5002 *Inorg. Chem.* **1993,** *32,* 5002-5003

Photochemistry of Peroxotitanium(IV) porphyrin. A Novel Photocleavage of the Oxygen-Oxygen Bond

Mikio Hoshino,* Kiyoko Yamamoto, Jerome P. Lillis, Tamiko Chijimatsu, and Jun Uzawa

The Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan

Received June 11, 1993

In recent decades, the reversible fixation and the activation of dioxygen by metal complexes have attracted continued attention in both biology and chemistry.[1-9] A number of studies have revealed that the dioxygen metal complexes play a crucial role in these processes.[1-9] The structures of dioxygen complexes with one metal center are roughly divided into two types: the peroxo and the superoxo structures.[2] Iron^{II} and cobalt^{II} porphyrins form the superoxo-type complexes,[10,11] while titanium^{IV} and molybdenum^{VI} porphyrins form peroxo complexes in which the central metal binds to both of the two oxygen atoms.[12-16]

The photochemistry of metalloporphyrin–dioxygen complexes has been the subject of extensive studies to aid in understanding of the mechanisms of storage and transportation of oxygen by hemoproteins.[17-20] The metalloporphyrin–dioxygen complexes studied hitherto undergo photodissociation of dioxygen. The present paper reports a novel photocleavage of the oxygen-oxygen bond in peroxotitanium(IV) tetraphenylporphyrin, $O_2Ti^{IV}TPP$, and peroxotitanium(IV) tetra-*p*-tolylporphyrin, $O_2Ti^{IV}TTP$: the photoproduct is identified as oxotitanium(IV) porphyrin *N*-oxide. The photochemistry of bis(peroxo)molybdenum(VI) tetraphenylporphyrin $O_4Mo^{VI}TPP$,[21] is reinvestigated for comparison.

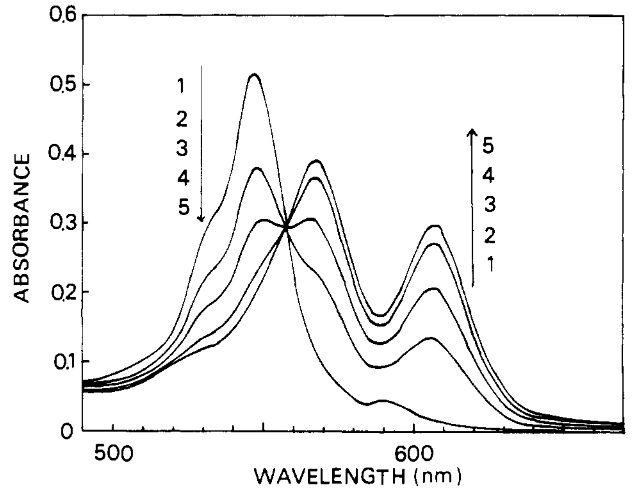


Figure 1. Spectral changes of 2.86 × 10^{-5} M $O_2Ti^{IV}TPP$ in aerated benzene upon irradiation with the mercury lamp and a cutoff filter (λ > 320 nm): (1) before irradiation; (2) after 1-min irradiation; (3) after 2-min irradiation; (4) after 4-min irradiation; (5) after 8-min irradiation.

Peroxotitanium(IV) tetraphenylporphyrin, $O_2Ti^{IV}TPP$, was synthesized and purified according to the literature.[14] The absorption spectrum of $O_2Ti^{IV}TPP$ in benzene exhibits absorption peaks at 423 ($\epsilon = 3.36 \times 10^5$ M^{-1} cm^{-1}) and 547 nm ($\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}). When an aerated solution was irradiated with a mercury lamp (250 W, USH 250D) using a cutoff filter ($\lambda >$ 320 nm), the spectrum gradually changes with isosbestic points, and new peaks appear at 438, 566, and 606 nm (Figure 1). The degassed benzene solution gave a photoproduct identical with that in aerated benzene, indicating that oxygen in air is not involved in the photoreaction of $O_2Ti^{IV}TPP$. Irradiation of $O_2Ti^{IV}TPP$ in toluene at 77 K also gave the same photoproduct. Since diffusion is suppressed at 77 K, the photoreaction seems unimolecular

The photoproduct in benzene was isolated and purified by column chromatography with silica gel. Chloroform and then a 95:5 (v/v) mixture of chloroform and ethanol were used as eluent: the former removes unreacted $O_2Ti^{IV}TPP$, and the latter gives the pure photoproduct. Fine crystals deposited from the concentrated solution of the photoproduct in a 95:5 (v/v) mixture of chloroform and ethanol. Efforts to obtain crystals suitable for X-ray structure determination, however, failed.

