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Photochemistry of (μ-Tetraphenylporphyrinato)bis[dicarbonylrhodium(I)] in Benzene–Carbon Tetrachloride Mixture. Formation of Chloro(tetraphenylporphyrinato)carbonylrhodium(III)

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Photolysis of (μ-tetraphenylporphyrinato)bis[dicarbonylrhodium(I)] (TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$) in a 5:1 mixture of benzene and carbon tetrachloride gives rise to the formation of chloro(tetraphenylporphyrinato)carbonylrhodium(III) (Cl(TPP)Rh$^{\mathrm{III}}$(CO)). The quantum yield (Φ) for the photodecomposition of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$ is markedly dependent on the excitation wavelength (λ): $\Phi = 0.075 \pm 0.04$, $\lambda < 320$ nm; $\Phi = 0.04 \pm 0.02$, 320 nm $< \lambda <$ 420 nm; $\Phi < 10^{-4}$, $\lambda > 420$ nm. The laser photolysis studies of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$ using the second (532 nm) and the third (355 nm) harmonic of a Nd–YAG laser reveal that neither the lowest singlet nor the triplet state is responsible for the photodecomposition of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$. The homolysis of the Rh(I)–N bond in the higher excited singlet states of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$ is considered to result in the formation of a transient species, TPP-[Rh$^{\mathrm{II}}$(CO)$_2$]. The assumption that TPP[Rh$^{\mathrm{II}}$(CO)$_2$]$_2$ abstracts a chlorine atom from carbon tetrachloride gives an interpretation for the formation of Cl(TPP)Rh$^{\mathrm{III}}$(CO): (TPP)Rh$^{\mathrm{II}}$(CO)$_2$ + CCl$_4$ $\rightarrow$ Cl(TPP)Rh$^{\mathrm{III}}$(CO) + CO + CCl$_3$.

Introduction

X-ray structure determination of dinuclear metalloporphyrins demonstrated that two metal atoms are located on each side of the porphyrin plane.[1,2] Since the porphyrin plane is considerably distorted, both the photophysics and the photochemistry of dinuclear metalloporphyrins are expected to differ significantly from those of the usual metalloporphyrins that have one central metal atom incorporated in a porphyrin ligand.

In a previous paper,[3] we reported that the photolysis of TPP-[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$ in benzene solutions gives a diamagnetic dimer of rhodium(II) tetraphenylporphyrin, [(TPP)Rh$^{\mathrm{II}}$]$_2$, as a photoproduct. On the basis of the quantum yield measurements for the photodecomposition as well as laser photolysis studies, the homolysis of a Rh(I)–N bond is considered to occur primarily in the higher excited singlet states, S$_n$ ($n > 2$), of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$.

Metalloporphyrins dissolved in alkyl halide solutions are known to be readily photooxidized to yield one-electron-oxidation products.[4,5] This method of photooxidation has also been frequently applied to prepare one-electron-oxidation products of metal complexes.[6-8] The present work deals with the photochemical reaction of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$ in a mixture of 5:1 benzene–carbon tetrachloride. The photooxidation product isolated from the reaction mixture is identified as chloro(tetraphenylporphyrinato)-carbonylrhodium(III), Cl(TPP)Rh$^{\mathrm{III}}$(CO). The mechanism of the Cl(TPP)Rh$^{\mathrm{III}}$(CO) formation is studied by steady light and laser flash photolysis.

Experimental Section

(μ-Tetraphenylporphyrinato)bis[dicarbonylrhodium(I)] was prepared from tetraphenylporphyrin and Rh$_2$(CO)$_4$Cl$_2$ as described previously.[9,10] Reagent grade benzene and carbon tetrachloride were used as supplied. Sample solutions were degassed by freeze–pump–thaw cycles.

The absorption spectra were recorded on a Hitachi 330 spectrophotometer. A xenon lamp incorporated in a Hitachi MPF 4 spectrofluorimeter was used as a source of monochromatic light for measurements of the quantum yields. The relative light intensity distribution of the xenon lamp was determined by the measurements of the fluorescence excitation spectrum of rhodamine B (8 g/L) in ethylene glycol.[3] The photon flux at 310 nm was obtained by using an aerated cyclohexane solution of methyldiphenylamine as a chemical actinometer.[3,11] From the relative light intensity distribution and the photon flux at 310 nm, we obtained the photon flux at a given wavelength over the range 250–600 nm. A 250-W mercury lamp (USH-250 D) was employed as a light source for the preparative photolysis of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$. The solvent used in the present study was a 5:1 mixture of benzene and carbon tetrachloride, unless otherwise stated.

