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Photodecarboxylation of chromone-2-carboxylic acid in aerated and deaerated ethanol solution

Hiroki Kawata [a,*], Tsutomu Kumagai [b], Tadayoshi Morita [b], Shigeya Niizuma [a]

[a] *Faculty of Humanities and Social Sciences, Iwate University, Morioka 020-8550, Japan*
[b] *Graduate School of Science, Tohoku University, Sendai 980-0845, Japan*

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Abstract

The typical photodecarboxylation of chromone-2-carboxylic acid occurs in aerated and deaerated ethanol solutions to afford 4-hydroxycoumarin and 2-(1′-hydroxyethyl)-chromone, respectively. The former proceeds through an addition of the ground state oxygen molecule, while the latter through the recombination between the ketyl radical and the 1-hydroxyethyl radical followed by the release of CO_2.

Chemiluminescence technique was successfully applied to detect ketohydroperoxide intermediates assumed in the photoreaction of the aerated system. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chromone-2-carboxylic acid; Ketyl radical; Photooxygenation; Decarboxylation; CIDEP; Chemiluminescence

1. Introduction

Flavone and flavonol derivatives are well known as a pale yellow or an orange color chromophores involved in higher plants. We previously investigated the photoreaction of flavone itself, the photoproducts being diastereomers, the dimers of flavanone [1]. This reaction proceeds via a ketyl radical formed by the hydrogen abstraction from the solvent. It naturally occurs only in deaerated system. Nakayama et al. [2] reported the photoreaction of chromone in 3-methylpentane and ethanol solutions, where the photoproduct was the chromanone derivatives. All the photoproducts for the above reactions have the flavanone structure. On the other hand, some of the flavone derivatives show the photooxygenation in oxygen saturated solutions [3,4], though the reaction does not proceed without a sensitizer such as rose bengal or methylene blue which makes a singlet oxygen molecule.

On irradiation of chromone-2-carboxylic acid (**1**), the photoproduct in aerated ethanol (4-hydroxycoumarin) is quite different from that in deaerated condition (2-(1′-hydroxyethyl)-chromone) though both are the decarboxylated compounds of **1**. The photodecarboxylation reactions are grouped into two types; one is the direct cleavage of C–COOH bond as observed in the reaction of phenylacetic acid [5] and the other is the photosensitized reaction to yield the carboxyl radical [6,7]. In our case, however, the carboxyl group of **1** is replaced by an oxygen molecule or a solvent molecule both in aerated and deaerated systems, which being so called the photoreplacement reaction. The product in deaerated system is not a reductant of **1** contrary to the predicted species in the reaction of flavone derivatives involving the ketyl radical intermediate, while the product of the photolysis of 2-methoxycarbonylchromone is the chromanone derivatives, just the same with the case of chromone itself. On the photoreaction in aerated system, the chemiluminescence technique was applied to detect a ketohydroperoxide intermediate postulated in the photoreaction of **1**. We now report the intriguing photoreaction of **1** in aerated and deaerated ethanol solutions using the continuous light irradiation, the chemiluminescence, the flash photolysis and the ESR techniques.

2. Experimental

Chromone-2-carboxylic acid (Aldrich Chem. Co.) was recrystallized twice from ethanol on activated charcoal in red light. 2-Methoxycarbonyl-chromone was synthesized according to the literature [8]. 500 W Xe lamp (USHIO Inc.) with a Pyrex filter was used for the large scale steady state irradiation of **1** in a cylindrical quartz cell of 200 cm^3, cooled with water. The solutions are aerated under bubbling air or deaerated with argon. The feature of the photoreaction in argon saturated sample is quite the same as that

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[*] Corresponding author.

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degassed by the freeze-pump-thaw cycles. The reaction was monitored by HPLC with methanol–water–acetic acid (60:40:3 v/v/v) solvent. For a quantitative inspection of the photoreaction of **1**, the light from the 150 W xenon lamp was irradiated to the solution in a 1 cm × 1 cm × 4 cm quartz cell. The photoproducts were separated by TLC of silica gel 60 with benzene and methanol in the ratio of 8:2.

