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Mechanistic investigations of the photosensitized reactions of iron arene complexes

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Abstract

The decomposition of cyclopentadienyliron(II) cumene hexafluorophosphate ([CpFe(Cum)]PF_6) was investigated by singlet and triplet sensitization. [CpFe(Cum)]PF_6 quenched the excited state of various sensitizers, and decomposition of [CpFe(Cum)]PF_6 efficiently took place in CH_2Cl_2. The quenching rate constants of fluorescence or T–T absorption of the sensitizers by [CpFe(Cum)]PF_6 were close to the diffusion rate constants. The rate constants were independent of the exo- or endo-thermicity of the photoinduced electron transfer process assumed to take place. However, they were dependent on the singlet and triplet excitation energies of [CpFe(Cum)]PF_6 and the sensitizers. Thus, the major quenching process would be the singlet and triplet energy transfer. In the case of using 3,3′-carbonyl-*bis*(7-diethylamino-coumarin) (KC-DA) as a visible-light-sensitizer, the decomposition of [CpFe(Cum)]PF_6 is inefficient, and a photochemically unstable intermediate was generated. © 1997 Elsevier Science S.A.

Keywords: Iron arene complex; Keto-coumarin; Photoreaction; Sensitization; Energy transfer

1. Introduction

A combination of an electron donor dye and cyclopentadienyl iron(II) arene complexes have been used as a photo-initiator of radical polymerization for a multi-functional acrylate monomer with high sensitivity (0.18 mJ cm^{-2}, 488 nm) [1]. Nesmeyanov et al. reported that the irradiation of a solution of iron arene complexes led to a release of arene and the formation of ferrocene [2]. Using this property, iron arene complexes have been used as a visible-light-sensitive photo-initiator for the polymerization of epoxides [3]. In addition, 9-methylanthracene as a sensitizer enhanced sensitivity (40 mJ cm^{-2}, 365 nm) for the photo-polymerization of epoxides [3]. The cationic polymerization is not inhibited by oxygen, therefore, the photo-crosslinking of epoxies has became a field of increasing interest.

Gill and Mann discovered that this reaction can be used to exchange the iron-bound arene for other ligands [4]. Further investigation of this reaction revealed that its quantum yield strongly depended on the counter ion [5], the polarity of the solvent [5], and arene substituents [6]. It was proposed that the photo-active species in this reaction is the $^3E_{1g}$ ligand field state of the iron arene complex [6]. This arene exchange reaction was sensitized by benzyl and anthracene in CH_2Cl_2 [6]. But, the mechanism of the sensitization and a quantitative analysis have not been examined.

In this study, the mechanism of the sensitized reaction of cyclopentadienyliron(II) cumene hexafluorophosphate ([CpFe(Cum)]PF_6) in the presence of several sensitizers having various excitation energies and redox potentials was investigated by the measurement of the quenching rate constant and reaction quantum yield. The possibility of a photo-induced electron transfer (PET) reaction is also discussed. In addition, the relations between the mechanism of sensitization and the decomposition of [CpFe(Cum)]PF_6 were investigated by product analysis. In the case of a combination of [CpFe(Cum)]PF_6 and 9,10-diphenylanthracene (DPA) or 3,3′-carbonyl-*bis*(7-diethylaminocoumarin) (KC-DA) as an excellent visible-light-sensitive sensitizer, the mechanism of sensitization was investigated in detail.

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2. Experimental

2.1. *Materials*

[CpFe(Cum)]PF_6 (Ciba-Geigy) was recrystallized from ethanol. KC-DA and coumarin-6 (C-6) (Eastman Kodak) were used without further purification. Spectroscopic grade dichloromethane (Dotite) or guaranteed grade dichloromethane (Wako) was used after distillation. Guaranteed grade sensitizers, anthracene (AN), benz[*a*]anthracene (BA), DPA, 9,10-dicyanoanthracene (DCA), perylene (PE), and tetracene (TE) were used after recrystallization from the appropriate solvent [7]. Michler's ketone (MK) was purified as reported [7].

2.2. *Light sources for photochemical reactions*

Light for the photochemical reaction was obtained from a 450-W Xe lamp with combinations of a Y-47 cut-off filter and a KL-49 interference filter (regarded as monochromatic light at 488 nm (the half-band width was 479–495 nm)) or a L-37 cut-off filter and a UV-D36B band-pass filter (regarded as monochromatic light at 365 nm (364–382 nm)). The intensity was measured using potassium ferrioxalate chemical actinometry [8] and a thermocouple detector (Eppley Lab., Model E6). The light was also obtained from a 150-W xenon lamp in a HITACHI F-4010 fluorescence spectrophotometer (band width = ±20 nm). The intensity was measured using actinometry and a Rhodamine B photon-counter.

2.3. *Direct photolysis of [CpFe(Cum)]PF$_6$ and photolysis by KC-DA sensitization*

A solution of [CpFe(Cum)]PF_6 in CH_2Cl_2 (2.5×10^{-2} M) prepared in a 1 cm × 1 cm quartz cuvette and saturated with argon was irradiated at 488 nm in a water bath to keep the temperature constant (18 ± 3 °C) and magnetically stirred during the irradiation.

The decomposition yield of [CpFe(Cum)]PF_6 was determined by a HPLC (JASCO 880-PU and 875-UV, monitored at 254 nm using an ODS column: ODS-1251-N, Senshu Pak, eluted by methanol:H_2O = 95:5) or by measurement of the absorbance at 242 nm of [CpFe(Cum)]PF_6 ($\varepsilon_{242} = 1.4\times10^4$ M^{-1} cm^{-1}).

An assignment of the photochemical products was carried out by a GC–MS (Shimadzu QP-2000). Yields of cumene and ferrocene were determined by GC (Shimadzu GC-14A) with a capillary column (Shimadzu CBP1-M25-025, equivalent to OV-1).

The yield of Fe^{2+} was determined by the measurement of absorbance of $Fe(phen)_3$ at 510 nm after the addition of a solution of 1,10-phenanthroline (phen, 0.1 wt%) in CH_2Cl_2 [8].