The laser photolysis studies were carried out by using the second (532 nm) and the third (355 nm) harmonic of the Nd–YAG laser (model HY 500 from J. K. Lasers): the duration of a laser pulse was ca. 20 ns. The detection system of the transient spectra was composed of (1) a 150-W xenon lamp as an analyzing light beam source, (2) a monochromator (Model MC-20N from Ritsu), (3) a photomultiplier (Hamamatsu R 758), and (4) an oscilloscope (Tektronix Model 7904). The details of the detection system have already been described earlier.[3,12]

Results

Preparative Photolysis of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$. One hundred milligrams of TPP[Rh$^{\mathrm{I}}$(CO)$_2$]$_2$ dissolved in the mixture (50 cm^3) of benzene and carbon tetrachloride was placed in a Pyrex tube with a round bottom. After being degassed on a vacuum line, the solution was irradiated by the mercury lamp for 8 h. The color of the solution changed from dark brown to pale brown, and fine precipitates were found to deposit on the wall of the reaction vessel with the irradiation time. After the complete photolysis, the solvents in the reaction mixture were distilled off and the residues were dried under reduced pressure. The residues contained soluble and insoluble substances in methanol. Therefore, the methanol solution of the residues was filtered: the filtrate showed green color, and the precipitates on a filter paper were pale pink. The pale pink precipitates were dissolved in chloroform and chromatographed on an alumina column with the use of chloroform as developing solvent. The first elutant, brilliant red, was collected, and chloroform was distilled off under reduced pressure. The solid material (45 mg) thus obtained shows an IR spectrum with a sharp absorption band at 2070 cm^{-1} due to the stretching mode of CO. The absorption spectrum of the benzene solution indicates that the solid material is a mixture of Cl(TPP)Rh$^{\mathrm{III}}$(CO) and chlororhodium(III) tetraphenylporphyrin, Cl(TPP)Rh$^{\mathrm{III}}$.

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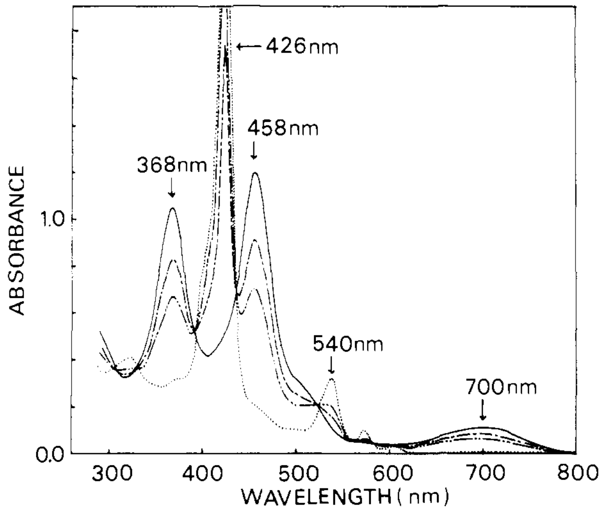

Figure 1. Absorption spectral changes by 370-nm irradiation observed for $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in a 5:1 mixture of benzene and carbon tetrachloride: (—) before irradiation; (— — —) after 5-min irradiation; (— · · —) after 10-min irradiation; (· · ·) after 40-min irradiation.

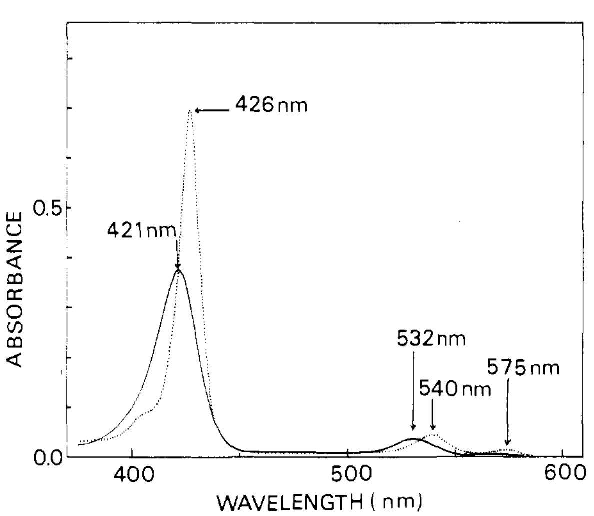

Figure 2. Absorption spectra of $\mathrm{Cl(TPP)Rh^{III}}$ (—) and $\mathrm{Cl(TPP)Rh^{III}(CO)}$ (· · ·) in benzene solutions. The latter spectrum is observed for the benzene solution of $\mathrm{Cl(TPP)Rh^{III}}$ after CO bubling for 1.0 min.