The quantum yield for the disappearance of **1** was measured with the irradiation of UXL-150D (USHIO Inc.) xenon short arc lamp equipped with a 313 nm interference filter (Nihon Shinku Kogaku Inc.). The light intensity was determined by a potassium trisoxalatoferrate(III) actinometer.

The microsecond flash photolysis was carried out using a conventional apparatus. The flash energy was about 90 J and full width at half-maximum was about 20 μs. A Pyrex filter was used for the excitation. Nanosecond laser flash photolysis was performed using 266 nm light pulse from a Nd^{3+}-YAG laser. The concentration of **1** in flash photolysis was 1.0×10^{-3} mol dm^{-3}. The chemiluminescence was measured using a chemiluminescence detector model CLD-110 (Tohoku Electronic Ind. Co., Ltd.) based on a single photon-counting method and the amount detected corresponds to the total photons over the wavelength region between 300 and 650 nm. CIDEP spectrum was measured by cw-TRESR method for the solution of **1** of 0.001 mol dm^{-3} in ethanol with bubbling nitrogen gas. 308 nm pulse from an eximer laser (LPX205icc, Lambda Physik) was used for the excitation light.

*2.1. Preparation of 4-hydroxycoumarin (**2**) and 2-(1′-hydroxyethyl)-chromone (**13**)*

Irradiation of **1** (70 mg in 200 cm^3) bubbling with air for 6 h gives **2** of 41.8 mg (70%) through the silica gel column. Irradiation of **1** of 50 mg in 200 cm^3 argon saturated ethanol for 5 h gives **13** of 28 mg (56%).

3. Results and discussion

3.1. Steady irradiation in air saturated system [9][1]

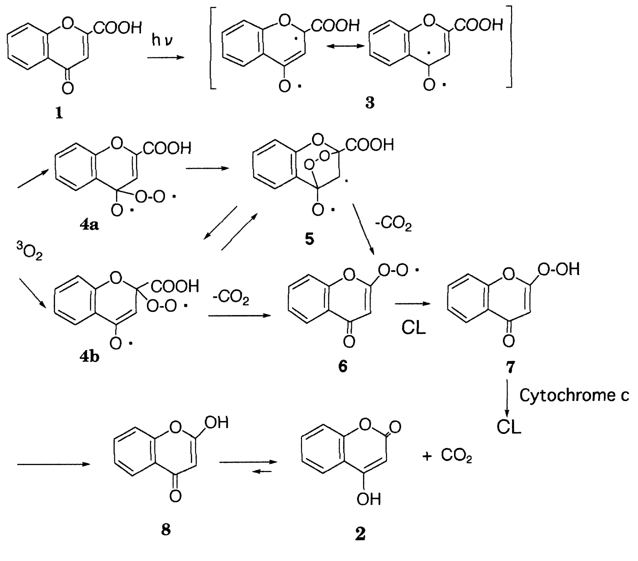
Irradiation of **1** in air saturated ethanol gives only 4-hydroxycoumarin (**2**).[2] The time course of the photoreaction is monitored by HPLC shown in Table 1. The quantum yield for the disappearance of **1** with 313 nm irradiation is 0.02 at 20°C. Quite the same photoreaction occurs in aerated alcohols other than ethanol, such as methanol and 2-propanol. Upon irradiation of chromone, flavone and 2-methoxycarbonylchromone in aerated ethanol solutions, little changes in the absorption spectra are observed, though they react in deaerated systems. Clearly, the carboxyl group at 2 position is prerequisite for the photoreaction of **1**. In spite of the decarboxylation product of **1**, **2** contains an extra oxygen atom. **2** was also confirmed not to be generated by means of the photosensitized oxygenation, e.g. the photoexcitation of oxygen saturated ethanol solution of **1** under the existence of methylene blue or rose bengal. These facts indicate that the singlet oxygen does not take part in the photoreaction of **1**.

