Photoinduced Cleavage of the Carbon–Indium Bond in Ethylindium(III) Tetraphenylporphyrin

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The photochemistry of ethylindium(III) tetraphenylporphyrin, $C_2H_5In^{III}TPP$, in benzene solutions was studied by steady light and laser flash photolysis. From the analysis of the products, the C₂H₅-In bond in C₂H₅In^{III}TPP was confirmed to be photodissociated. The quantum yields for the photodecomposition of $C_2H_3In^{III}TPP$ were found to be diminished by the addition of ferrocene. However, 2,4,7-trinitro-9-fluorenone, a strong electron acceptor, was found to increase the quantum yields. The laser photolysis studies revealed that the photoreaction of $C_2H_3In^{III}TPP$ occurs via the triplet state originating from the porphyrin ligand.

Introduction

Carbon dioxide insertion into the carbon-metal bond is considered to be an interesting and important subject in the photochemistry of alkylmetalloporphyrins. In 1977, Inoue and Takeda reported the photoinduced carbon dioxide insertion into the ethyl-aluminum bond of ethylaluminum(III) tetraphenylporphyrin.¹ More recently, Cocolios and his co-workers have found that photolysis of methylindium(III) tetraphenylporphyrin in the presence of cabon dioxide gives acetatoindium(III) tetraphenylporphyrin as a photoproduct of the carbon dioxide insertion into the methyl-indium bond.² Despite these interesting findings, the photochemistry and photophysics of alkylmetalloporphyrins have received less attention. We, therefore, aimed to carry out systematic studies on the photochemistry of alkylmetalloporphyrins.

In a previous paper, we reported the photochemical reaction of methylrhodium(III) octaethylporphyrin, CH₃Rh^{III}OEP, by steady light photolysis and laser flash photolysis.³ The photoproduct is identified as a diamagnetic dimer of rhodium(II) octaethylporphyrin. The photoreaction is considered to be the homolysis of the CH₃-Rh bond in CH₃Rh^{III}OEP. On the basis of (1) quantum yield measurements for the photodecomposition of CH₃Rh^{III}OEP, (2) detection of the transient species by laser photolysis, and (3) the temperature and wavelength dependence of the phosphorescence yields, we conclude that (1) Soret band excitation gives rise to the direct homolysis of the CH3-Rh bond and (2) Q band excitation leads to the formation of an intermediate X from which the homolysis of CH₃-Rh bond occurs.

The present paper reports the photochemical reaction of ethylindium(III) tetraphenylporphyrin, C₂H₅In^{III}TPP, in benzene solutions. The detailed mechanisms for the photoinduced cleavage of the carbon-indium bond are discussed in comparison with the photochemistry of CH₃Rh^{III}OEP.

Experimental Section

Materials. Ethylindium(III) tetraphenylporphyrin was synthesized by a Grignard reaction: chloroindium(III) tetraphenylporphyrin was added into the ether solution of an excess amount of ethylmagnesium iodide under a nitrogen atmosphere. After the ether solution was stirred for 2 h, cold water was added into the reaction mixture. The crude $C_2 H_5 In^{III} TPP$ extracted with benzene from the reaction mixture was chromatographed on alumina columns by using benzene as a developing solvent. The yield of C₂H₅In^{III}TPP is approximately 20%. The NMR spectrum of C₂H₃In^{III}TPP is in good accord with that reported previously.⁴

Anal. Calcd for C₂H₅In^{III}TPP: C, 73.19; H, 4.34, N, 7.37. Found: C, 73.03; H, 4.31; N, 7.27.

Ferrocene was purified by sublimation. Reagent-grade 2,4,7trinitro-9-fluorenone (TNF) and benzene were used without further purification.

Spectroscopic Measurements and Laser Photolysis. Absorption spectra were recorded on a Hitachi 330 spectrophotometer. ESR spectra were measured by a Jeol JES-FE-3AX X-band spectrophotometer.