A solution of [CpFe(Cum)]PF_6 in CH_2Cl_2 (5.0×10^{-3} M) in the presence of KC-DA (2.7×10^{-4} M) was irradiated in the same manner as for the direct photolysis.

To determine the molar extinction coefficient (ε) of the intermediate photochemically generated, a solution of KC-DA in CH_2Cl_2 (2.5×10^{-4} M) in the presence of [CpFe(Cum)]PF_6 (2.0×10^{-3} M) was irradiated by a 450-W xenon lamp through a L-39 filter. The absorption spectra of the irradiated solution was measured after a 30× dilution with CH_2Cl_2.

2.4. *Spectroscopic measurements*

Fluorescence spectra and fluorescence lifetimes were measured using a HITACHI F-4010 and a Horiba NEAS-1100 (single photon counting) fluorescence spectrometer, respectively. For NEAS-1100, excitation light was passed through a monochromator, and the emission was passed through the appropriate cut-off filter. The sample was saturated with nitrogen or argon.

The transient absorption spectra were measured using a laser-flash photolysis system composed of a Nd^{3+}:YAG laser (Continuum Surelite I-10) with detectors of a photodiode array (Princeton Instruments IRY-512G/RB SMA detector, gate: 18 ns) or a photomultiplier (Hamamatsu photonics, R636). In the case of T–T absorptions of DPA or PE measurement, the quantum yield of the intersystem crossing (Φ_{isc}) was very low, therefore, MK (1.7×10^{-5} M) was used as a triplet sensitizer.

To estimate the structure of a photochemical intermediate, IR spectra were measured by a Horiba FT-200 FT–IR spectrophotometer. [CpFe(Cum)]PF_6 (5.1×10^{-3} M) was prepared in the presence of KC-DA (4.9×10^{-3} M) in CH_2Cl_2, and irradiated with a 450-W xenon lamp through a L-39 cut-off filter. The solution after the irradiation was transferred to a liquid cell with 0.1 mm spacer.

2.5. *Redox potentials*

Cyclic voltammetry (BAS voltammograph CV-1B) was used to determine the redox potentials of the sensitizers and [CpFe(Cum)]PF_6. The sample was prepared in acetonitrile (0.01 M) in the presence of $(n\text{-}C_4H_9)_4N^+BF_4^-$ (0.1 M) as the supporting electrolyte and purged by nitrogen before and during the measurement. A Pt and an Ag/Ag^+ (RE-5 for nonaqueous solvent) electrodes were used as the working and reference electrodes, respectively.

3. Results

3.1. *Direct photolysis of [CpFe(Cum)]PF$_6$*

Table 1 shows the conversions and the quantum yields of the direct photolysis (488 nm) of [CpFe(Cum)]PF_6 (2.5×10^{-2} M) in CH_2Cl_2. The decomposition quantum

Table 1
Conversions and quantum yields of direct photolysis [a] of $[CpFe(Cum)]PF_6$ [b] in CH_2Cl_2

Irradiation time/min	Conversion/%	Production quantum yield (yield [c]/%)			
		Φ_{decomp}	Φ_{cumene}	$\Phi_{ferrocene}$	Φ_{Fe2+}
15	4.17	(1.41)	0.98(69)	–	0.27(38)
30	6.04	1.02	0.92(91)	0.24(47)	0.20(39)

[a] Using a 450-W xenon lamp through a Y-47 and a KL-49 filters.
[b] 2.5×10^{-2} M.
[c] Conversion yield.

Table 2
Excitation energies, fluorescence quantum yields and lifetimes of the singlet-excited state of sensitizers and their quenching rate constants (k_q^S) by $[CpFe(Cum)]PF_6$

Sens	E_S [a]/kcal mol^{-1}	Φ_f [b]	τ_S^0 [c]/ns	k_q^S [c]/M^{-1} s^{-1}
AN	74.4	0.27	2.44	8.2×10^9
DPA	69.3	0.95	7.93	1.3×10^{10}
DCA	65.5	0.87	12.9	1.4×10^{10}
PE	64.2	0.87	5.03	1.8×10^{10}
KC-DA	59.6 [d]	0.0064 [e]	0.41 [e]	– [f]
TE	59.5	0.16	2.99	8.4×10^9

[a] Calculated by λ_{0-0} band of fluorescence measured in CH_2Cl_2 at room temperature.
[b] Ref. [9].
[c] Measured by a single photon counting method in CH_2Cl_2 at room temperature.
[d] Estimated by the absorption and fluorescence spectra.
[e] Ref. [10].
[f] Fluorescence lifetime is too short to do a quenching experiment.

yields (Φ_{decomp}) were similar to the production quantum yield of cumene (Φ_{cum}) for all irradiation times. Φ_{decomp} and Φ_{cum} decreased with increasing irradiation time. At a short time irradiation, Φ_{decomp} and Φ_{cum} were greater than unity, and the production quantum yields of ferrocene (Φ_{ferro}) was unable to be detected since they were under the detection limit. The conversion yields of cumene were close to 100%, however, those of ferrocene and Fe^{2+} were rather small.

3.2. Fluorescence quenching of [CpFe(Cum)]PF$_6$

The fluorescence of AN, DPA, DCA, PE, TE, and KC-DA used as a sensitizer were quenched by $[CpFe(Cum)]PF_6$. The Stern–Volmer's equation (Eq. (1)) applies to the relation of the fluorescence lifetime of the sensitizer and the concentration of $[CpFe(Cum)]PF_6$,

$$\frac{\tau_S^0}{\tau_S} = 1 + k_q^S\tau_S^0[[CpFe(Cum)]PF_6] \qquad (1)$$

where τ_S^0 and τ_S are the fluorescence lifetimes of sensitizer in the absence and presence of $[CpFe(Cum)]PF_6$, k_q^S is the quenching rate constant of the singlet-excited sensitizer by $[CpFe(Cum)]PF_6$. The slope of the Stern–Volmer plots (τ_S^0/τ_S vs. concentration of $[CpFe(Cum)]PF_6$) of the fluorescence quenching of various sensitizers by $[CpFe(Cum)]PF_6$ corresponds to $k_q^S\times\tau_S^0$. The τ_S^0 and k_q^S are listed in Table 2. The k_q^S values obtained in this study are close to diffusion-controlled rate constant (k_{diff}) reported as 1.5×10^{10} M^{-1} s^{-1} in CH_2Cl_2 at 22 °C [11].