The photoproduct was found to react quantitatively with triphenylphosphine to give oxotitanium(IV) porphyrin, $O{=}Ti^{IV}TPP$, and triphenylphosphine oxide. This finding suggests that the photoproduct has an oxygen atom which can be removed by triphenylphosphine. When 6.6 × 10^{-2} M triphenylphosphine is added into the solution of the photoproduct, the spectrum gradually changed to that of $O{=}Ti^{IV}TPP$ with isosbestic points: the pseudo first order rate constant for the reaction was 9.2 × 10^{-4} s^{-1} at room temperature. With the use of the molar absorption coefficients of $O{=}Ti^{IV}TPP$, the amount of $O{=}Ti^{IV}TPP$ produced from the photoproduct can be determined. On the assumption that 1 mol of photoproduct gives 1 mol of $O_2Ti^{IV}TPP$, the molecular weight of the photoproduct is 746.8 ± 0.6. Chemical analysis of the photoproduct affords the following values: C, 74.02; H, 4.70; N, 7.40. These are in good agreement with those (C, 73.91; H, 4.68; N, 7.49) calculated for $C_{44}H_{28}N_4O_2Ti{\cdot}C_2H_5OH{\cdot}{}^1/_2H_2O$. The molecular weight of $C_{44}H_{28}N_4O_2Ti{\cdot}C_2H_5OH{\cdot}{}^1/_2H_2O$ is 746.95, identical with that determined above. The IR spectrum of $O_2Ti^{IV}TPP$[14] shows ν_{O-O} at 900 cm^{-1} in KBr pellet. However, the photoproduct displays no ν_{O-O} in the region around 900 cm^{-1}. It is probable that the oxygen–oxygen bond of $O_2Ti^{IV}TPP$ is photodissociated in the photoproduct.

The ^1H NMR spectrum of the photoproduct in $CDCl_3$ shows marked temperature dependence as shown in Figure 2. All the proton signals in the NMR spectrum of the photoproduct from

---

(1) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980,** *13,* 353–360.
(2) Vaska, L. *Acc. Chem. Res.* **1976,** *9,* 175–183.
(3) Martell, A. E. *Acc. Chem. Res.* **1982,** *15,* 155–162.
(4) Henrici-Olive, G.; Olive, S. *Angew. Chem., Int. Ed. Engl.* **1974,** *13,* 29–38.
(5) Collman, J. P.; Brauman, J. I.; Iverson, B. L.; Sessler, J. L.; Morris, R. M.; Gibson, Q. H. *J. Am. Chem. Soc.* **1983,** *105,* 3052–3064.
(6) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984,** *84,* 137–203.
(7) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988,** *110,* 3690–3692.
(8) Linard, J. E.; Ellis, P. E.; Budge, J. R.; Jones, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1980,** *102,* 1896–1904.
(9) Chang, C. K.; Traylor, T. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975,** *72,* 1160–1170.
(10) James, B. R. In *The Porphyrins*; Dolphin, D. Ed.; Academic Press: New York, 1978; Vol. 5, Chapter 6.
(11) Wayland, B. B.; Minkiewicz, J. V.; Abd Elmageed, M. E. *J. Am. Chem. Soc.* **1974,** *96,* 2795–2801.
(12) Latour, J.-M.; Galland, B.; Marchon, J.-C. *J. Chem. Soc., Chem. Commun.* **1979,** 570–571.
(13) Guilard, R.; Fontesse, M.; Fournar, P. *J. Chem. Soc., Chem. Commun.* **1976,** 161–162.
(14) Guilard, R.; Latour, J.-M.; Lecomte, C.; Marchon, J.-C. *Inorg. Chem.* **1978,** *17,* 1228–1273.
(15) Ellinger, Y.; Latour, J.-M.; Marchon, J.-C.; Subra, R. *Inorg. Chem.* **1978,** *17,* 2024–2026.
(16) Chevrier, B.; Diebold, Th.; Weiss, R. Inorg. Chim. Acta **1976,** *19,* L57–L58.
(17) Chernoff, D. A.; Hochstrasser, R. M.; Steele, A. W. *Proc. Natl. Acad. Sci. U.S.A.* **1980,** *77,* 5606.
(18) Hoshino, M. *Chem. Phys. Lett.* **1985,** *120,* 50–52.
(19) Collman, J. P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T. *J. Am. Chem. Soc.* **1975,** *97,* 1427–1439.
(20) Petrich, J. W.; Poyart, C.; Martin, J. L. *Biochemistry* **1988,** *27,* 4049–4060.
(21) Ledon, H.; Bonnet, M. *J. Chem. Soc., Chem. Commun.* **1979,** 702–704.

