1998 (Chapter 7).
[12] T. Koga, K. Ohara, K. Kuwata, H. Murai, J. Phys. Chem. A 101 (1997) 8021.
[13] K. Ohara, N. Hirota, D.M. Martino, H. van Willigen, J. Phys. Chem. A 102 (1998) 5433.

[14] K. Ohara, K. Mukai, Chem. Phys. Lett. 317 (2000) 619.
[15] K. Ohara, S. Nagaoka, K. Mukai, Bull. Chem. Soc. Jpn. 73 (2000) 37.
[16] Y. Yamada, S. Yamauchi, N. Hirota, Bull. Chem. Soc. Jpn. 55 (1982) 2046.
[17] K. Hamanoue, T. Nakayama, T. Miyake, H. Teranishi, Chem. Lett. (1981) 39.
[18] D.M. Martino, H. van Willigen, J. Phys. Chem. A 104 (2000) 10701.
[19] K. Ohara, N. Hirota, C.A. Steren, H. van Willigen, Chem. Phys. Lett. 232 (1995) 169.
[20] P.R. Levstein, H. van Willigen, J. Chem. Phys. 95 (1991) 900.
[21] M. Igarashi, Y. Sakaguchi, H. Hayashi, Y. I'Haya, Chem. Phys. Lett. 181 (1991) 187.
[22] Y. Sakaguchi, M. Igarashi, H. Hayashi, Zeitschrift fur Physikalische Chemie 182 (1993) 77.
[23] A. Kawai, T. Okutsu, K. Obi, Chem. Phys. Lett. 174 (1990) 213.
[24] K. Ohara, N. Hirota, Bull. Chem. Soc. Jpn. 69 (1996) 1517.
[25] P.J. Wagner, A.E. Kemppainen, H.N. Schott, J. Am. Chem. Soc. 95 (1973) 5604.
[26] H. Hayashi, Y. Sakaguchi, H. Murai, Y. I'Haya, J. Phys. Chem. 90 (1986) 4403.
[27] S. Tero-Kubota, A. Katsuki, Y. Kobori, J. Photochem. Photobiol. C: Photochem. Rev. 2 (2001) 17.
[28] K. Katsuki, K. Akiyama, Y. Ikegami, S. Tero-Kubota, J. Am. Chem. Soc. 116 (1994) 12065.