Table 1
Photolysis of **1** at various times[a]

Irradiation time (min)	Consumption of **1** (%)	Yield of **2** (%)
20	11.5	9.2
50	28.4	23.5
90	47.8	41.3
130	64.7	57.1

[a] 20 mg of **1** in 200 ml ethanol was irradiated.

From the above results, Scheme 1 is offered for the photoreaction of **1** in aerated ethanol solution. We take notice of the biradical property of n-π* triplet state of **1** and propose **3** first as a transient analogous to that in the photorearrangement reaction of cyclohexenone or cyclohexadienone [10]. Oxygen molecule is a good quencher of the excited triplet states of most organic compounds through the formation of an exciplex or an energy transfer. In this case, the rate of the reaction between $^3\mathbf{1}^*$ and oxygen molecule is quite fast compared to that of the hydrogen abstraction from the solvent, so the ketyl radical is not detected in flash photolysis in



Scheme 1.

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[1] Photoreaction in aerated system has been briefly mentioned in a preliminary report.

[2] Spectral data for **2**: mp 216–217°C (colorless powder). Anal: Calcd. for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.61; H, 3.86; HR Mass: 162.0267 (Calcd. for $C_9H_6O_3$: 162.0317); IR (KBr); 3083, 3059, 1648, 1614, 1543 cm^{-1}: ^{1}H NMR (DMSO-d6, 600 MHz); 5693 (H_4, s), 7.440 (H_6, dd, $J = 7.8, 7.5$ Hz), 7.464 (H_8, d, $J = 8.5$ Hz), 7.737 (H_7, dd, $J = 8.5, 7.5$ Hz), 7.916 (H_5, d, $J = 7.8$ Hz), 12.03 (OH): ^{13}C NMR (DMSO-d6, 150 MHz); 90.996 (C_3), 115.806 (C_{4a}), 116.391 (C_8), 123.225 (C_5), 123.952 (C_6), 132.734 (C_7), 153.537 (C_{1a}), 161.922 (C_3 and C_4), 165.710 (C_2).

aerated system (see Section 3.3). Two pathways to **2** are considered; one is that the ground state oxygen molecule attacks the 2-position of the biradical generating peroxy radical **4b** and the other is the attack at C_4-position giving peroxy radical **4a** followed by cyclization to endo-peroxide **5** [11]. Both the biradical **4b** and **5**, are precursors for the peroxyradical **6** and the ketoperoxid **7**. **7** is the end-product in the photoreaction and is relatively stable in the solution. When we try to separate and purify the photoproduct, however, **7** goes to 2-hydroxychromone (**8**) on a silica gel column or TLC plates (discussed later in Section 3.2). **2** is a tautomer form of **8** and the equilibrium may lie probably so far to the right side. Therefore, we obtain only **2** as a purified product. The photooxygenation by a superoxide may be eliminated because of the absence of the sensitizer to form a superoxide in this system. **1** itself cannot be an electron donor to the oxygen molecule due to the presence of the carboxyl group. Matsuura et al. [3] and Chou and Martinez [4] investigated the photosensitized oxygenation of 3-hydroxyflavone (3-HF). They postulated a hydroperoxide as an intermediate and concluded that the presence of a hydroxyl group is indispensable for the photooxygenation, because 3-methoxyflavone, which cannot be involved in an ESPT (excited state proton transfer) [12,13], did not show the photooxygenation. Especially, the direct excitation of 3-HF in oxygen saturated nonpolar solvents gave the same product as that of the sensitization experiment [4]. The idea of the addition of oxygen molecule to 2-position of flavone ring is the same as ours. We tried to identify the ketohydroperoxide postulated in Scheme 1 using a chemiluminescence method as given below.

3.2. Chemiluminescence

Chemiluminescence (CL) is observed as is often the case when the peroxides such as 1,2-dioxetane or hydroperoxide decomposes. Therefore, the CL method can be used for the demonstration of the presence of peroxide intermediates in the reaction. By this method we could successfully detect the peroxy radical **6** and hydroperoxide **7** postulated in the photoreaction of **1** as in Scheme 1. The weak CL was observed at 23°C immediately after the irradiation of **1** (1.0×10^{-3} mol dm^{-3}) in the course of the reaction as shown in Fig. 1(a). The decay of the CL intensities is a single exponential with the rate constant of 4.2×10^{-4} s^{-1}. In blank test as in Fig. 1(b), all samples before irradiation as well as only the solvent irradiated show no CL, that is, the background count is 110 counts s^{-1} and is subtracted from the sample chemiluminescence counts for the analysis of its decay.