Laser photolysis was carried out by using the second harmonic of a Nd-YAG laser (Model HY 500 from J. K. Lasers Ltd.): the duration and the energy of a 532-nm laser pulse were ca. 20 ns and ca. 100 mJ/pulse, respectively. The detection system of transient spectra was reported previously.5,6

Quantum Yield Measurements. Steady light photolysis of $C_2H_5In^{III}TPP$ in benzene solutions was performed by using a xenon lamp incorporated in a Hitachi MPF 4 spectrofluorimeter. Distribution of the relative light intensity of the xenon lamp was determined by measurement of the excitation spectrum of rhodamine B in ethylene glycol (8 g/L). The photon flux of the xenon lamp at 310 nm was measured by using N-methyldiphenylamine in an aerated methylcyclohexane solution as a chemical actinometer. It is established that N-methyldiphenylamine in the solution gives N-methylcarbazole with a quantum yield of 0.42 upon irradiation at 310 nm.⁷ The photon flux at a given wavelength can be determined from distribution of the light intensity and the photon flux at 310 nm.

Sample solutions used for the determination of quantum yields were degassed on a vacuum line (10⁻⁶ Torr). Concentrations of $C_2H_5In^{III}TPP$ used in the present study ranged from 1.3×10^{-5} to 7.7 \times 10⁻⁵ M. Preparative photolysis of C₂H₅In^{III}TPP in aerated and deaerated benzene solutions was performed with sunlight.

Results

Absorption Spectral Changes upon Irradiation. Figure 1 shows the absorption spectral changes observed for the degassed benzene solution of $C_2H_5In^{III}TPP$ upon irradiation at 580 nm. The absorption peaks located at 540, 580, and 625 nm decrease in intensity and new peaks appear at 520, 560, 600, 627, and 800 nm with an increase in the irradiation time. The same spectral changes were observed for the solution upon irradiation at 355, 455, 540, and 580 nm. This result indicates that the photoproduct is identical irrespective of the irradiation wavelengths.

After completion of photolysis, air was introduced into the degassed benzene solution of C₂H₅In^{III}TPP. The broad absorption

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Figure 1. Optical absorption spectral changes observed for the degassed benzene solution of $C_2H_3In^{III}TPP$ upon 580-nm irradiation: (1) before irradiation; (2) after 10-min irradiation; (3) after 20-min irradiation; (4) after 30-min irradiation; (5) after 40-min irradiation; (6) after 50-min irradiation; (7) after 90-min irradiation.



Figure 2. ESR spectrum of the irradiated degassed benzene solution of $C_2H_5In^{III}TPP$ observed after aeration at room temperature.

at 800 nm disappeared, accompanied by a slight increase in intensity at 520, 560, and 600 nm and by a slight decrease in intensity at 625 nm.

The NMR spectra were measured for the degassed deuterated benzene solution of $C_2H_5In^{III}TPP$ before and after photolysis. The proton NMR signals due to C_2H_5 in $C_2H_5In^{III}TPP$ are found to decrease in intensity with the irradiation time. We, therefore, consider that $C_2H_5In^{III}TPP$ undergoes photocleavage of the carbon-indium bond.

Absorption spectral changes were also observed for an aerated benzene solution of $C_2H_5In^{III}TPP$ upon irradiation. The absorption peak intensity of $C_2H_5In^{III}TPP$ decreased and new peaks appeared at 561, 600, and 627 nm. We found two major differences between the absorption spectra observed for the degassed and aerated solutions after the completion of photolysis: (1) the absorption peak intensity at 627 nm of the former solution is 3 times larger than that of the latter one; (2) the aerated solution gives no absorption band at 800 nm, in contrast to the degassed solution. It is noted that the rate of photoreaction in aerated solutions is markedly slower than that in degassed solutions.

