PHOTOCHEMICAL DISSOCIATION OF THE CARBON-INDIUM BOND IN ETHYLINDIUM(III) TETRAPHENYLPORPHYRIN. EVIDENCE FOR THE FORMATION OF ZWITTERIONIC PORPHYRIN IN 2-METHYLTETRAHYDROFURAN

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Ethylindium(III) tetraphenylporphyrin, $C_2H_5-In(III)TPP$, undergoes photoinduced homolytic cleavage of the C_2H_5-In bond to produce the zwitterionic indium(III) tetraphenylporphyrin, $In(III)^+TPP^-$, in which a positive charge is located on the central indium atom and a negative one on the tetraphenylporphyrin (TPP) ligand.

1. Introduction

A number of porphyrins having divalent central metals has been described [1-3]. These porphyrins can be represented as M(II)P, in which M and P stand for the central metal and the porphyrin ligand, respectively. They can also be expressed as a zwitterionic structure, M(III)⁺P⁻, where an electron is transferred from the central metal to the porphyrin ligand. However, metalloporphyrins having a M(III)⁺P⁻ structure have not yet been detected because the highest occupied orbital of the central metal in M(II)P is lower in energy than the lowest vacant π orbital, π^* , of the porphyrin ligand.

It is known that alkylmetalloporphyrins, R-M(III)P undergo photoinduced homolytic cleavage of the carbon-metal bond [4,5]:

$R-M(III)P \xrightarrow{h\nu} R' + M(II)P$.

Here, R' represents the alkyl radical. These results indicate that M(II)P can be produced by the photolysis of the alkylmetalloporphyrins. In the present study, we have carried out photolysis of ethylindium(III) tetraphenylporphyrin, C₂H₅--In(III)TPP, in 2-methyltetrahydrofuran at room temperature. From the optical and ESR measurements of the photoproduct, we

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found that [In(II) TPP] produced from the photolysis of $C_2H_5(III)$ TPP is formulated as a zwitterionic structure, In(III)⁺ TPP⁻. This finding leads to the conclusion that the 5s orbital of the central indium atom is higher in energy than the π^* orbital of the TPP ligand.

2. Experimental

Ethylindium(III) tetraphenylporphyrin was synthesized from ethylmagnesium iodide and chloroindium(III) tetraphenylporphyrin by Grignard reaction. The crude products were purified by column chromatography using benzene as a developing solvent. The IR, NMR, and UV-visible spectra of the purified C_2H_5 -In(III) TPP are in good agreement with those reported previously [6]. 2-methyltetrahydrofuran, MTHF, was purified by distillation and stored on Na-K alloy in vacuo in order to remove traces of water.

Optical absorption spectra were measured by Hitachi 330 and Cary 14 R spectrophotometers, ESR spectra were recorded on a JES-FE 3AX X-band spectrometer. Continuous photolysis of C_2H_5 -In(III) TPP was performed using a 250 W high-pressure mercury lamp (USH 250 D from Ushio Electric Co.). For NMR measurements of the photoproduct, the solvent of the irradiated solution, MTHF, was replaced by deuterated benzene on a vacuum line. Tetracyanoquinodimethane was purified by sublimation on a vacuum line.

3. Results and discussion

Fig. 1 shows an ESR spectrum observed for the degassed MTHF solution of $C_2H_5-In(III)$ TPP after irradiation using a cut-off filter ($\lambda < 400$ nm) for 30 s at room temperature. Since no ESR signal was observed for the MTHF solution before irradiation, the ESR spectrum is ascribed to the photoproduct from $C_2H_5-In(III)$ TPP. The spectrum exhibits ten hyperfine lines due to the interaction between an unpaired electron and an indium atom (I = 9/2). The ESR parameters, g value and hyperfine coupling constant (A_{iso}^{In}), were determined as g = 2.02 and $A_{iso}^{In} = 10.5$ G, respectively. The ESR signal was found to disappear immediately after aeration of the irradiated solution. This result indicates that the species giving the ESR signal reacts with oxygen to produce diamagnetic species.