Cytochrome c is known to be a good CL catalyst in the hydroperoxide assay [14]. It cleaves R–O–OH to activated oxygens (RO$^\bullet$, O_2^-, HO$^\bullet$, $^1O_2$, etc.) which emit CL. Fig. 2(a) shows the CL time profile of the solution to which

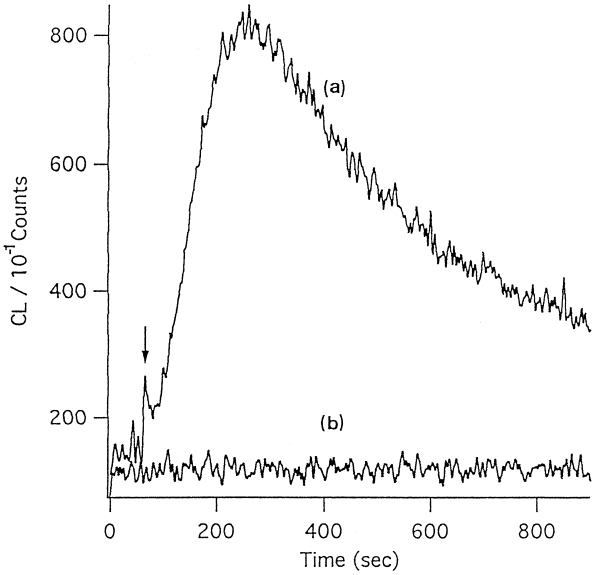

Fig. 2. Time profile of CL intensity with an addition (downward arrow point) of cytochrome c to (a) irradiated solution of **1** kept in the dark for 2 h; (b) the non-irradiated solution of **1** and the irradiated ethanol.

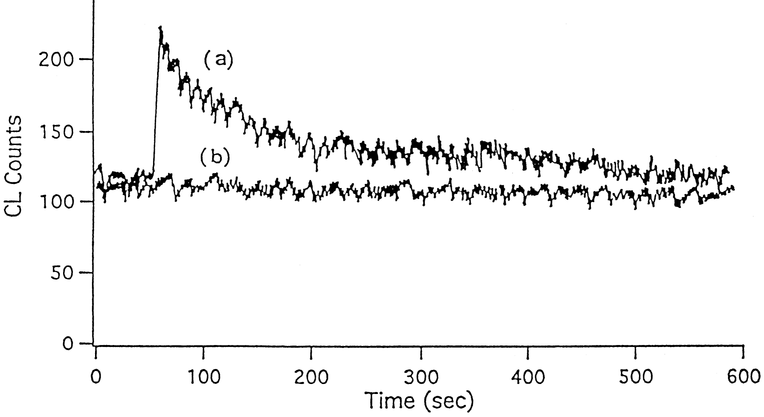

Fig. 1. Time profile of CL intensity: (a) CL of the solution immediately after the irradiation of **1**; (b) CL of the non-irradiated solution of **1** or the irradiated ethanol.

cytochrome c was added at the downward arrow point when the weak CL species in Fig. 1(a) had completely disappeared. The CL intensities are about 30 times strong compared with those of the original one and its decay rate constant ($2.5 \times 10^{-3}\,\mathrm{s}^{-1}$) is larger than that in Fig. 1(a). In blank test, samples before irradiation as well as the irradiated solvent ethanol show no CL when cytochrome c is added, as shown in Fig. 2(b). The traces of the emissive species or a new product formed by the irradiation of **1** containing cytochrome c were not observed except the trace of **2** in HPLC. No CL was observed when cytochrome c was added to the solution of **2**, which indicates the existence of the precursor of **2** (**7**) as a final product of the photoreaction.