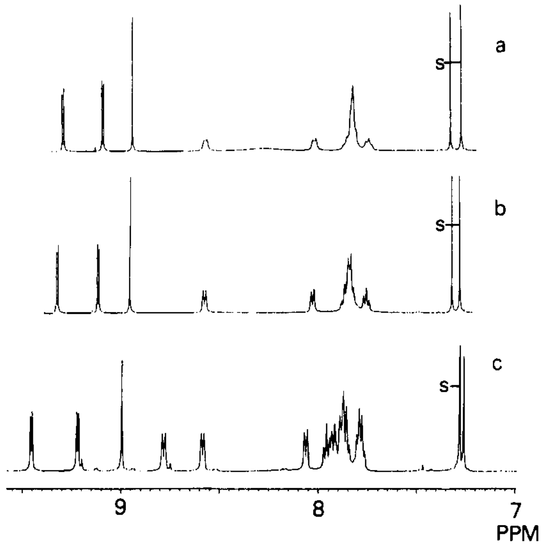
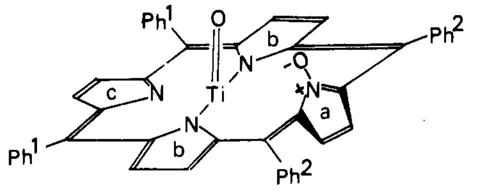


Figure 2. ^1H NMR spectra of the photoproduct of $O_2Ti^{IV}TPP$ in $CDCl_3$ taken by a JEOL JNM-GSX 500 at (a) 323, (b) 300, and (c) 223 K. The solvent $CDCl_3$ contains $CHCl_3$ as an impurity. The symbol, s, denotes the proton signal of $CHCl_3$.

$O_2Ti^{IV}TPP$ are well resolved at 223 K. The photoproduct from $O_2Ti^{IV}TPP$ was identified as oxotitanium(IV) tetraphenylporphyrin *N*-oxide, $O{=}Ti^{IV}TPPO$.[22]



The proton signals (7.26 ppm) of the pyrrole ring **a** are greatly shifted to higher field in comparison with those of thc pyrrole rings **b** and **c**.[22] The distortion of the pyrrole ring **a** out of the porphyrin plane would significantly reduce the ring current which affects the shift of the ^1H NMR signal of the pyrrole ring **a**. The temperature dependence of the NMR spectrum is interpreted in terms of the rotation of phenyl rings Ph^2: the rotation causes the line width changes for the ^1H signals of phenyl rings Ph^2 in the temperature range studied. Presumably, owing to less steric hindrance, the rotation of Ph^2 is more facile than that of Ph^1. NMR studies of the phenyl ring rotation of metallotetraphenylporphyrins have already been carried out in detail.[23,24]

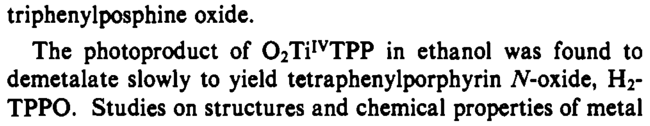
The preparative photolysis of $O_2Ti^{IV}TPP$ in benzene or in chloroform afforded $O{=}Ti^{IV}TPPO$ with ca. 80% yield. It was found that the solution of the photoproduct is further photodecomposed to yield $O{=}Ti^{IV}TPP$[25] and an unidentified brown polymer.

Peroxotitanium(IV) tetra-*p*-tolylporphyrin, $O_2Ti^{IV}TTP$, when irradiated in benzene with the mercury lamp, exhibits a photoreaction similar to that of $O_2Ti^{IV}TPP$. The absorption spectrum of $O_2Ti^{IV}TTP$ has peaks at 425 and 548 nm. The spectrum changed with isosbestic points upon irradiation to show new peaks at 439, 569, and 610 nm. The photoproduct was isolated and purified according to the method mentioned above. The molecular symmetry of the photoproduct from $O_2Ti^{IV}TTP$ was examined by measuring the H^1 signal of methyl groups at the four phenyl rings. Since two types of methyl protons (2.73 and 2.71 ppm) with equal intensities are observed for the H^1 NMR spectrum, the C_2 symmetry is safely assumed for the photoproduct of $O_2Ti^{IV}TTP$. From the analysis of NMR spectra measured in the temperature region 223–323 K, the photoproduct is identified as oxotitanium(IV) tetra-*p*-tolylporphyrin *N*-oxide.