The fluorescence quenching of KC-DA by $[CpFe(Cum)]PF_6$ was unsuccessful because Φ_f was very small and τ_S was below the detection limit of the nano-second single-photon counting instrument [10].

3.3. Quenching of T–T absorptions of sensitizers by [CpFe(Cum)]PF$_6$

T–T absorption spectra of BA, AN, DPA, PE, and KC-DA were measured in CH_2Cl_2 saturated with nitrogen. If quenching of the triplet sensitizer by $[CpFe(Cum)]PF_6$ occurred, the slope of the Stern–Volmer's plot gives $k_q^T\tau_T^0$ (k_q^T is the quenching rate constant of the triplet sensitizer by $[CpFe(Cum)]PF_6$) similar to Eq. (1) replacing τ_S^0 and τ_S by the τ_T^0 and τ_T, respectively, which indicate the lifetimes of the T–T absorption observed at the absorption maximum wavelength (λ_T, similar wavelength as already reported [12]) in the absence and presence of $[CpFe(Cum)]PF_6$, respectively. The λ_T and τ_T^0 values, and k_q^T of the various triplet sensitizers are summarized in Table 3.

The T–T absorption of DPA (5×10^{-4} M) and PE (5×10^{-4} M) were measured in CH_2Cl_2 in the presence of MK (3.4×10^{-5} M) as a triplet sensitizer since Φ_{isc} of DPA and PE were small.

The T–T absorption of KC-DA (4.5×10^{-5} M) in CH_2Cl_2 between 400 to 480 nm was not detected since the ground-state of KC-DA absorption was very strong. The T–T absorption peak was located near 510 nm [14]. The decay profile of the triplet-excited KC-DA at 510 nm decayed single-exponentially, and the lifetime of the triplet KC-DA was determined to be 5.9 μs. However, the sample was rapidly discolored by the laser pulse, and the persistent absorption due to the intermediate was observed in the presence of $[CpFe(Cum)]PF_6$. Therefore, a quenching experiment was performed with monitoring at 725 nm as already reported [15].

Table 3
Parameters of triplet state of various sensitizers and quenching rate constants (k_q^T) of triplet-excited state of sensitizers by [CpFe(Cum)]PF_6

Sens	E_T [a]/kcal mol	Φ_{isc} [a]	λ_T [b]/nm	τ_T^0 [b]/μs	k_q^T [b]/M^{-1} s^{-1}
KC-DA	50.8 [c]	0.92 [c]	725	5.9	4.6×10^9
BA	47.2	0.79	484	14.1	4.9×10^9
AN	42.5	0.66	426	30.6	4.5×10^9
DPA	40.9	0.02	424	6.6	8.1×10^8
PE	36.0	0.0088	483	7.0	2.8×10^8

[a] Ref. [9].
[b] Measurement in CH_2Cl_2 saturated with N_2 at room temperature.
[c] Ref. [13].

3.4. Photolysis of [CpFe(Cum)]PF_6 by DPA or KC-DA sensitization

The $\Phi_{cum(DPA)}$ for photolysis (365 nm, 150-W xenon lamp) of [CpFe(Cum)]PF_6 (1.0×10^{-3} M) by sensitization of DPA (1.0×10^{-3} M) is 0.16.

[CpFe(Cum)]PF_6 has weak and broad absorption bands (λ_{max} at 389 and 455 nm have ε of 80 and 66 M^{-1} cm^{-1}, respectively) and KC-DA has a strong absorption band ($\varepsilon_{459}=9.2\times10^4$ M^{-1} cm^{-1}) in the visible region.

The conversions and the quantum yields for photolysis (488 nm) of [CpFe(Cum)]PF_6 (5.0×10^{-3} M) in the presence of KC-DA (2.7×10^{-4} M) as a sensitizer are summarized in Table 4. $\Phi_{decomp(KC\text{-}DA)}$ is the decomposition quantum yield of [CpFe(Cum)]PF_6 in the presence of KC-DA. Since cumene and ferrocene were slightly produced, the yields of cumene and ferrocene by GC were unable to be determined. $\Phi_{decomp(KC\text{-}DA)}$ are decreased with increasing irradiation time.

The changes in the absorption spectra of KC-DA (2.7×10^{-4} M) in the presence of [CpFe(Cum)]PF_6 (5.0×10^{-3} M) by irradiation at 488 nm were measured in argon purged CH_2Cl_2 (after 50 times dilution). By irradiation, the absorption of KC-DA peak ($\lambda_{max}=459$ nm, $\varepsilon_{459}=9.2\times10^4$ M^{-1} cm^{-1}) decreased and a new absorption band assigned to a photochemical intermediate appeared at wavelengths longer ($\lambda_{max}=500$ nm) than the absorption band of KC-DA. The intermediate absorption band gradually disappeared after the irradiation was stopped. At the same time, the absorption band of KC-DA recovered, and the absorption of the intermediate disappeared. The absorption band at 242 nm, which is attributed to [CpFe(Cum)]PF_6, was slightly decreased by the irradiation.

Table 4
Conversions and quantum yields of direct photolysis [a] of [CpFe-(Cum)]PF_6 [b] sensitization in CH_2Cl_2

Irradiation time/min	Conversion/%	$\Phi_{decomp(KC\text{-}DA)}$	Φ_{im} [c](yield [d]/%)
60	6.4	0.21	0.009(21)
120	12.9	0.14	0.008(19)
240	17.1	0.08	0.007(25)

[a] Using a 450-W xenon lamp through a Y-47 and a KL-49 filters.
[b] Concentrations of [CpFe(Cum)]PF_6 and KC-DA were 5.0×10^{-3} and 2.7×10^{-4} M, respectively.
[c] Quantum yield of formation of intermediate.
[d] Conversion yield.