It is evident there exists two peroxide species in the photolysis of **1**. We conclude the weak CL originates from the radical **6** and it goes to **7** with the rate constant of $4.2 \times 10^{-4}\,\mathrm{s}^{-1}$. The increasing and decreasing of CL intensities in Fig. 2(a) results from the amount change of the activated oxygens by the decomposition of ketohydroperoxide **7** with the addition of cytochrome c.

3.3. Photoreaction in deaerated system

On the steady irradiation of **1** in argon saturated ethanol, 2-(1′-hydroxyethyl)-chromone (**13**)[3] is the main photoproduct. The same reaction occurs in deaerated 2-propanol but its yield is rather low compared to that in ethanol [15]. The quantum yield for the disappearance of **1** in ethanol is 0.045 with 313 nm irradiation. In general, the photoproducts via a ketyl radical are mainly grouped into two types, one is the pinacol type coupling between ketyl radicals as observed in the reactions of xanthone [16,17] and *N*-methylacridone [18] and the other is the enol type coupling or the solvent radical addition at β position as those of flavone [1] and chromone [2]. The photoreaction of **1** seems to belong to the latter case, though the reaction mechanism is quite different in respect that the product is not the reduced form. The UV spectral changes on irradiation of 2-methoxycarbonylchromone (**9**) in ethanol are quite the same as that of chromone, where the photoproduct is 2-(1′-hydroxyethyl)-chromanone, the reductant of the chromone. The UV spectra of the chromanone itself and the product of the photoreaction of **9** are very similar to each other and their wavelength maxima are 322 and 321 nm, respectively. We can infer safely the product of the photoreaction of **9** to be a chromanone type. On the other hand, the UV spectral changes for the photoreaction of **1** are quite different from those of chromone and **9**, and that, the UV spectrum of the photoproduct is very similar to that of chromone itself, having the absorption maxima at the same wavelength (297 and 302 (sh) nm). The difference of the photolysis between **1** and **9** seems to be due to the difference of the properties between carboxyl and methoxy carbonyl group, the former being able to leave CO_2 but the latter not. The carboxyl group plays also a significant role in the photoreaction of the deaerated system just the same in that of aerated one.

The flash photolysis of **1** in argon saturated ethanol gives a transient which decays of the second order with the rate constant of $4.0 \times \varepsilon \times 10^3\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, where ε is the molar extinction coefficient of the transient at 355 nm, while no transient was observed in aerated system. Fig. 3 shows the transient absorption spectrum 100 μs after flashing and the decay curve of this transient at 355 nm. This spectrum resembles that of flavone ketyl radical. The amount of the ketyl radical by a dose decreases with increasing the concentration of ferrocene, a triplet quencher, though its decay rate is not affected by the additive. This means the photoreactive excited state is the triplet state of **1**. It was confirmed by the CIDEP experiment as discussed later. The reaction proceeds as follows (Scheme 2).

From the above scheme, Φ_0 and Φ (the yields of **10** in the absence and the presence of ferrocene, respectively) are represented as $\Phi_{\mathrm{isc}}\cdot k_{\mathrm{r}}[\mathrm{AH}]/(k_{\mathrm{r}}[\mathrm{AH}] + k_{\mathrm{d}})$ and $\Phi_{\mathrm{isc}}\cdot k_{\mathrm{r}}[\mathrm{AH}]/(k_{\mathrm{r}}[\mathrm{AH}] + k_{\mathrm{d}} + k_{\mathrm{q}}[\mathrm{Q}])$, respectively. AH, Q, **10**, k_{d}, k_{r} and k_{q} stand for ethanol, ferrocene, ketyl radical and the rate constants for processes in the scheme.

