Examples of trans-chelating ligands in platinum complexes are rare. Use of diethylenetriamine (dien) with the central N methylated allowed isolation of a complex containing trans-chelating dien (thus also an eight-membered ring) by a complicated procedure involving reduction from Pt(IV) to Pt(II).[20] Similarly, phosphines with bulky substituents have been used to produce complexes such as *trans*-[PtCl$_2$(t-Bu$_2$P(CH$_2$)$_n$P-t-Bu$_2$)] (n = 9, 10).[21] Systems such as *trans*-[PtCl$_2$(L)] and *trans*-[PtHCl(L)], where L is a bidentate ligand with the phosphine or arsine donor atoms bridged by the rigid benzo[c]phenanthrene skeleton have also been examined in detail.[22,23] Complex II thus represents the simplest reported example of a trans-chelating ligand. The mechanism of substitution and the generality of the reaction are being studied further.

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Contribution from the Science and Engineering Laboratory,
Waseda University, Shinjukuku, Tokyo 160, Japan,
Department of Chemistry, Toyo University,
Kujirai, Kawagoe, Saitama 350, Japan, and
The Institute of Physical and Chemical Research,
Wako, Saitama 351-01, Japan

Photochemical Formation of Oxochromium(IV) Tetraphenylporphyrin from Nitritochromium(III) Tetraphenylporphyrin in Benzene

Minoru Yamaji,† Yoshimasa Hama,† Yoshio Miyazaki,‡ and Mikio Hoshino*,§

It has been well recognized that synthetic metalloporphyrins with central metals Fe, Co, Rh, and Mn react with simple diatomic molecules O$_2$, CO, and NO to yield their adducts. Laser photolysis studies have revealed that these adducts readily liberate the diatomic molecules to give metalloporphyrins upon photoexcitation.[1-8] The photoreaction is simply interpreted in terms of the photoinduced dissociation of the axial diatomic molecules from the central metal.

In the present work, we have carried out photochemical studies of nitritochromium(III) tetraphenylporphyrin, ONO–Cr^{III}TPP, which is considered to be an adduct of a triatomic molecule NO$_2$ of chromium(II) tetraphenylporphyrin, Cr^{II}TPP.
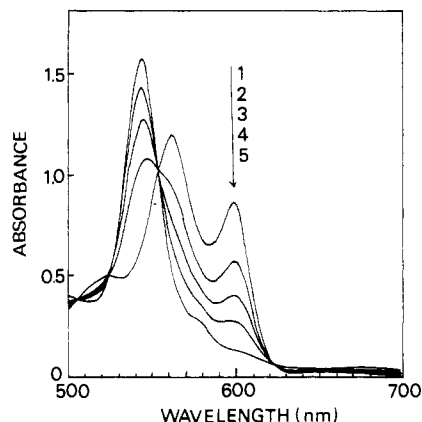
Experimental Section

Chlorochromium(III) tetraphenylporphyrin, ClCr^{III}TPP, was synthesized and purified according to the literature.[9] Further purification

† Waseda University.
‡ Toyo University.
§ The Institute of Physical and Chemical Research.

Figure 1. Absorption spectral changes observed for a benzene solution of 1.12 × 10^{-4} M ONO–Cr^{III}TPP upon irradiation with the mercury lamp with a cutoff filter (λ > 420 nm): 1, before irradiation; 2, after ‘10 min; 3, after 30 min; 4, after 70 min; 5, after 150 min.

of ClCr^{III}TPP was carried out by column chromatography with the use of Sephadex LH 20 resin and acid methanol containing 0.1 M HCl as an eluent.

ONO–Cr^{III}TPP was prepared by the anion-exchange method:

