

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

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

Available online 24 January 2006

## 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<sub>0</sub> 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.

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**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 <sup>3</sup>ππ\* and <sup>3</sup>nπ\* states gives rise to unique features of triplet Xn (<sup>3</sup>Xn\*), 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 (<sup>3</sup>Xn\* or <sup>3</sup>CRCA\*), giving rise to emissive polarization. (2) The ST<sub>0</sub> mixing (ST<sub>0</sub>M) 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

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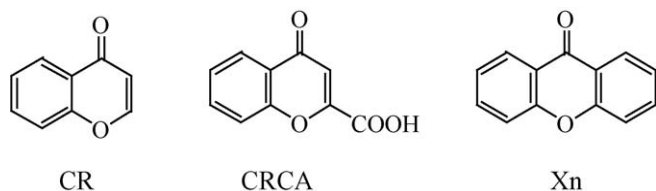


Fig. 1. Molecular structures of chromone (CR), chromone-2-carboxylic acid (CRCA), and xanthone (Xn).

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  ${}^3\text{CRCA}^*$  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  $(2\text{--}3) \times 10^{-8}$  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  $1.0 \times 10^{-2}$  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  $\mu\text{s}$  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 ( ${}^3\text{CR}^*$ ) 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  $\text{ST}_0\text{M}$  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  ${}^3\text{CR}^*$  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

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