In the Stern–Volmer plots for the initial amount of ketyl radical by a dose shown in Fig. 4, the slope, $k_{\mathrm{q}}\tau$, is $3.0 \times 10^3\,\mathrm{dm^3\,mol^{-1}}$, where τ is equal to $(k_{\mathrm{r}}[\mathrm{AH}] + k_{\mathrm{d}})^{-1}$. If the quenching is a diffusion controlled reaction (k_{q} is calculated as $5.4 \times 10^9\,\mathrm{dm^3\,mol^{-1}}$ in ethanol), τ can be estimated to be $5.6 \times 10^{-6}\,\mathrm{s}$. The hydrogen abstraction reaction from ethanol also occurs in the flash photolysis of **9** but the subsequent reaction is quite different from that of **1** as mentioned above. The T–T absorption of **1** in argon saturated ethanol is observed with the same wavelength region of the ketyl radical absorption shown in Fig. 5. The decay is of first order with the rate constant of $2.4 \times 10^5\,\mathrm{s}^{-1}$, nearly equal to the calculated τ. After the disappearance of T–T absorption, the long-lived transient absorption of the ketyl radical (Fig. 5(c)) remains in the same wavelength region. The peak of the absorption band shifts to longer wavelength, the absorption peak of ketyl radical. No transient was observed in aerated system.

The CIDEP spectrum justifies the above argument as shown in Fig. 6(a) (1.2 μs after 308 nm pulse irradiation of $10^{-3}\,\mathrm{mol\,dm^{-3}}$ of **1** at −50°C). It consists of two components. One is the chromone ketyl radical and the other is the solvent radical, 1-hydroxyethyl radical; the former has a broad singlet emissive line (E signal) with $g = 2.0040$ induced by the triplet mechanism, the latter is emissive at

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[3] Spectral data for **13**: mp 89–90°C. Anal: Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; Found: C, 68.99; H, 5.41; Mass: 190 (M^+ 77.9%), 175 (14.1), 148 (10.6), 147 (base), 121 (15.3): IR (KBr) 3200, 300, 2850, 1651, 1628, 1468, 1121 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz); 1.607 (Me, d $J = 7.0$ Hz), 2.416 (OH, s), 4.748 (CHOH, broad q, $J = 7.0$ Hz), 6.475 (d, $J = 1.0$ Hz), 7.398 (ddd, 8.0, 7.0, 1.0 Hz), 7.446 (dd, 8.5, 1.0 Hz), 8.190 (dd, 8.0, 2.0 Hz); ^{13}C NMR (MeOH-d4, 150 MHz); 21.426 (Me), 67.335 (CHOH), 107.323 (C_3), 117.920 (C_8), 123.918 (C_{4a}), 125.199 (C_5), 125.790 (C_6), 133.760 (C_7), 156.199 (C_{1a}), 170.558 (C_2), 178.542 (C_4); UV (EtOH); 228 (log ε 4.12), 242 (sh 3.98), 297 (3.88), 302 (sh 3.85).

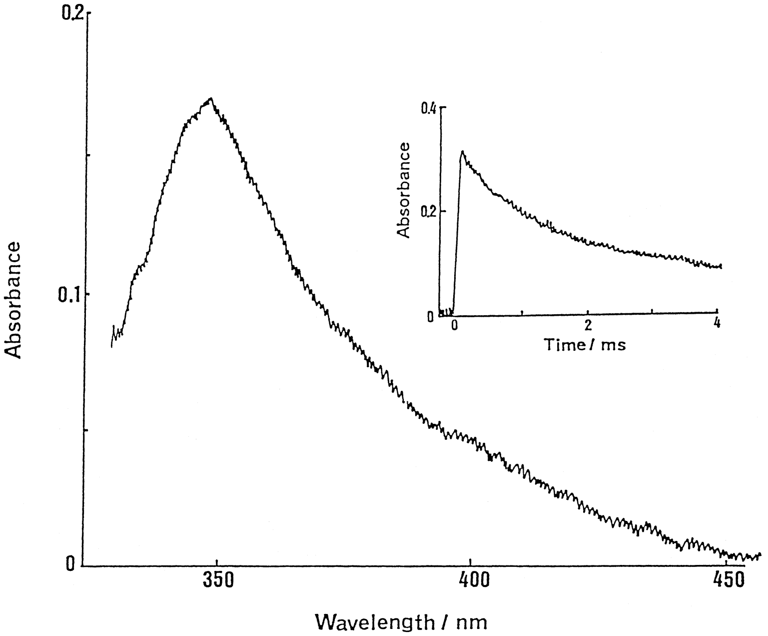


Fig. 3. Transient absorption spectrum 100 μs after flashing and the decay curve at 355 nm in deaerated ethanol solution observed by a microsecond flash photolysis.