$$ClCr^{III}TPP + NaNO_2 \rightarrow ONO-Cr^{III}TPP + NaCl$$
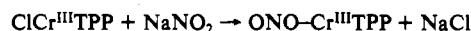
A dichloromethane solution of ClCr^{III}TPP and an aqueous solution of NaNO$_2$ were mixed and stirred for 3 h at room temperature. After removal of the aqueous phase by a funnel, the dichloromethane solution was washed several times with distilled water. The solvent, dichloromethane, was evaporated under reduced pressure, and the resulting solid was dissolved in benzene. After filtration, the solvent, benzene, was evaporated from the filtrate under reduced pressure. The dark solids obtained were dissolved again in boiling diethyl ether. Solids insoluble in diethyl ether were filtered off, and the filtrate was kept in the dark for 2 days to give black needle crystals. Anal. Calcd for ONO–Cr^{III}TPP·(C$_2$H$_5$)$_2$O·H$_2$O: C, 71.8; H, 4.98; N, 8.73. Found: C, 71.51; H, 4.78; N, 8.64. The absorption spectrum of ONO–Cr^{III}TPP is similar to that of ClCr^{III}TPP. The molar absorption coefficients in benzene are obtained as 2.1 × 10^5 and 1.12 × 10^4 M^{-1} cm^{-1} at 447 and 560 nm. IR spectrum of ONO–Cr^{III}TPP in KBr pellet, in comparison with that of ClCr^{III}TPP, is found to show characteristic absorption at 727, 1010, and 1622 cm^{-1}.

Laser photolysis was performed with a Nd–YAG laser (HY 500 from JK Lasers, Ltd.) equipped with second, third, and fourth harmonic generators. The detection system of transient spectra was described elsewhere.[10]

Quantum yield measurements by the steady light photolysis method were made with the use of monochromatic light from a xenon lamp incorporated in a Hitachi MPF 4 spectrofluorometer. The relative light intensity distribution of the xenon lamp in the region 290–600 nm was determined by measuring the excitation spectrum or rhodamine B in ethylene glycol (8 g/L). The photon flux at 313 nm was measured by actinometry with an aerated cyclohexane solution of *N*-methyldiphenylamine: the quantum yield for the formation of *N*-methylcarbazole from *N*-methyldiphenylamine has been determined as 0.45.[11] From the light intensity distribution and the photon flux at 313 nm, a photon flux at a given wavelength was obtained.

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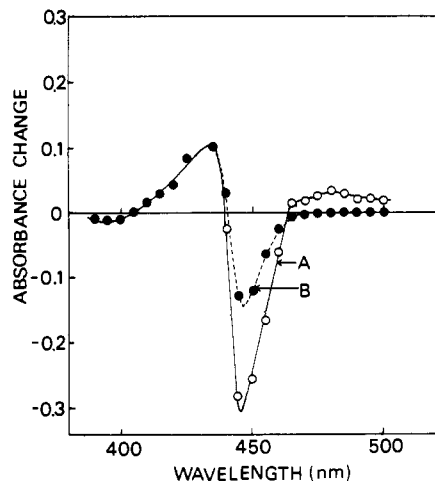
Figure 2. Transient absorption spectra observed for a benzene solution of (A) ONO–Cr^{III}TPP at 50 ns and (B) solution A 1.5 μs after 355-nm laser pulsing.

The quantum yields for photolysis of ONO–Cr^{III}TPP were also measured by the laser photolysis method, which is reported in previous papers.[4,12,13] The light intensity of a laser pulse was monitored by measuring the triplet–triplet absorption of zinc(II) tetraphenylporphyrin, Zn^{II}TPP, in a benzene solution: the yield and the molar absorption coefficient of the triplet Zn^{II}TPP have been determined as 7.4×10^4 M^{-1} cm^{-1} at 470 nm and 0.83, respectively.[14]

Results and Discussion

Figure 1 shows the absorption spectral changes in the Q band region observed for a degassed benzene solution of 1.12×10^{-4} M ONO–Cr^{III}TPP upon irradiation by a 250-W high-pressure mercury lamp with a cutoff filter ($\lambda > 450$ nm). The absorption peaks of ONO–Cr^{III}TPP located at 560 and 598 nm decrease in intensity, and a new peak appears at 533 nm. The spectral changes exhibit isosbestic points during the course of photolysis. The spectrum obtained at the end of the photolysis was found to be identical with that of oxochromium(IV) tetraphenylporphyrin, O=Cr^{IV}TPP, in benzene, which was prepared by the method reported previously.[15–17] The photochemical reaction is, therefore, represented by

$$\text{ONO–Cr}^{III}\text{TPP} \xrightarrow{h\nu} \text{O=Cr}^{IV}\text{TPP} + \text{NO}$$
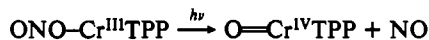
The formation of NO was confirmed by the following experiment. When gaseous photoproducts from ONO–Cr^{III}TPP in degassed benzene were introduced into the benzene solution of cobalt(II) tetraphenylporphyrin, Co^{II}TPP, by using a vacuum line, the spectrum of Co^{II}TPP was instantaneously changed to that of nitrosylcobalt tetraphenylporphyrin.[4]

The spectral changes observed for ONO–Cr^{III}TPP in aerated benzene upon irradiation were the same as those in degassed benzene. The rate for the disappearance of ONO–Cr^{III}TPP was not affected by oxygen.