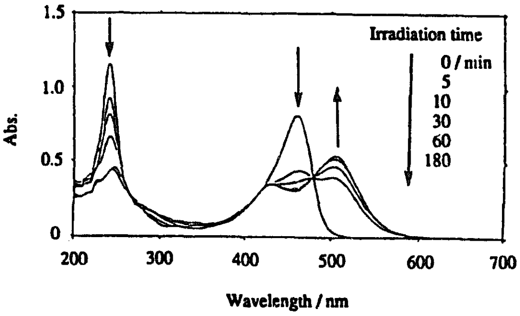


Fig. 1. Absorption spectra of KC-DA (2.5×10^{-4} M) in the presence of [CpFe(Cum)]PF_6 (2.0×10^{-3} M) before and after irradiation (by 450-W xenon lamp through a L-39 filter) in CH_2Cl_2 (Each spectrum was measured after 30 times dilution).

The molar extinction coefficient (ε) of the intermediate was determined by the procedures described in the experimental section. Fig. 1 shows that the change in the absorption spectra of KC-DA (2.5×10^{-4} M) in the presence of [CpFe(Cum)]PF_6 (2.0×10^{-3} M) by irradiation using a 450-W xenon lamp through a L-39 filter in argon purged CH_2Cl_2 (after 30 times dilution). The clear isosbestic points were observed at 426 and 478 nm. When the intermediate absorption had been saturated, it was assumed that all the KC-DA was converted into the intermediate. The absorbance was measured and ε were calculated; $\varepsilon_{459}=3.7\times10^4$ M^{-1} cm^{-1}, and $\varepsilon_{500}=6.1\times10^4$ M^{-1} cm^{-1}. Table 4 also shows Φ_{im}; the formation quantum yield of the intermediate.

3.5. Estimation of structure of intermediate

Fig. 2(a) shows that IR-spectral change of the solution of KC-DA (4.9×10^{-3} M) and [CpFe(Cum)]PF_6 (5.1×10^{-3} M) in CH_2Cl_2 by irradiation. Since a transparent area of CH_2Cl_2 solution expands from 2300 to 1500 cm^{-1}, the sample solution was monitored in this region. The IR spectrum of [CpFe(Cum)]PF_6 did not strongly appear in this region. The two stretching bands (ν(C=O)) of the δ-lactone carbonyl and ketone which combines two coumarin chromophores were observed at 1715 and 1588 cm^{-1}, respectively.

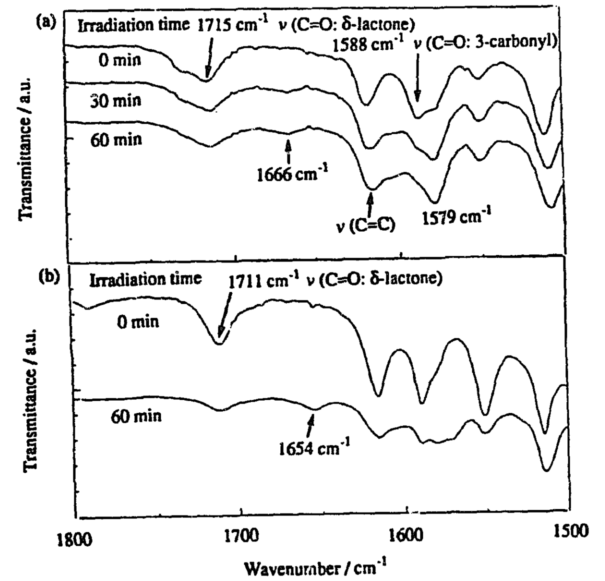


Fig. 2. IR spectra of KC-DA (4.9×10^{-3} M) in the presence of [CpFe(Cum)]PF_6 (5.1×10^{-3} M) (a), and IR spectra of C-6 (2.5×10^{-3} M) in the presence of [CpFe(Cum)]PF_6 (2.5×10^{-3} M) (b) before and after irradiation (by 450-W xenon lamp through a L-39 filter) in CH_2Cl_2.

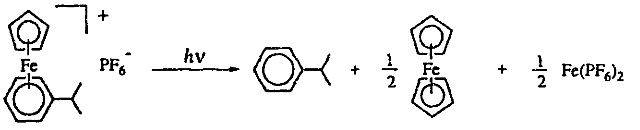
After irradiation, the two carbonyl bands at 1715 and 1588 cm^{-1} decreased in intensity and the absorption at 1666 and 1579 cm^{-1} increased in intensity.

A similar experiment was carried out for C-6. Fig. 2(b) shows the IR-spectral change in the solution of C-6 (2.5×10^{-5} M) in the presence of [CpFe(Cum)]PF_6 (2.5×10^{-5} M) in CH_2Cl_2 by irradiation. After irradiation, μ(C=O) of the δ-lactone of C-6 at 1711 cm^{-1} decreased in intensity with increasing the absorption at 1654 cm^{-1}.

4. Discussion

4.1. Direct photolysis of [CpFe(Cum)]PF_6

It is reported that the irradiation of [CpFe(Arene)]$^+$ leads to the dissociation of arene and the formation of ferrocene [2]. According to this, in the case of [CpFe(Cum)]PF_6 studied in this work, cumene must be dissociated after photoexcitation, and the two generated cyclopentadienyl iron cations must react each other to produce ferrocene. In the direct photolysis of [CpFe(Cum)]PF_6 in CH_2Cl_2, cumene and ferrocene were the only GC-detectable photoproducts and the quantum yield of decomposition of [CpFe(Cum)]PF_6 (Φ_{decomp}) and the formation of cumene (Φ_{cum}) were close to unity as shown in Table 1 (The Φ_{decomp} exceeded 1 at 15 min irradiation. However, it contained a large error (±30%) since the conversion was small). The conversion yield of cumene was approximately 100%, but those of ferrocene and Fe^{2+}, which are related to the recovery of iron, were lower than 50%. These results indicate that the decomposition of [CpFe(Cum)]PF_6 must be accompanied by the dissociation of cumene, however, the decomposition of [CpFe(Cum)]PF_6 would not occur according to the stoichiometry given in Scheme 1. The iron must be involved in the other products such as photo-generated precipitate which had not been assigned.