After photolysis, the degassed benzene solution of $C_2H_5In^{III}TPP$ showed a weak ESR signal of unidentified species with a peakto-peak width of 7.5 G around g = 2.0. When the solution was exposed to air, an intense ESR signal having 10 well-resolved hyperfine lines was observed as shown in Figure 2. Taking account of the fact that an In atom has a nuclear spin of $I = {}^{9}/_{2}$, we consider that the species that gives the ESR signal is presumably ascribed to the oxygen adduct, O₂-InTPP. The g value and hyperfine coupling constant of the indium atom were obtained as 2.004 \pm 0.001 and 27.5 G, respectively. The ESR signal intensity was found to decrease when the air-exposed solution was preserved at room temperature. This result suggests that O₂-InTPP is transformed to a diamagnetic species.

Preparative Photolysis. An aerated benzene solution of 35 mg of $C_2H_3In^{III}TPP$ was irradiated by sunlight for 2 days. After evaporation of the benzene, the amorphous residue was dissolved in an ethanol solution of 0.6 M HCl. This procedure affords fine, purple crystals. From IR and UV-vis spectral measurements the crystals are identified as ClIn^{III}TPP. The yield of ClIn^{III}TPP is found to be 98%. We have tried to purify the photoreaction products without dissolving them in acid ethanol. However, column chromatigraphy or recrystallization does not give a pure product. Presumably, the residue is considered to be a mixture



Figure 3. Transient absorption spectrum observed for the degassed benzene solution of $C_2H_5In^{III}TPP$ at 50 ns after a 532-nm laser flash.

of [In^{III}TPP]O₂, [In^{III}TPP]₂O, C₂H₅-O-In^{III}TPP, etc., which are easily transformed to ClIn^{III}TPP by being dissolved in acid ethanol.

The degassed benzene solution of 100 mg of $C_2H_5In^{III}TPP$ was irradiated by sunlight for 2 days. After exposure of the irradiated solution to air, benzene was distilled off under reduced pressure. The amorphous solid obtained was dissolved into an ethanol solution of 0.6 M HCl. The solvents were distilled off again under reduced pressure. Then, the solid was chromatographed on alumina by using chloroform as the developing solvent. The major species separated by column chromatography were (1) ClIn^{III}TPP (85%) and (2) an unidentified blue amorphous solid (15%), which showed an intense absorption peak at 627 nm in benzene.

Quantum Yield Measurement. Quantum yields for the photodecomposition of $C_2H_5In^{III}TPP$ were determined according to the procedure described previously. Changes in the concentration of $C_2H_5In^{III}TPP$ upon irradiation were monitored by the measurement of the absorbance at 623 nm. For the degassed solution, the quantum yields, Φ , are obtained as 0.047 ± 0.007 , $0.038 \pm$ 0.006, and 0.046 ± 0.007 at irradiation wavelengths, 355, 455, and 580 nm, respectively. Contrary to the case of CH₃Rh^{III}OEP,³ no wavelength dependence of the quantum yields is observed for the photodecomposition of $C_2H_5In^{III}TPP$. The aerated benzene solutions give $\Phi < 0.002$ for the photodecomposition of C_2H_5 -In^{III}TPP. This result suggests that an intermediate, which can be quenched by oxygen, plays a key role in the photoreaction of $C_2H_5In^{III}TPP$.

Laser Photolysis. Laser photolysis studies were carried out in order to elucidate the primary processes of the photoreaction of $C_2H_5In^{III}TPP$. Figure 3 shows the transient absorption spectrum observed for the degassed benzene solution of $C_2H_5In^{III}TPP$ at 50 ns after a 532-nm laser flash. The transient spectrum having peak maxima at 480 and 800 nm is ascribed to the photoexcited triplet state of $C_2H_5In^{III}TPP$, as will be discussed later. The rate constants for the decay of the transient in degassed and aerated benzene solutions of 1.3×10^{-5} M $C_2H_5In^{III}TPP$ were determined as 1.43×10^4 and 9.52×10^5 s⁻¹, respectively.