lower field/absorptive at higher field lines (E/A signals) with $g = 2.0035$ by the radical pair mechanism (RPM). The g-value of 1-hydroxyethyl radical agrees closely with that in the literature [19]. Fig. 6(b) shows the simulation of CIDEP spectrum of 1-hydroxyethyl radical using the hfc from Fig. 6(a). The features of E phase CIDEP is very similar to that of flavone ketyl radical [1]. This implies that the photoreactive state is the triplet state of **1** and the first transient of the reaction is a ketyl radical formed by the hydrogen abstraction from ethanol.

We propose Scheme 3 for the photoreaction of **1** in deaerated system. The ketyl radical, 1-hydroxyethyl radical and **13** are identified as mentioned above and the carboxyl group of **1** is consequently substituted by 1-hydroxyethyl group. The first step of the reaction is the hydrogen abstraction from

$$^{1}\mathbf{1}^{*} \xrightarrow{k_{isc}} {}^{3}\mathbf{1}^{*}$$

$$^{3}\mathbf{1}^{*} \xrightarrow{k_{d}} \mathbf{1}$$

$$^{3}\mathbf{1}^{*} + \mathrm{AH} \xrightarrow{k_{r}} \mathbf{10}$$

$$^{3}\mathbf{1}^{*} + \mathrm{Q} \xrightarrow{k_{q}} \mathbf{1} + \mathrm{Q}^{*}$$

Scheme 2.

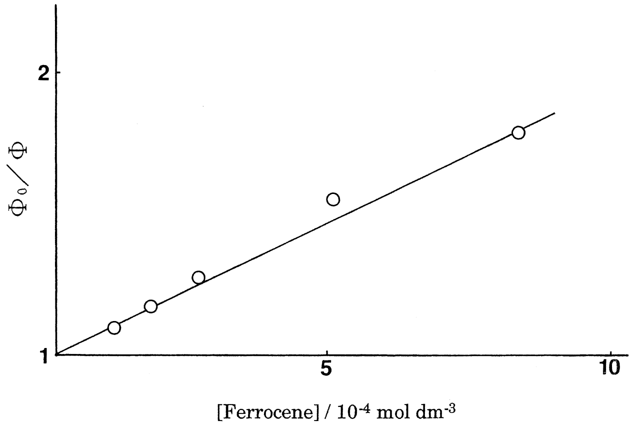


Fig. 4. Stern–Volmer plots of quenching by ferrocene for the initial yield of the ketyl radical formed by a dose of flashing.

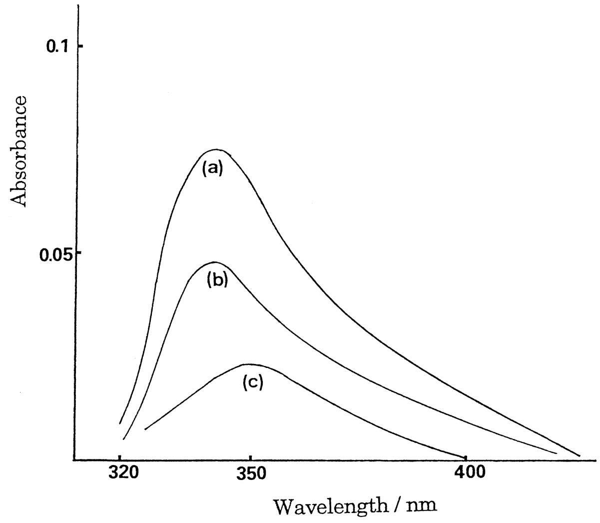


Fig. 5. T–T absorption spectra of **1**: (a) 1 μs, (b) 5 μs, (c) 50 μs after laser flashing.