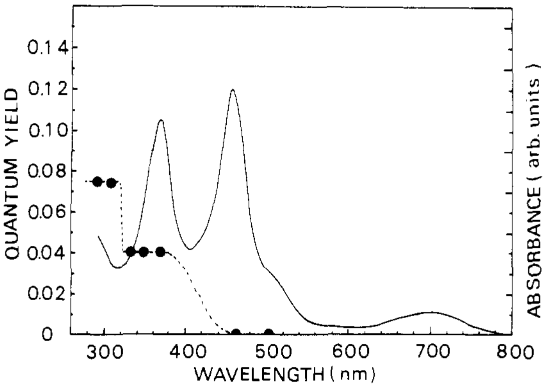

Figure 3. The absorption spectrum of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ (—) and the quantum yields (●) for the photodecomposition of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in a 5:1 mixture of benzene and carbon tetrachloride.

Addition of sodium acetate into the green filtrate generated metal-free tetraphenylporphyrin, indicating that the green species is ascribed to protonated tetraphenylporphyrin, $\mathrm{TPPH^+}$. Presumably, hydrogen chloride, which is expected to be produced in the irradiated solution, reacts with $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ to form $\mathrm{TPPH^+}$.

Absorption Spectral Changes of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ upon Irradiation. Figure 1 shows the absorption spectral changes of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in the benzene–carbon tetrachloride mixture upon irradiation at 370 nm. The absorption peaks are located at 368, 458, and 700 nm before irradiation. These peaks decrease in intensity with irradiation time, and new bands appear at 426, 540, 572, and 605 nm. The same absorption spectral changes were observed with an irradiation light of $\lambda < 420$ nm, indicating that the photoproducts from $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ are identical irrespective of the irradiation wavelengths.

The studies on the photochemistry of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in benzene revealed that the absorption peaks of the final product, $\mathrm{[(TPP)Rh^{II}]_2}$, are located at 412 and 512 nm[3]. Accordingly, the photoproducts obtained by photolysis of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in the mixture of benzene and carbon tetrachloride are concluded to differ from $\mathrm{[(TPP)Rh^{II}]_2}$. Figure 2 shows the absorption spectra of $\mathrm{Cl(TPP)Rh^{III}}$ and $\mathrm{Cl(TPP)Rh^{III}(CO)}$ in benzene solutions. The absorption peaks of the former are located at 421, 532, and 563 nm, and those of the latter at 426, 540, and 573 nm. On the basis of the comparison of the absorption spectra of the photoproduct and authentic $\mathrm{ClRh^{III}TPP(CO)}$, we consider that the absorption bands of the photoproduct located at 426, 540, and 573 nm are ascribed to $\mathrm{ClRh^{III}TPP(CO)}$. Since a chloride atom in $\mathrm{ClRh^{III}TPP(CO)}$ originates from carbon tetrachloride, the photoreaction is represented as

$$\mathrm{TPP[Rh^{I}(CO)_2]_2 + CCl_4 \xrightarrow{h\nu} ClRh^{III}TPP(CO)}$$

The quantum yields for the photodecomposition of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in the benzene–carbon tetrachloride mixture were found to be dependent on the excitation wavelengths (λ). The photoreaction takes place when $\lambda < 420$ nm, whereas it does not take place when $\lambda > 420$ nm. Figure 3 shows the absorption spectrum of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ and the quantum yields for the photodecomposition of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ represented as a function of λ. The yields, Φ, are determined to be $\Phi < 10^{-4}$ ($\lambda > 420$ nm), $\Phi = 0.04 \pm 0.02$ (320 nm $< \lambda <$ 420 nm), and $\Phi = 0.075 \pm 0.004$ ($\lambda < 320$ nm). The wavelength dependence of the quantum yields for the photodecomposition of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ indicates that the lowest excited singlet state is not responsible for the photoreaction.

Laser Photolysis Studies. The laser photolysis studies of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in the benzene–carbon tetrachloride mixture were carried out in order to elucidate the primary processes of the photoreaction. The transient spectrum observed after a 532-nm laser pulse has absorption peaks at 570 and 800 nm, in agreement with that observed for a pure benzene solution of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$. The transient spectrum, therefore, is ascribed to the triplet state of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$. The decay of the transient spectrum follows first-order kinetics: the decay rate constant, k, is obtained as $k = (4.0 \pm 0.4) \times 10^6\ \mathrm{s^{-1}}$. Since the lifetime, $\tau = 167$ ns measured in a benzene solution,[3] we conclude that the triplet state is not quenched by carbon tetrachloride molecules.