Photoreaction in the Presence of Quenchers. The transient spectrum of $C_2H_5In^{III}TPP$ measured by laser photolysis is very similar to the triplet-triplet (T-T) absorption spectra of other metallotetraphenylporphyrins.^{8,9} This fact indicates that the transient is attributed to the photoexcited $\pi - \pi^*$ triplet state of $C_2H_5In^{III}TPP$ originating from the porphyrin ligand. The rate constant for the decay of the transient in aerated benzene is found to be much larger than that in degassed benzene because of the quenching of the triplet state by oxygen

$${}^{3}[C_{2}H_{5}In^{III}TPP] + O_{2} \rightarrow C_{2}H_{5}In^{III}TPP + {}^{1}O_{2}$$

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Figure 4. Plots of Φ_0/Φ (•) and k_T/k_T^0 (O) as a function of ferrocene concentration (see text).



Figure 5. Plots of the triplet decay rates as a function of TNF concentration.

Here ${}^{3}[C_{2}H_{5}In^{III}TPP]$ and ${}^{1}O_{2}$ are the excited triplet state of $C_{2}H_{5}In^{III}TPP$ and singlet oxygen, respectively.

We have examined the reactive state of $C_2H_5In^{III}TPP$, which leads to the homolytic cleavage of the carbon-In bond, by measuring the quantum yields for the photodecomposition and the decay rate of the triplet state in the presence of ferrocene and TNF as quenchers. Ferrocene was found to quench the photoreaction of $C_2H_5In^{III}TPP$: the yield for the photodecomposition decreased with an increase in the concentration of ferrocene. The laser photolysis studies revealed that the photoexcited triplet state of $C_2H_5In^{III}TPP$ was also quenched by ferrocene. The assumption that the triplet state is the reactive state responsible for the photodecomposition gives the following equation:

$$\Phi_0/\Phi = k_{\rm T}/k_{\rm T}^0 = 1 + k_{\rm g}/k_{\rm T}^0[{\rm Q}] \tag{1}$$

Here $k_{\rm T}$ and $k_{\rm T}^0$ are the rate constants for the decay of the triplet state in the presence and in the absence of ferrocene and Φ and Φ_0 are the quantum yields for the photodecomposition of C_2H_5 -In^{III}TPP in the presence and in the absence of ferrocene, respectively. Figure 4 shows Φ_0/Φ as well as $k_{\rm T}/k_{\rm T}^0$ represented as a function of the ferrocene concentration. The plot of $k_{\rm T}/k_{\rm T}^0$ vs. ferrocene concentration gives a straight line. From the slope of the line, $k_q/k_{\rm T}^0$ is determined as $1.46 \times 10^5 \,{\rm M}^{-1}$. On the other hand the plot of Φ_0/Φ vs. ferrocene concentration gives $k_q/k_{\rm T}^0$ = $1.8 \times 10^5 \,{\rm M}^{-1}$. The two values of $k_q/k_{\rm T}^0$ are very close to each other. This result shows that the photoexcited triplet state is responsible for the photoreaction of $C_2H_5In^{\rm III}TPP$.

Further examination for the reactive state of $C_2H_3In^{III}TPP$ was carried out with the use of TNF as a quencher. Since the absorption spectrum of $C_2H_3In^{III}TPP$ in benzene is not altered by the addition of TNF in the concentration range $0-1 \times 10^{-3}$ M, no formation of the ground-state complex of $C_2H_5In^{III}TPP$ with TNF is concluded. Figure 5 shows the plot of k_T vs. the concentration of TNF. From the slope and the intercept of the line, we obtain k_q/k_T as 2.2×10^4 M⁻¹. Figure 6 shows the quantum yields for the photodecomposition of $C_2H_5In^{III}TPP$ represented as a function of the TNF concentration. The yields initially increase with the increase in the concentration of TNF and become



Figure 6. Plots of quantum yields for the photodecomposition of $C_2H_5In^{III}TPP$ as a function of TNF concentration.

constant when the TNF concentration exceeds 1.5×10^{-4} M. Therefore, TNF molecules are concluded to quench the triplet state of C₂H₃In^{III}TPP but enhance the quantum yields for the photodecomposition. The quantum yield, Φ , for the photodecomposition in the presence of TNF is represented as

$$\Phi = \Phi_{\rm r}(k_{\rm r} + \gamma k_{\rm q}[{\rm TNF}]) / (k_{\rm R}^0 + k_{\rm q}[{\rm TNF}])$$
(2)