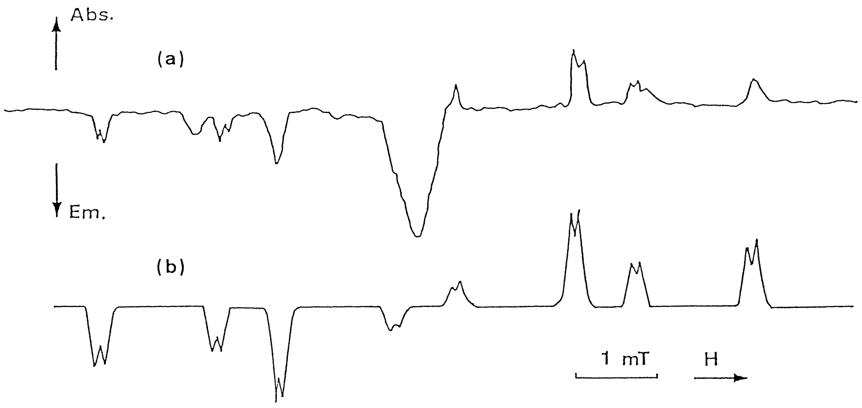
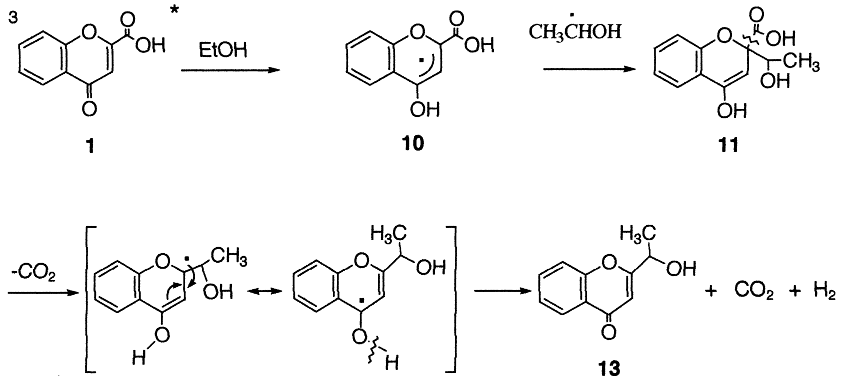
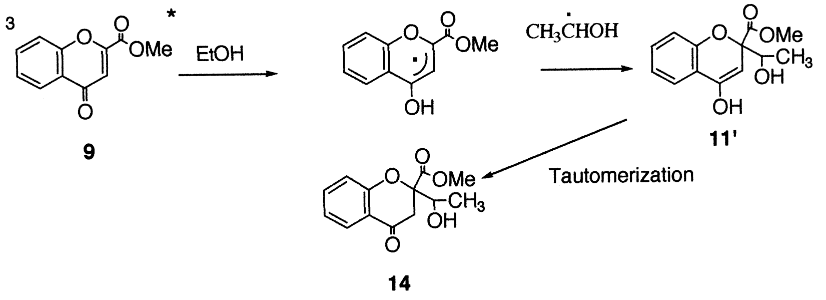


Fig. 6. (a) CIDEP spectrum of 1.2 μs after 308 nm pulse irradiation of the solution of **1** in ethanol at −50°C (0.8 mW). The overlap of a broad singlet line of ketyl radical with E phase pattern ($g = 2.0040$) and E/A RPM signals of 1-hydroxyethyl radical ($g = 2.0035$) is observed. (b) Simulation spectrum of 1-hydroxyethyl radical.



Scheme 3.



Scheme 4.

ethanol to yield the ketyl and 1-hydroxyethyl radical and then the alcohol radical attacks the ketyl radical at C_2 to **11**. The decarboxylation probably occurs simultaneously with the attack. In the photolysis of **9**, in contrast to **1**, **11**′ undergoes the tautomerization to the stable **14** similar to that of chromone itself shown in Scheme 4, since the methoxycarbonyl cannot release CO_2.

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