Figure 2 shows the transient absorption spectra in the Soret band region observed for an aerated benzene solution of 1.0×10^{-5} M ONO–Cr^{III}TPP. The first transient spectrum observed at 50 ns after 355-nm laser pulsing decays according to first-order kinetics with the rate constant 7.0×10^6 s^{-1}, leaving the second

spectrum, which exhibits no decay over a few tens of milliseconds. Since the second spectrum is identical with the difference spectrum obtained by subtracting the spectrum of ONO–Cr^{III}TPP from that of O=Cr^{IV}TPP, the product which gives the second spectrum is ascribed to O=Cr^{IV}TPP. Because of the fact that the product does not decay, we conclude that O=Cr^{IV}TPP cannot recombine with NO. The transient spectra observed in degassed benzene were the same as those in aerated benzene. However, the rate constant for the decay of the first transient became as small as 1.6×10^6 s^{-1}. No formation of Cr^{II}TPP was detected by the present laser photolysis study, suggesting that, even if Cr^{II}TPP and NO$_2$ are produced as a radical pair like ONO···Cr^{II}TPP, ONO–Cr^{III}TPP can be readily regenerated within the pulse duration (20 ns) by the very fast recombination reaction between NO$_2$ and Cr^{II}TPP in the solvent cage.

On the basis of our previous laser photolysis study of chromium(III) porphyrin,[18] the first transient which decays with the rate constant 1.6×10^6 s^{-1} in degassed benzene is assigned to the lowest excited state of ONO–Cr^{III}TPP, $^6T_1$. The $^6T_1$ state is in thermal equilibrium with the $^4T_1$ state, which locates slightly higher than the $^6T_1$ state in energy.[19] Both the $^6T_1$ and $^4T_1$ states originate from the weak interaction between the excited triplet ligand and d-electrons located in the central Cr(III) atom.[19]

With the use of the laser photolysis method, the quantum yields for the photodecomposition of ONO–Cr^{III}TPP in benzene are determined as 0.10 ± 0.01 at 355 nm (CT band) and 0.054 ± 0.005 at 532 nm (Q band). Steady light photolysis of ONO–Cr^{III}TPP gives the yields 0.11 ± 0.01 and 0.06 ± 0.01 at the excitation wavelengths 447 (Soret band) and 550 nm (Q band), respectively. These results imply that CT and Soret band excitations give the identical quantum yield, 0.10 ± 0.01, and Q band excitation affords the lower yield, 0.06 ± 0.01. The yields in degassed benzene were identical with those in aerated benzene.

As described above, the quantum yields for the photodecomposition of ONO–Cr^{III}TPP are independent of the presence or the absence of oxygen, while the lifetime of the $^6T_1$ state is markedly quenched by oxygen. This fact indicates that neither the $^6T_1$ nor the $^4T_1$ state is responsible for the photodecomposition of ONO–Cr^{III}TPP.

The photolysis of ONO–Cr^{III}TPP is established to yield O=Cr^{III}TPP as a unique product. It is frequently observed that the product by photolysis differs from that by thermolysis. Thermolysis of solid ONO–Cr^{III}TPP in vacuum was carried out at ca. 550 K. The product was solely O=Cr^{IV}TPP.

$$\text{ONO–Cr}^{III}\text{TPP} \rightarrow \text{NO} + \text{O=Cr}^{IV}\text{TPP}$$
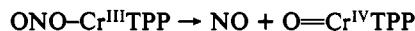
No formation of Cr^{II}TPP was detected, indicating that the bond-dissociation energy of the ONO–Cr bond is much larger than that of the ON–O bond in ONO–Cr^{III}TPP.