Here Φ_r is the quantum yield of the reactive state responsible for the photoreaction of $C_2H_5In^{III}TPP$, k_r , the rate constant for the decomposition of $C_2H_5In^{III}TPP$ from the reactive state, k_q , the rate constant for the quenching of the reactive state by TNF, γ , the ratio of the rate for decomposition of $C_2H_5In^{III}TPP$ to that for the whole deactivation processes of the reactive state when a TNF molecule attacks the reactive state, and k_R^0 , the decay rate constant of the reactive state in the absence of TNF. The quantum yields, Φ_0 and Φ_{∞} , in the absence of TNF and at an infinite concentration of TNF are represented respectively as

$$\Phi_0 = \Phi_r k_r / k_R^0 \tag{3}$$

and

$$\Phi_{\infty} = \Phi_{\rm r} \gamma \tag{4}$$

From eq 2-4, we obtain

$$Y = (\Phi_{\infty} - \Phi_0) / (\Phi_{\infty} - \Phi) = 1 + k_q [\text{TNF}] / k_R^0 \qquad (5)$$

From the slope of the line, the value of k_q/k_R^0 is estimated as 3.20 $\times 10^4 \text{ M}^{-1}$. This value is moderately in agreement with $k_q/k_T^0 = 2.2 \times 10^4 \text{ M}^{-1}$, supporting that the photodecomposition of $C_2H_5In^{III}TPP$ takes place via the triplet state as mentioned previously.

Discussion

Primary processes of the photoreaction of $C_2H_5In^{11}TPP$ in benzene solutions are concluded to be homolysis of the carbonindium bond. A similar photodissociation of the carbon-metal bond in CH₃Rh^{III}OEP has been reported³

$$CH_3Rh^{III}OEP \xrightarrow{\mu\nu} CH_3 + Rh^{II}OEP$$

In benzene solutions, $C_2H_3In^{III}TPP$ has two major absorption bands, a Soret band around 444 nm and a Q band around 580 and 610 nm. The quantum yields for the photodecomposition of $C_2H_3In^{III}TPP$ are found to be independent of the excitation wavelengths: no differences in the quantum yields are observed between the Soret and the Q band excitation. This result markedly differs from the photochemistry of $CH_3Rh^{III}OEP$: the quantum yields, Φ , for the photodecomposition of $CH_3Rh^{III}OEP$ have been demonstrated to be dependent on the excitation wavelength, λ : $\Phi = 0.22 \pm 0.02$ (410 nm $< \lambda < 550$ nm) and $\Phi = 0.16 \pm 0.02$ (300 nm $< \lambda < 410$ nm).³ The wavelength dependence is interpreted by assuming that no electronic relaxation occurs from the Soret band to the Q band of $CH_3Rh^{III}OEP$. This assumption is also used for the interpretation of the wavelength-dependent photochemistry of chloro(tetraphenylporphynato)carbonylrhodium(III) in benzene.¹⁰ From the comparison in photochemistry between CH₃Rh^{III}OEP and C₂H₅In^{III}TPP, we concluded that no wavelength dependence of the quantum yields for the photocomposition of C₂H₅In^{III}TPP implies that electronic relaxation from the Soret to the Q band occurs efficiently in case of the excited molecules of C₂H₅In^{III}TPP.