Photochemistry of C_2H_5 —In (III) TPP was found to be homolysis of the C_2H_5 —In bond by the NMR measurements of the irradiated product as described below. It was therefore expected that the paramagnetic species observed for the irradiated MTHF solution of C_2H_5 —In(III) TPP was [In(II) TPP] in which an unpaired electron is located in the 5s orbital of the central indium atom. However, we conclude that the un-



Fig. 1. ESR spectrum observed for the MTHF solution of 10^{-3} M C₂H₅-In(III) TPP after irradiation for 30 s at room temperature.

paired electron is not located in the central indium atom on the basis of the fact that the hyperfine coupling constant of In(II) atoms doped in KCl crystals is as large as 0.46 cm⁻¹ [7]. It is likely that the unpaired electron is located in the porphyrin ligand: the paramagnetic species is described as a zwitterionic structure of In(III)⁺TPP⁻. This structure implies that the optical absorption spectrum of the species is very similar to that of the anion radicals of metallotetraphenylporphyrin such as the anion radical of zinc(II) tetraphenylporphyrin, Zn(II)TPP⁻. In order to examine this prediction, the optical absorption spectra of the photoproducts from C₂H₅–In(III)TPP were studied at room temperature and at 77 K.

Fig. 2 shows the absorption spectra of C₂H₅-In(III) TPP in MTHF solutions before irradiation, after 30 s irradiation and after aeration of the 30 s irradiated solution at room temperature. The same spectral changes were observed for the MTHF solutions of C_2H_5 -In(III) TPP independent of the excitation wavelength (300-650 nm). The absorption spectrum of C_2H_5 -In(III) TPP in MTHF exhibits the peak maxima at 622, 578, and 573 nm in the O-band region. After 30 s irradiation, these peaks disappear and new peaks appear at 860, 748, 630, 615, and 562 nm. When the irradiated solution is exposed to air, the absorption bands located at 860 and 748 nm disappeared, leaving a broad absorption band around 850 nm in the nearinfrared region. These results indicate that irradiation of C₂H₅-In(III) TPP in MTHF results in the formation of, at least, two species: one is easily decomposed by aeration and the other is not decomposed by aeration. The former, which has peak wavelengths at 860 and



Fig. 2. Absorption spectra of C_2H_5 -In(III) TPP in MTHF before irradiation (----), after 30 s irradiation (---), and after aeration of the 30 s irradiated solution (---) at room temperature.

748 nm, is considered to have strong reducing power. In order to confirm the reductive properties of the species, we added TCNQ into the irradiated degassed solution. Immediately after the addition of TCNQ, the absorption bands at 860 and 784 nm disappeared and new strong absorption due to TCNQ anion radicals, TCNQ⁻, was observed. The ESR measurements also confirmed that the paramagnetic species which gives the ESR spectrum shown in fig. 1 were changed to TCNQ⁻. These results imply that the paramagnetic species produced in the MTHF solution by photolysis has absorption bands at 860 and 748 nm. The addition of TCNQ into the irradiated solution reveals that In(III)⁺TPP⁻ readily transfers an electron to TCNQ:

$In(III)^+TPP^- + TCNQ \rightarrow In(III)^+TPP + TCNQ^-$.

Fig. 3 shows the absorption spectra observed at 77 K for the MTHF solution of C_2H_5 —In(III) TPP after irradiation at room temperature for 5.0 s. The solution was frozen in liquid nitrogen immediately after 5.0 s irradiation. The absorption peaks in the near-infrared region are located at 870 and 748 nm, in agreement with those measured at room temperature. After introduction of air into the irradiated solution and cooling it to 77 K, we have measured the absorption spectrum of the air-stable product: the peak maxima were found to be located at 875 and 790 nm. By subtracting the spectrum of the air-stable product from



Fig. 3. Absorption spectra observed at 77 K for the MTHF solution of 10^{-3} M C₂H₅-In(III) TPP after irradiation for 5.0 s at room temperature (A) and after aeration of the 5 s irradiated solution (B). The difference spectrum C is obtained by subtracting the spectrum B from spectrum A.

that of the irradiated degassed solution, the absorption spectrum of the paramagnetic species is found to have the absorption peaks at 870 and 748 nm at 77 K.