To the best of our knowledge, there have been only a few studies on the photochemical reaction of nitritometalloporphyrins. Steady light photolysis of nitritomanganese(III) tetraphenylporphyrin, ONO–Mn^{III}TPP, in benzene has been found to give NO and oxomanganese(IV) tetraphenylporphyrin, O=Mn^{IV}TPP, with a low quantum yield 5.3×10^{-4} at room temperature:[20]

$$\text{ONO–Mn}^{III}\text{TPP} \xrightarrow{h\nu} \text{NO} + \text{O=Mn}^{IV}\text{TPP}$$
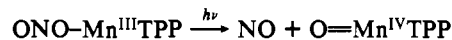
However, in low-temperature matrices, the product is identified as Mn^{II}TPP, which is yielded by the photoinduced homolysis of the O–Mn bond in ONO–Mn^{III}TPP:[21]

$$\text{ONO–Mn}^{III}\text{TPP} \xrightarrow{h\nu} \text{NO}_2 + \text{Mn}^{II}\text{TPP}$$
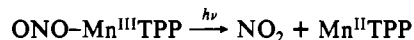
We have carried out laser photolysis of ONO–Mn^{III}TPP in benzene at 355 and 532 nm at room temperature. The transient

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spectrum observed after pulsing is almost identical with the difference spectrum obtained by subtracting the spectrum of $ONO-Mn^{III}TPP$ from that of $Mn^{II}TPP$. Thus, the principal photoproduct from $ONO-Mn^{III}TPP$ is considered to be $Mn^{II}TPP$ independent of excitation wavelengths studied. The transient, $Mn^{II}TPP$, decays according to second-order kinetics, probably due to the recombination reaction between NO_2 and $Mn^{II}TPP$. The stable photoproduct, $O=Mn^{IV}TPP$, observed with steady light photolysis at room temperature is suggested to be a minor one.

Very recently, we found that oxonitritomolybdenum(V) tetraphenylporphyrin undergoes photodissociation of NO_2 to yield oxomolybdenum(IV) tetraphenylporphyrin, $O=Mo^{IV}TPP$.[22] The yield for the photodissociation was determined as 0.3 upon excitation at both 532 and 355 nm.

As mentioned above, nitritometallotetraphenylporphyrins, ONO-MTPP, undergo α- or β-cleavage depending on the nature of the central metal, M: α-cleavage leads to the formation of NO_2 and MTPP, while β-cleavage gives NO and oxometalloporphyrin, $O=MTPP$. Homolytic α-cleavage of the axial anion in metalloporphyrins has been discussed on the basis of the intramolecular electron transfer from the axial anion to the central metal.[12,23] The photodissociation of NO_2 is, therefore, considered to result from intramolecular electron transfer from ONO^- to the central metal M in the excited state. On the other hand, β-cleavage as

observed for $ONO-Cr^{III}TPP$ is hardly interpreted in terms of intramolecular electron transfer in the excited state. Thermolysis of $ONO-Cr^{III}TPP$ confirmed that the ON–O bond is much weaker than the ONO–Cr bond. It, therefore, is expected that, even in the excited state, the weaker bond ON–O of $ONO-Cr^{III}TPP$ is preferentially dissociated. The laser photolysis studies of $ONO-Cr^{III}TPP$ reveal that the photodissociation of NO occurs via excited states higher than the $^4T_1$ state in energy. Studies on the quantum yield measurements for β-cleavage are summarized as follows. (1) Since CT band excitation at 355 nm[19] gives the yield identical with that obtained with Soret band excitation ($^4S_2 \leftarrow {}^4S_0$) at 447 nm, the internal conversion from the CT to the $^4S_2$ state is considered to occur very efficiently without dissociation of NO. (2) The dissociation of NO from $ONO-Cr^{III}TPP$ in the $^4S_2$ state takes place in competition with the fast internal conversion process from the $^4S_2$ to the $^4S_1$ state. (3) The $^4S_1$ state dissociates NO with the yield of 0.06. It is likely that the $^4S_2$ and $^4S_1$ states have excess energy and lifetime enough to dissociate NO from $ONO-Cr^{III}TPP$.

In conclusion, it is confirmed that the photolysis of $ONO-Cr^{III}TPP$ in benzene gives rise to the formation of $O=Cr^{IV}TPP$. No formation of $Cr^{II}TPP$ was detected, indicating that the β-cleavage is the predominant reaction in the excited state of $ONO-Cr^{III}TPP$, presumably owing to a small bond-dissociation energy of the ON–O bond in comparison with that of the ONO–Cr bond.

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