A 355-nm laser pulse gives the same transient spectrum as that observed with a 532-nm laser pulse. Accordingly, the lowest triplet state of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ is considered to be produced by excitation light of both 355 and 532 nm. The fact that the photoreaction occurs only by the excitation light $\lambda < 420$ nm implies that the lowest triplet state observed in laser photolysis is not responsible for the photodecomposition of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$.

Discussion

Our previous study[3] on the photochemistry of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in benzene solutions shows that the photoproduct is a diamagnetic dimer of $\mathrm{Rh^{II}TPP}$. However, preparative photolysis of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in benzene–carbon tetrachloride mixture gives $\mathrm{ClRh^{III}TPP}$, $\mathrm{Cl(TPP)Rh^{III}(CO)}$, and protonated tetraphenylporphyrin. The formation of $\mathrm{Rh^{III}TPP}$ products indicates that carbon tetrachloride acts as an oxidizing reagent.

The spectral changes shown in Figure 1 confirm that the major photoproduct is $\mathrm{Cl(TPP)Rh^{III}(CO)}$. This result suggests that $\mathrm{ClRh^{III}TPP}$ obtained in the preparative photolysis is produced on alumina during column chromatography.

The quantum yields for the photodecomposition of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in the benzene–carbon tetrachloride mixture are markedly dependent on the excitation wavelengths. The similar wavelength dependence is observed for the quantum yields measured with the pure benzene solution of $TPP[Rh^I(CO)_2]_2$.[3] However, the absolute values of the quantum yields differ significantly between those measured for the benzene solution and those for the mixture of benzene and carbon tetrachloride: $\Phi_m/\Phi_b \sim 1.6$, 320 nm $< \lambda <$ 420 nm; $\Phi_m/\Phi_b \sim 1.4$, $\lambda <$ 320 nm. Here Φ_m and Φ_b, respectively, are the quantum yields for the photodecomposition of $TPP[Rh^I(CO)_2]_2$ in the benzene–carbon tetrachloride mixture and in a pure benzene solution. The fact that Φ_m is larger than Φ_b gives a clue for the consideration of the primary photochemical processes of $TPP[Rh^I(CO)_2]_2$, as will be discussed later.

The laser photolysis studies of $TPP[Rh^I(CO)_2]_2$ in the benzene–carbon tetrachloride mixture show that the triplet state is not responsible for the photoreaction. The triplet–triplet (T–T) absorption spectrum as well as the triplet lifetime is very different from that of the usual metallotetraphenylporphyrin.[12,14] In particular, the lifetime of the triplet state (~160 ns)[3] is markedly shorter than that of $ClRh^{III}TPP$ (120 μs).[14] Taking account of the fact that $TPP[Rh^I(CO)_2]_2$ gives no phosphorescence, we consider that the short lifetime of the triplet state is ascribed to the increase in the rate constant for the nonradiative processes from the triplet to the ground state. Presumably, the distorted structure of the porphyrin plane in $TPP[Rh^I(CO)_2]_2$ gives a T–T absorption spectrum different from that of $ClRh^{III}TPP$ and gives the short lifetime of the triplet state.

The photochemistry of $TPP[Rh^I(CO)_2]_2$ in benzene solutions is represented as[3]

$$TPP[Rh^I(CO)_2]_2 \xrightarrow{h\nu} [Rh^{II}TPP]_2 + [Rh(0) + 4CO]$$

Here $[Rh^{II}TPP]_2$ stands for the diamagnetic dimer of $Rh^{II}TPP$, and $[Rh(0) + 4CO]$ is assumed to be formed on the basis of the stoichiometry. The primary photochemical process is considered to involve the homolysis of the Rh(I)–N bond in $TPP[Rh^I(CO)_2]_2$.

The photochemical reaction product from $TPP[Rh^I(CO)_2]_2$ in the benzene–carbon tetrachloride mixture is identified as $Cl(TPP)Rh^{III}(CO)$. The chloride atom in $Cl(TPP)Rh^{III}(CO)$ is undoubtedly regarded as originating from carbon tetrachloride. It, therefore, is important to determine the species with which a carbon tetrachloride molecule reacts, leading to the formation of $Cl(TPP)Rh^{III}(CO)$.