Scheme 1.

4.2. Quenching study of sensitizers by [CpFe(Cum)]PF_6

To investigate the sensitization mechanism of decomposition of [CpFe(Cum)]PF_6 via a singlet-excited state, the quenching studies for fluorescence of sensitizers by [CpFe(Cum)]PF_6 were performed. AN, DPA, DCA, PE, and TE were used as a sensitizer. The Stern–Volmer plots of the fluorescence lifetimes against concentration of [CpFe(Cum)]PF_6 were linear for all sensitizers. As shown in Table 2, k_q^S takes values between 1.8×10^{10} (PE) and $8.2\times10^{9}\ M^{-1}\ s^{-1}$ (AN). The E_S of [CpFe(Cum)]PF_6 was reported as 58.6 kcal mol^{-1}, therefore, the singlet energy transfer from all sensitizers used to [CpFe(Cum)]PF_6 are exothermic.

To consider the possibility of the PET between the excited state of sensitizers and [CpFe(Cum)]PF_6, the change of free energy (ΔG) by the PET is calculated by Rehm–Weller equation (Eq. (2)) [16]. ΔG_S for the PET from singlet-excited state of sensitizer to [CpFe(Cum)]PF_6 or vice versa PET from [CpFe(Cum)]PF_6 to singlet-excited state of sensitizer is given by

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06(E_{ox} - E_{red}) - E_{ex} \qquad (2)$$

where E_{ox} and E_{red} are an oxidation and a reduction potential of a sensitizer and [CpFe(Cum)]PF_6 ($E_{red} = -1.45$ V and $E_{ox} = 1.70$ V). E_{ex} (kcal mol^{-1}) is the excitation energy of the sensitizers, therefore this can be expressed here as E_S (the singlet excitation energy). As ΔG_S for various sensitizers summarized in Table 5, ΔG_S take negative values in the case of the PET from singlet-excited AN, DPA, and PE to [CpFe(Cum)]PF_6 and from [CpFe(Cum)]PF_6 to singlet-excited DCA. The data suggest that PET is not the mechanism of fluorescence quenching. These results indicate that [CpFe(Cum)]PF_6 acts as a singlet quencher and undergoes the singlet energy transfer from sensitizers whose E_S is larger than E_S of [CpFe(Cum)]PF_6. The fluorescence of sensitizers overlap to the weak absorption of [CpFe(Cum)]PF_6. However, it is thought that the energy transfer mechanism may be a collisional mechanism rather than resonance mechanism (Förster's mechanism) because $k_q^S \leq k_{diff}$.

Next, to investigate a triplet-state path of the sensitized reaction, quenching of T–T absorptions of various sensitizers by [CpFe(Cum)]PF_6 were examined. BE, AN, DPA, PE, and KC-DA were used as the sensitizers. Similar to the fluorescence quenching, the change in free energy (ΔG_T) for PET between the triplet sensitizers and [CpFe(Cum)]PF_6

Table 5
Redox potentials of [CpFe(Cum)]PF_6 and sensitizers and estimated change of free energies (ΔG) [a] by photoinduced electron transfer process

Sens	E_{ox} vs. SCE/V	E_{red} vs. SCE/V	ΔG/kcal mol^{-1}			
			Sens*/[CpFe(Cum)]PF_6 [b]		[CpFe(Cum)]PF_6/Sens* c	
			ΔG_S [d]	ΔG_T [e]	ΔG_S [d]	ΔG_T [e]
AN	1.16	−1.93	−14.2	17.7	9.3	41.2
DPA	1.18	−1.91	−8.7	19.7	13.9	42.3
DCA	–	−0.89	-	–	−5.8	17.9
PE	1.06	−1.68	−6.3	21.9	13.7	41.9
KC-DA	1.07	−1.23	−1.5	7.3	8.0	16.8
BA	1.18	−2.00	−12.8	13.4	11.9	38.1
TE	0.77	−1.58	−8.3	21.8	16.1	46.2

[a] Calculated by Rehm–Weller's equation. E_{ox} and E_{red} of [CpFe(Cum)]PF_6 are 1.70 and −1.45 V vs. SCE, respectively.
[b] PET from excited state of sensitizers to [CpFe(Cum)]PF_6 (sensitizers act as electron donor).
[c] PET from [CpFe(Cum)]PF_6 to excited state of sensitizers (sensitizers act as electron accepter).
[d] S indicates that the electron transfer reaction occured through the singlet excited state of sensitizers. Calculated using E_S listed in Table 2.
[e] T indicates that the electron transfer reaction occured through the triplet excited state of sensitizers. Calculated using E_T listed in Table 4.

are also calculated using Eq. (2), where E_{ex} can be replaced by E_T (kcal mol^{-1}, a triplet energy of sensitizer). ΔG_T takes positive values in all cases.

As listed in Table 3, k_q^T decreased with decreasing E_T of the sensitizers. Thus, the triplet quenching process is the only triplet energy transfer from these sensitizers. The k_q^T of AN ($E_T = 42.5$ kcal mol^{-1}) [19] is large, however, k_q^T of DCA ($E_T = 40.9$ kcal mol^{-1}) [19] and PE ($E_T = 36.0$ kcal mol^{-1}) [19] are much smaller than the k_{diff} (1.5×10^{10} M^{-1} s^{-1}) in CH_2Cl_2. By fitting k_q^T measured to Sandros's equation ($k_q^T/k_{diff} = (1+\exp(-\Delta E/RT))^{-1}$) [17], it is proposed that the E_T of [CpFe(Cum)]PF_6 would be 42 kcal mol^{-1}. It is slightly smaller than that of [CpFe(Cum)]PF_6 reported as 44 kcal mol^{-1} (estimated from the S–T absorption located at 650 nm) [6].

The decomposition must take place by T–T energy transfer through the excited triplet state of [CpFe(Cum)]PF_6 whose triplet state is reported to have an extremely short lifetime [18,19].