Laser photolysis studies show that the photoexcited triplet state of C₂H₃In^{III}TPP has a T-T absorption spectrum with peak maxima around 480 and 800 nm. Ferrocene is found to quench the triplet state. The quenching rate constant by ferrocene is obtained as 1.0×10^9 M⁻¹ s⁻¹. Since the triplet energy level of the ligand in metallotetraphenylporphyrins¹¹ is known to range from 12.5 to 14×10^3 cm⁻¹ and that of ferrocene is ca. 15.0 \times 10^3 cm⁻¹, ¹² C₂H₅In^{III}TPP is expected to have a $\pi - \pi^*$ triplet energy slightly lower than that of ferrocene. Herkstroeter et al.¹² have studied the quenching rate constants by ferrocene with the variation of the triplet energy levels of the sensitizers. According to their results, when the triplet energy level ranges from 12.5 to 14×10^3 cm⁻¹, the quenching rate constant is expected to be 5×10^{8} -2 $\times 10^{9}$ M⁻¹ s⁻¹. This value is rather in good accord with the rate constant for quenching of the triplet $C_2H_5In^{III}TPP$ by ferrocene. We, therefore, consider that the quenching mechanism by ferrocene, Fer, is expressed by triplet energy transfer

 ${}^{3}[C_{2}H_{5}In^{III}TPP] + Fer \rightarrow C_{2}H_{5}In^{III}TPP + {}^{3}Fer$

The quantum yields for the photodecomposition of C_2H_5 -In^{III}TPP are decreased with the addition of ferrocene. The triplet state of $C_2H_5In^{III}TPP$ is concluded to be responsible for the photoreaction on the basis of the quantum yield and the triplet decay rate measurements in the presence of ferrocene. This conclusion is further supported by the quenching experiment performed with the use of TNF as a quencher: TNF quenches the photoexcited triplet state of $C_2H_5In^{III}TPP$ but enhances the quantum yields for photodecomposition of $C_2H_5In^{III}TPP$. The variation in the quantum yields at various concentration of TNF can be explained by assuming the following reaction:

$$P[C_2H_5In^{III}TPP] + + TNF \rightarrow C_2H_5 + (In^{II}TPP) + TNF$$

The π - π * triplet state interacts with TNF, resulting in the increase in the quantum yields for the photodecomposition of C₂H₃In^{III}TPP. Since the electron affinity of TNF is considered to be large, it is expected that TNF interacts with the porphyrin plane of the triplet state as in the case of the charge-transfer complexes of metalloporphyrins and trinitrobenzene.^{13,14} Consequently the electron density on the central In atom diminishes, and therefore, the strength of the carbon-indium bond tends to decrease, resulting in the facile dissociation of the carbon-indium bond.

Registry No. TNF, 129-79-3; $C_2H_5In^{111}TPP$, 63036-65-7; ferrocene, 102-54-5.

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Nanosecond Transient Processes in the Triethylamine Quenching of Benzophenone Triplets in Aqueous Alkaline Media. Substituent Effect, Ketyl Radical Deprotonation, and Secondary Photoreduction Kinetics¹

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In the course of benzophenone triplet quenching by triethylamine (TEA) at high concentrations in alkaline aqueous acetonitrile, two temporally distinct processes are observed for ketyl radical anion formation. The fast component occurs on a nanosecond time scale, has kinetics sensitive to basicity and water content of the medium, and is ascribed to the deprotonation of the diphenylhydroxymethyl radical initially produced as a result of subnanosecond intra-ion-pair proton transfer. The slow process occurs on a microsecond time scale and is characterized by pseudo-first-order rate constants linearly dependent on ketone ground-state concentration; this is assigned to the one-electron reduction of the ketone by the methyl(diethylamino)methyl radical (derived from TEA). Substituent effects on the kinetics of the two processes follow trends expected from those of the acidity of diarylhydroxymethyl radicals and of the behavior of diaryl ketones as oxidants. Neither of the two processes is observed with N_iN -dimethylaniline (DMA) and 1,4-diazabicyclo[2.2.2]octane (DABCO) as quenchers. The electron or hydrogen transfer yields in the course of diaryl ketone triplet quenching by the three amines are all close to unity, suggesting that the back electron transfer in the triplet ion pairs is relatively unimportant.

Introduction

For nearly two decades, the electron-transfer quenching of aromatic carbonyl triplets by amines has been an active area of photochemical investigations.²⁻¹⁵ On the basis of photoreduction

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quantum yields and phosphorescence quenching studies, Cohen and co-workers^{2,5,6} first proposed that the initial step in the

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