Since the absorption spectrum of $TPP[Rh^I(CO)_2]_2$ in the benzene–carbon tetrachloride mixture was identical with that in pure benzene, it is concluded that $TPP[Rh^I(CO)_2]_2$ and carbon tetrachloride do not form the ground-state complex. As stated earlier, neither the lowest excited singlet nor the triplet state is responsible for the photoreaction. Consequently, the species that reacts with carbon tetrachloride molecules is presumed to be an intermediate which is produced by homolysis of the Rh(I)–N bond in $TPP[Rh^I(CO)_2]_2$. Since the wavelength dependence of the quantum yields for the photodecomposition of $TPP[Rh^I(CO)_2]_2$ in the mixture of benzene and carbon tetrachloride is very similar to that observed for the benzene solution, an intermediate produced by homolysis of the Rh(I)–N bond is suggested to be a possible candidate to react with a carbon tetrachloride molecule. Taking account of the fact that the quantum yields for the photodecomposition in the presence of carbon tetrachloride are 1.4–1.6 times as large as those in the absence of carbon tetrachloride, we consider that the photochemical reaction mechanism for the formation of $Cl(TPP)Rh^{III}(CO)$ is represented as

$$TPP[Rh^I(CO)_2]_2 \xrightarrow{h\nu} (TPP)Rh^{II}(CO)_2 + [Rh^0(CO)_2] \quad (1)$$

$$(TPP)Rh^{II}(CO)_2 + [Rh^0(CO)_2] \rightarrow TPP[Rh^I(CO)_2]_2 \quad (2)$$

$$(TPP)Rh^{II}(CO)_2 + CCl_4 \rightarrow Cl(TPP)Rh^{III}(CO) + CO + CCl_3 \quad (3)$$

Here, dicarbonylrhodium(II) tetraphenylporphyrin, $(TPP)Rh^{II}(CO)_2$, is assumed to be produced as an intermediate according to reaction 2. The CCl_3 radical in reaction 3 is also assumed to be produced on the basis of stoichiometry, as in the case of photooxidation of ferrocene.[6] In the absence of carbon tetrachloride, an intermediate, $(TPP)Rh^{II}(CO)_2$, is converted to $[(TPP)Rh^{II}]_2$ by

$$2(TPP)Rh^{II}(CO)_2 \rightarrow [(TPP)Rh^{II}]_2 + 4CO \quad (4)$$

The above reaction scheme seems plausible for the interpretation of the increase in the quantum yields for the photodecomposition in the presence of carbon tetrachloride: recombination reaction 2 between $(TPP)Rh^{II}(CO)_2$ and $Rh^0(CO)_2$ to regenerate $TPP[Rh^I(CO)_2]_2$ is suppressed owing to the formation of $Cl(TPP)Rh^{III}(CO)$, as indicated by reaction 3.

The quantum yields for the photodecomposition of $TPP[Rh^I(CO)_2]_2$ seem to be a step function of the excitation wavelengths. Since the yields start to increase around 420 nm on going from long to short excitation wavelengths, the dissociation energy of the Rh(I)–N bond is estimated to be ca. 2.9 eV on the assumption that the bond dissociation takes place when the energy of an incident photon absorbed by the molecule exceeds the dissociation energy of the Rh(I)–N bond.

The wavelength dependence of the quantum yields for the photodecomposition of $TPP[Rh^I(CO)_2]_2$ differs significantly from that observed for the photodissociation of iodine molecules in solutions.[15] The quantum yields for the photodissociation of iodine molecules are strongly dependent on the excitation wavelength: the yield increases monotonously with the increase in the energy of the incident photon absorbed by iodine. The result is well intepreted by using a simple model proposed by Noyes.[15] The model indicates that the excess energy, E, defined by $E = h\nu - E_d$ ($h\nu$ is the energy of the incident photon: E_d is the dissociation energy of iodine molecule) is converted to the translational energy of the iodine atoms, resulting in the separation of the two atoms. In this case, the quantum yields depend on the energy of the incident photon but not on the character of the electronic band excited. On the contrary, the quantum yields for the photodecomposition of $TPP[Rh^I(CO)_2]_2$ are represented as a step function of the excitation wavelength. Furthermore, each electronic band, when excited, seems to give its own quantum yield. This result suggests that the quantum yields depend on the electronic character of the absorption band excited as well as the incident photon energy. The wavelength dependence observed in the present study can be interpreted on the basis of the assumption that the photoreaction occurs at the lowest vibrational level of each higher excited state S_n ($n > 2$). The lowest triplet state of $TPP[Rh^I(CO)_2]_2$ is considered to be formed from the lowest excited singlet state, as discussed previously.[3]

Registry No. $TPP[Rh^I(CO)_2]_2$, 88083-36-7; CCl_4, 56-23-5; $ClRh^{III}TPP(CO)$, 42892-91-1.

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