4.3. Sensitization mechanism for [CpFe(Cum)]PF_6 by DPA

Scheme 1 shows that the mechanism of decomposition of [CpFe(Cum)]PF_6 by sensitization. The Φ_S, Φ_T, and Φ_{isc} in the presence of [CpFe(Cum)]PF_6 are given by Eqs. (3)–(7).

$$\Phi_q^S = \frac{k_q^S[[\mathrm{CpFe(Cum)}]\mathrm{PF_6}]}{k_d^S + k_{isc} + k_q^S[[\mathrm{CpFe(Cum)}]\mathrm{PF_6}]} \tag{3}$$

$$\Phi_{isc} = \frac{k_{isc}}{k_d^S + k_{isc} + k_q^S[[\mathrm{CpFe(Cum)}]\mathrm{PF_6}]} \tag{4}$$

$$\Phi_q^T = \frac{k_q^T[[\mathrm{CpFe(Cum)}]\mathrm{PF_6}]}{k_d^T + k_q^T[[\mathrm{CpFe(Cum)}]\mathrm{PF_6}]} \tag{5}$$

$$k_{isc} = \Phi_{isc}^0 \times (k_d^S + k_{isc}) \tag{6}$$

$$k_{isc} = \frac{\Phi_{isc}^0 \times k_d^S}{1 - \Phi_{isc}^0} \tag{7}$$

where k_q^S is the quenching rate constant of the singlet-excited sensitizer by [CpFe(Cum)]PF_6, k_d^S is the deactivation rate constant of the singlet-excited sensitizer, k_{isc} is the intersystem crossing rate constants of the sensitizer, Φ_{isc}^0 is the quantum yields of the intersystem crossing in the absence of [CpFe(Cum)]PF_6, k_q^T is the quenching rate constant of the triplet sensitizer by [CpFe(Cum)]PF_6, and k_d^T is the deactivation rate constant of the triplet sensitizer.

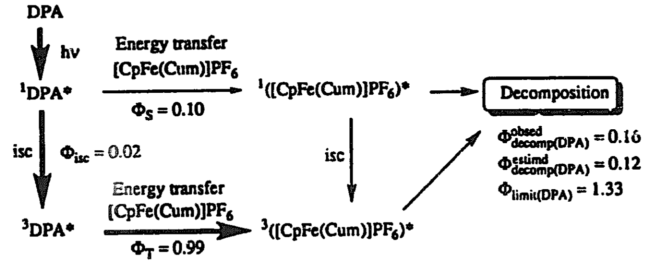
In the case of using DPA as a sensitizer ($k_q^S = 1.3\times10^{10}$ M^{-1} s^{-1}, $k_q^T = 8.1\times10^8$ M^{-1} s^{-1}) in the presence of [CpFe(Cum)]PF_6 (1.0×10^{-3} M), Φ_q^S, Φ_q^T and Φ_{isc} are determined to be 0.10, 0.99 and 0.02, respectively. The production quantum yield of cumene for photolysis (365 nm, 150-W xenon lamp) of [CpFe(Cum)]PF_6 (1.0×10^{-3} M) by sensitization of DPA (1.0×10^{-3} M) is 0.16.

To consider the sensitized mechanism for [CpFe(Cum)]PF_6, the efficiencies of quenching of the singlet-excited and triplet states of DPA by [CpFe(Cum)]PF_6 (Φ_q^S, Φ_q^T) are calculated. As shown in Table 6, in the case of the concentration of [[CpFe(Cum)]PF_6] = 1.0×10^{-3} M, Φ_q^S of DPA by [CpFe(Cum)]PF_6 is small, 0.10, because τ_S is short. Since τ_T of DPA is long and k_q^T is large, Φ_q^T is estimated to be 0.99. However, Φ_{isc} of DPA is very low (0.02), therefore, the efficiency of quenching via the triplet state of DPA ($\Phi_{isc}\times\Phi_q^T$) is 0.02. The total efficiency of quenching of the excited state DPA by [CpFe(Cum)]PF_6 ($\Phi^{estmd}{}_{decomp(DPA)}$) estimated from various rate constants ($\Phi_q^S + \Phi_{isc}\times\Phi_q^T$) is 0.12. In this case, the $\Phi_{cum(DPA)}$ was 0.16 (365 nm, a 150-W xenon lamp through a monochromator). The $\Phi^{obsed}{}_{decomp(DPA)}$ is assumed to be 0.16 because the Φ_{decomp} is almost the same Φ_{cum} as seen in the direct photolysis of [CpFe(Cum)]PF_6. The limiting decomposition quantum yield ($\Phi_{limit(DPA)}$) by the sensitization of [CpFe(Cum)]PF_6 is expressed as $\Phi^{obsed}{}_{decomp(DPA)}/\Phi^{estmd}{}_{decomp(DPA)}$, and is 1.33. This contains a small error because the absorption spectrum of [CpFe(Cum)]PF_6 spreads over the visible region and direct absorption by

Table 6
Efficiencies of sensitization of [CpFe(Cum)]PF_6 by DPA and KC-DA in CH_2Cl_2

Sens	Φ_{decomp}	Φ_q^S	Φ_{isc}	Φ_q^T	$\Phi_{isc} \times \Phi_q^T$	$\Phi_q^S + (\Phi_{isc} \times \Phi_q^T)$	Φ_{limit} [a]
DPA	0.16	0.10	0.02	0.99	0.02	0.12	1.33
KC-DA	0.21	0.17	0.76	0.99	0.75	0.92	0.23

[a] $\Phi_{limit} = \Phi_{decomp} / [\Phi_q^S + (\Phi_{isc} \times \Phi_q^T)]$.



Scheme 2.

[CpFe(Cum)]PF_6 which lead photo-degradation is unavoidable. These results indicate that [CpFe(Cum)]PF_6 is efficiently decomposed by DPA sensitization and a contribution of sensitization via a singlet-excited state is large when using DPA as a sensitizer. The mechanism of DPA sensitization is shown in Scheme 2.