It is well known that the anion radicals of metallotetraphenylporphyrins exhibit absorption bands in the wavelength region 600–900 nm. These bands correspond to the electronic transitions ${}^{2}E_{g} \rightarrow {}^{2}A_{1u}$, ${}^{2}E_{g} \rightarrow$ ${}^{2}B_{2u}$ and ${}^{2}E_{g} \rightarrow {}^{2}B_{1u}$ [8,9]. For example, Zn(II) TPP⁻ in MTHF shows two major absorption bands at 710 and 920 nm at 77 K [10]. On this basis we considered that the absorption bands at 870 and 748 nm observed for the irradiated solution of C₂H₅-In(III) TPP at 77 K are ascribed to the ligand-reduced species of indium porphyrin, i.e. the paramagnetic species is formulated as In(III)⁺TPP⁻.

For comparison of the absorption spectra, we have carried out optical measurements of one-electron reduced C₂H₅-In(III) TPP which were produced by γ -ray irradiation of the MTHF solutions at 77 K. Previous work has demonstrated that γ -irradiation of MTHF solutions at 77 K gives rise to the formation of the solute anion radicals as stable products which can be subjected to conventional spectroscopic measurements [11-13]. The absorption spectrum of one-electron reduced C_2H_5 -(III) TPP, $[C_2H_5$ -(III) TPP], produced by γ -radiolysis of the MTHF solution at 77 K, showed peak maxima at 890 and 775 nm in the near-infrared region. The spectrum of $[C_2H_5-In(III)TPP]^{-1}$ is similar to that of the paramagnetic species produced by photolysis of C₂H₅-In(III) TPP. However, the wavelengths of the peak maxima are evidently different. From these results, we concluded that the paramagnetic species is not ascribed to $[C_2H_5-In(III)TPP]^{-1}$. This conclusion suggests that no electron transfer occurs from $In(III)^{+}TPP^{-}$ to $C_{2}H_{5}In(III)TPP$ in the irradiated solution.

As described previously, we have carried out NMR measurements of the irradiated products of C_2H_5 -In(III) TPP. Characteristic proton signals from C_2H_5 of $C_2H_5In(III)$ TPP located at -2.53 and -4.27 ppm decreased in intensity with the irradiation time. This result indicates that the C_2H_5 group is removed from C_2H_5 -In(III) TPP upon irradiation. On the basis of optical, ESR, and NMR studies of the irradiation products of C_2H_5 -In(III) TPP, the homolytic cleavage of the C_2H_5 -In bond is considered to occur upon irradiation.

4. Conclusion

The chemical bond of C_2H_5 —In is considered to be composed of a sp³ orbital of a carbon atom in C_2H_5 and a 5s orbital of an indium atom. The primary photochemistry of C_2H_5 —In(III) TPP is expressed as

$$C_2 H_5 In(III) TPP \xrightarrow{hv} C_2 H_5 + In(III)^+ TPP^-.$$
(1)

Here C_2H_5 is assumed to convert to C_2H_6 by hydrogen abstraction from MTHF. The unpaired electron in $In(III)^+TPP^-$ is concluded to be located in the tetraphenylporphyrin ligand by ESR measurements of the photoproduct in MTHF. In fact, the spectrum of the paramagnetic species shows the near-infrared absorption bands characteristic to the anion radicals of metallotetraphenylporphyrins.

The lowest vacant orbital of In(III) tetraphenylporphyrin is considered to be either the 5s orbital of the central indium atom or the π^* orbital of the porphyrin ligand. The fact that the unpaired electron in In(III)⁺TPP⁻ is located in the porphyrin ligand indicates that the 5s orbital of the central indium atom is higher in energy than the π^* orbital of the tetraphenylporphyrin ligand.

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