The quantum yields, Φ, for the formation of the photoproduct from $O_2Ti^{IV}TPP$ in benzene were measured: $\Phi < 10^{-3}$ at 545 nm and $\Phi = 0.095 \pm 0.005$ at 425, 320, and 310 nm. This result indicates that excitation of the Soret and other short wavelength bands gives rise to the formation of the photoproduct. A benzene solution of $O_2Ti^{IV}TPP$ was subjected to laser pulses (20 ns in duration) at 355 nm. The transient spectrum observed at 50 ns after a pulse did not decay over a few milliseconds. Since the spectrum is in good agreement with the difference spectrum obtained by subtracting the spectrum of $O_2Ti^{IV}TPP$ from that of the photoproduct, the photoreaction of $O_2Ti^{IV}TPP$ is concluded to occur within 50 ns after a pulse, resulting in the formation of $O{=}Ti^{IV}TPPO$.

An earlier photochemical study showed that excitation of $O{=}Ti^{IV}TPP$ in ethanol gives the excited triplet state with the lifetime of 35 μs and exhibits fluorescence.[27] However, neither the fluorescence nor the triplet state was detected for $O_2Ti^{IV}TPP$. NMR studies of $O_2Ti^{IV}TPP$ have revealed that dioxygen located at the Ti atom rotates thermally.[14] The thermal rotation of dioxygen presumably accelerates the rates for radiationless transitions in the excited states of $O_2Ti^{IV}TPP$.

The initial photochemical event of O_2Ti^{IVTPP} is probably the fission of either the Ti–O or the O–O bond. The cleavage of a Ti–O bond leads to the formation of the superoxo complex. According to an earlier study of the superoxo complex of titanium(III) tetraphenylporphyrin, the superoxo complex readily changes to $O_2Ti^{IV}TPP$.[28] It, therefore, seems that the photochemical fission of the Ti—O bond does not give $O{=}Ti^{IV}TPPO$. The photochemistry for the formation of the photoproduct, $O{=}Ti^{IV}TPPO$, is



The oxygen–oxygen bond in $O_2Ti^{IV}TPP$ is initially photodissociated, followed by intramolecular oxygen atom transfer to yield $O{=}Ti^{IV}TPPO$. Since $O{=}Ti^{IV}TPPO$ has an oxygen atom bound to the pyrrole nitrogen, the oxygen atom is readily abstracted by triphenylposphine, leading to the formation of $O{=}Ti^{IV}TPP$ and triphenylposphine oxide.

The photoproduct of $O_2Ti^{IV}TPP$ in ethanol was found to demetalate slowly to yield tetraphenylporphyrin *N*-oxide, H_2-TPPO. Studies on structures and chemical properties of metal complexes of tetraphenylporphyrin *N*-oxide are in progress.

---

(22) ^1H NMR (δ, $CDCl_3$ at 223 K): pyrrole **a**, 7.26 (2H, s); pyrrole **b**, 9.45 (2H, d, J = 4.7 Hz), 9.22 (2H, d, J = 4.7 Hz); pyrrole **c**, 8.99 (2H, s); Ph^1 *o*-H, 8.58 (2H, br. d, J = 7.3 Hz), 8.08 (2H, d, J = 7.3 Hz), Ph^2 *o*-H, 8.78 (2H, d, J = 7.0 Hz). Other phenyl protons appear in the range δ 7.7–7.9 (14 H, m). Absorption peaks, λ in mm (ϵ, M^{-1} cm^{-1}), in benzene: 605 (1.01×10^4), 567 (1.33×10^4), 483 (3.0×10^5). IR (cm^{-1}, KBr pellet): 1330, 886 (N—O), 960 (Ti═O).

(23) Eaton, S. S.; Eaton, G. R. *J. Chem. Soc., Chem. Commun.* **1974**, 576–577.

(24) Eaton, S. S.; Eaton, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 3660–3666.

(25) An earlier report[26] on the photochemistry of $O_2Ti^{IV}TPP$ describes that the photoproducts from $O_2Ti^{IV}TPP$ are $O{=}Ti^{IV}TPP$ and O_2. Presumably, these products are yielded from further photolysis of $O{=}Ti^{IV}TPPO$.

(26) Boreham, C. J.; Latour, J.-M.; Marchon, J.-C. *Inorg. Chim. Acta* **1980**, *45*, L69–L71.

(27) Hoshino, M.; Imamura, M.; Watanabe, S.; Hama, Y. *J. Phys. Chem.* **1984**, *88*, 45–49.

(28) Latour, L.-M.; Marchon, J.-C.; Nakajima, M. *J. Am. Chem. Soc.* **1979**, *101*, 3974–3976.