Gill and Mann discovered that the reaction of arene release and ferrocene formation from [CpFe(Arene)]$^+$ can generally be used to exchange the iron-bound arene for other ligands [4]. They proposed that the photoactive species in this reaction was a $^3E_{1g}$ ligand field state of [CpFe(Arene)]$^+$ [6]. They also observed that triplet sensitizers (benzyl and AN) initiated the ligand substitution reaction [6]. It is thought that the triplet state of [CpFe(Cum)]PF_6 may quickly decompose, because the reported triplet lifetime of [CpFe(Cum)]PF_6 was shorter than 1.5 ns [18,19]. However, in our study, even the singlet-excited sensitizers also initiated the decomposition of [CpFe(Cum)]PF_6.

4.4. Photolysis of [CpFe(Cum)]PF$_6$ by KC-DA sensitization and estimation of intermediate structure

KC-DA has excellent properties as a triplet sensitizer for visible light; a large extinction coefficient ($\varepsilon_{459} = 9.2 \times 10^4$ M^{-1} cm^{-1}), very efficient intersystem crossing ($\Phi_{isc} = 0.92$ in benzene) [13], and long triplet lifetime (5.9 μs).

The decomposition quantum yields ($\Phi_{decomp(KC\text{-}DA)}$) for KC-DA sensitization of [CpFe(Cum)]PF_6 are decreased with increasing irradiation time. At conversion, 6.4, 12.9 and 17.1% (1, 2, 4 h irradiation time, respectively), $\Phi_{decomp(KC\text{-}DA)}$ is 0.21, 0.14 and 0.08, respectively. However, Φ_{im} is constant, ca. 0.01, at each irradiation time. The formation of the intermediate might prevent the decomposition of [CpFe(Cum)]PF_6.

The photoreaction of [CpFe(Cum)]PF_6 with KC-DA in CH_2Cl_2 produced an intermediate which had a long lifetime and a strong absorption band at $\lambda_{max} = 500$ nm as shown in Fig. 1. The isosbestic point was observed during these changes. These changes occurred when the irradiation of the weak absorption of [CpFe(Cum)]PF_6 at $\lambda \geq 600$ nm (using a 450-W xenon lamp through a R-62 filter) to directly excite [CpFe(Cum)]PF_6. These results indicate that the intermediate will be produced between KC-DA and the cyclopentadienyl iron cation which was formed by the photodissociation of cumene from [CpFe(Cum)]PF_6.

The possibilities of the production of the intermediate by PET or a kethyl radical generated by a hydrogen abstraction are investigated in the following way. KC-DA (1.0×10^{-5} M) in the presence of dimethylaniline ($E_{ox} = 0.73$ V) as an electron donor or dimethylfumarate ($E_{red} > -1.23$ V) as an electron accepter in CH_2Cl_2 were irradiated using a 355 nm laser. The change in the absorption was then monitored using a spectrophotometer. However, the absorption similar to the intermediate was not observed. Next, cumene or dimethylamine as a hydrogen donor was added to KC-DA (1.0×10^{-5} M) in CH_2Cl_2. When the sample solution was irradiated, the absorption of the intermediate did not appear. Therefore, the intermediate neither resulted from the electron transfer which is related to the excited state of KC-DA nor the kethyl radical which was produced by hydrogen abstraction by KC-DA.

In addition, the absorption of the intermediate did not quickly disappear by the introduction of air or by the irradiation of laser pulses (532 nm, Nd^{3+}:YAG). These results indicate that the intermediate was stable against oxygen and the irradiation by light.

The IR spectra measurement was used to estimate the structure of the intermediate. Koefod and Mann proposed a structure of the intermediate generated in the thermal and photochemical reactions of coumarin dyes in the presence of cyclopentadienylruthenium(II) complexes, ([CpRu(η^4-Coumarin)]$^+$) [20]. The structure of [CpRu(η^4-Coumarin)]$^+$ as shown in Fig. 3(a), was proposed on the basis of the IR spectra of Coumarin and the intermediate.

To reveal whether a similar intermediate is formed in this case, the same experiment was carried out for

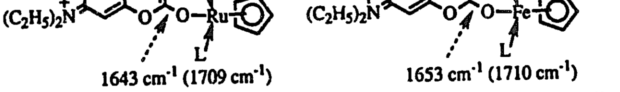


Fig. 3. Proposed structure for the intermediate generated photochemically from C-6 and [CpRu(CH_3CN)$_3$]$^+$ adopted from Ref. [20] (a) and the proposed structure for the intermediate of C-6 in the presence of [CpFe(Cum)]PF_6 in this study (b). The values indicated in wave number are observed by IR spectra before (parenthesis) and after irradiation.

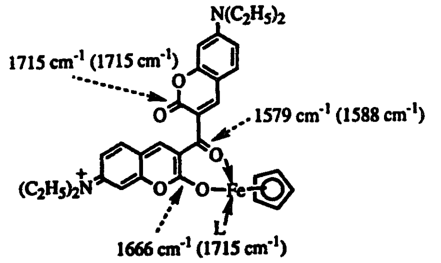


Fig. 4. Proposed structure for the intermediate generated photochemically from KC-DA in the presence of [CpFe(Cum)]PF$_6$ in CH$_2$Cl$_2$. The values indicated in wave number are observed by IR spectra before (parenthesis) and after irradiation.

[CpFe(Cum)]PF$_6$ and C-6. By irradiation of C-6 (2.5×10^{-5} M) and [CpFe(Cum)]PF$_6$ (2.5×10^{-5} M) in CH$_2$Cl$_2$, a new absorption band ($\lambda_{max}=530$ nm) appeared and the absorption of C-6 ($\lambda_{max}=462$ nm) decreased in intensity in the visible region. At the same time, an absorption band at 1711 cm^{-1} (assigned to the stretching band of δ-lactone of C-6) decreased in intensity and a new absorption band at 1654 cm^{-1} appeared as shown in Fig. 2(b). This might be the shift of the stretching band from 1711 to 1654 cm^{-1} due to the complexation. This fact confirms the formation of the photochemical intermediate, [CpFe(η^4-C-6)]$^+$, similar to [CpRu(η^4-C-6)]$^+$. Fig. 3(b) shows the proposed structure of [CpFe(η^4-C-6)]$^+$.

A similar experiment was then examined for KC-DA and [CpFe(Cum)]PF$_6$. By light irradiation ($\lambda>360$ nm), then IR spectra of KC-DA (4.9×10^{-3} M) in the presence of [CpFe(Cum)]PF$_6$ (5.1×10^{-3} M) changed as shown in Fig. 2(a). The IR spectra of [CpFe(Cum)]PF$_6$ did not significantly appear between 1800 and 1500 cm^{-1}. The bands at 1715 cm^{-1} and 1588 cm^{-1} are assigned to ν(C=O) of the δ-lactone and 3-ketone stretching bands of KC-DA, respectively. These bands decreased in intensity and the absorption bands of 1666 and 1579 cm^{-1} increased after the irradiation. It appears that the absorption bands at 1715 and 1588 cm^{-1} would shift to 1666 and 1579 cm^{-1}, respectively. According to the analogy with [CpRu(η^4-C-6)]$^+$ and [CpFe(η^4-C-6)]$^+$, it is proposed that the cyclopentadienyl-iron cation (CpFe$^+$) combines in the intramolecular charge-transfer state of KC-DA at a δ-lactone in the intermediate. The center iron may have had a weak interaction with oxygen of the 3-ketone, since the 3-ketone band shifts to a smaller wavenumber than the δ-lactone band. KC-DA has two δ-lactones in the molecule, but it is impossible that CpFe$^+$ combines with two δ-lactones, because of the twisted structure of KC-DA whose two δ-lactones are far apart. According to these explanations, the structure of the photochemical intermediate between KC-DA and [CpFe(Cum)]PF$_6$ is proposed as shown in Fig. 4.

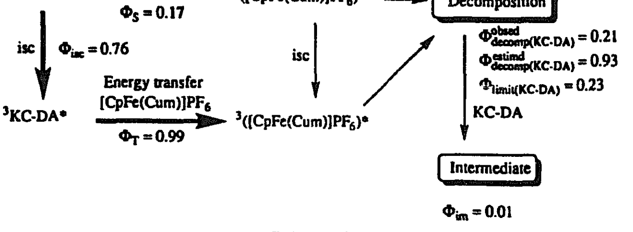
4.5. Sensitization mechanism of [CpFe(Cum)]PF$_6$ by KC-DA

To understand the mechanism of the sensitized reaction of [CpFe(Cum)]PF$_6$ by KC-DA, the redox potential, excitation energies and kinetic characteristics of KC-DA and [CpFe(Cum)]PF$_6$ are summarized in Table 6 and Table 5. The singlet energy (E_S) of [CpFe(Cum)]PF$_6$ is estimated by the absorption spectrum of [CpFe(Cum)]PF$_6$ and the fluorescence spectrum [21] of [CpFe(p-xylene)]PF$_6$. The reduction of [CpFe(Cum)]PF$_6$ was reversible and E_{red} was determined to be -1.45 V, however, the oxidation was irreversible and E_{ox} was determined to be 1.70 V. The energy transfer from KC-DA to [CpFe(Cum)]PF$_6$ is exothermic at the singlet and the triplet states. Rehm–Weller's equation (Eq. (2)) is used to estimate the change in free energy (ΔG) for the photoinduced electron transfer process. These values are summarized in Table 5. ΔG_S for PET from the singlet-excited KC-DA to [CpFe(Cum)]PF$_6$ is slightly negative ($\Delta G_S=-1.5$ kcal mol^{-1}).

The k_q^S of KC-DA by [CpFe(Cum)]PF$_6$ could not be determined, however, these values can be reasonably estimated. The k_q^S is estimated to be 8×10^9 M^{-1} s^{-1} because k_q^S of TE, whose E_S (59.5 kcal mol^{-1}) is similar to that of KC-DA (59.6 kcal mol^{-1}), by [CpFe(Cum)]PF$_6$ is 8.4×10^9 M^{-1} s^{-1}. The T–T absorption of KC-DA was quenched by [CpFe(Cum)]PF$_6$ with a rate constant as 4.6×10^9 M^{-1} s^{-1}, because the triplet energy transfer from KC-DA to [CpFe(Cum)]PF$_6$ is quite exothermic. As shown in Table 6, in this case, the concentration of [CpFe(Cum)]PF$_6$ is 5.0×10^{-3} M, Φ_q^S, Φ_q^T and Φ_{isc} of [CpFe(Cum)]PF$_6$ by KC-DA sensitization were 0.17, 0.99 and 0.76, respectively. The decomposition quantum yield of [CpFe(Cum)]PF$_6$ by KC-DA sensitization (${\Phi^{obsed}}_{decomp(KC\text{-}DA)}$) is 0.21, therefore, $\Phi_{limit(KC\text{-}DA)}$ (${\Phi^{obsed}}_{decomp(KC\text{-}DA)}/{\Phi^{estmd}}_{decomp(KC\text{-}DA)}$) is 0.23. These mechanisms are shown in Scheme 3.

It seems that the decomposition of [CpFe(Cum)]PF$_6$ by sensitization of the triplet state of KC-DA did not efficiently occur, irrespective of the expectation by the quenching rate constant. However, $\Phi_{decomp(KC\text{-}DA)}$ decreased due to the formation of the intermediate. For the photolysis (365 nm) of [CpFe(Cum)]PF$_6$ (2.4×10^{-3} M) by sensitization of benzophenone (1.5×10^{-1} M, $\Phi_{isc}=1$) in CH$_2$Cl$_2$, the production quantum yield of cumene was 0.28 in spite of the hydrogen abstraction of benzophenone from CH$_2$Cl$_2$. Thus, the reason why Φ_{limit} is small might be partly due to the hydrogen abstraction reaction of KC-DA.

The above proposed mechanism suggests that photosensitized decomposition of iron–arene complexes is interesting



Scheme 3.

and useful from mechanistic and applied aspects. However, there is still a lot to be solved in the case of KC-DA sensitization.

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