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Photochemical Reactions of Dioxygen containing Metalloporphyrins

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ABSTRACT

Optical absorption and laser photolysis studies reveal a similarity in the nature and reactivity in the peroxo dioxygen metalloporphyrin complexes of Ti, and Mo. This reactivity is compared with that observed for the superoxo dioxygen Co(II) tetraphenylporphyrin complex.

A. INTRODUCTION

The reversible fixation and the activation of dioxygen by metal complexes have attracted considerable attention as systems to model biological oxygen transport and oxidase function as well as to develop homogeneous analogs of the heterogeneous oxidation catalysts. In a number of systems dioxygen metal complexes have been implicated as intermediates in these processes (1,2). The structures of dioxygen complexes with one metal center are roughly divided into two types; the peroxo and superoxo type complexes (3,4). Titanium(IV) and molybdenum(VI) porphyrins form the peroxo complexes in which the central metal binds to both of the two oxygen atoms (5). Cobalt(II) porphyrins are known to form the superoxo form in which the metal binds to only one of the oxygen atoms (6). In particular, the photochemistry of metalloporphyrin-dioxygen complexes has been used extensively to aid in the understanding of the mechanisms of storage and transportation of oxygen by hemoproteins (7).

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Previous studies indicated that metalloporphyrin dioxygen complexes preferentially undergo the photodissociation of dioxygen. The present paper presents the photocleavage of the oxygen-oxygen bond in peroxotitianium(IV) tetraphenylporphyrin, O_2Ti^{IV}(TPP), and the paratolylporphyrin derivative O_2Ti^{IV}(TTP) in which the photoproducts were identified as oxotitanium(IV)porphyrin N-oxide, O=Ti(TPP)O (8). The photochemistry of bisperoxomolybdenum(VI)tetraphenylporphyrin, O_4Mo^{VI}TPP exhibits similar reactivity. The photochemistry of the dioxygen adduct of Co(II)tetraphenylporphyrin was investigated for comparison.

B. EXPERIMENTAL

All reagents were purchased with the highest purity possible from Wako Chemicals and used as received. Oxygen gas was purchased from Nihon Sanso and used as received. Steady state photolyses were conducted using a high pressure mercury lamp (250 W USH250D) and a cutoff filter (λ >320nm). N-Methyldiphenylamine was used as the actinometer.

The peroxotitianium(IV)tetraphenylporphyrin, O_2Ti^{IV}(TPP), cobalt(II)tetraphenylporphyrin, and bisperoxo-molybdenum(VI)tetraphenylporphyrin, O_4Mo^{VI}TPP were synthesized and purified according to literature methods (4,5c).

Laser photolysis was conducted using the second and third harmonics of a Nd-YAG laser with a detection system previously described (9). Low temperature measurements were done using a cryostat (Oxford Instruments Model DN 10200).

C. RESULTS AND DISCUSSION

The absorption spectrum of O_2Ti^{IV}(TPP) in benzene exhibits absorption peaks at 423 (ε= 3.3 x 10^5 M^{-1} cm^{-1}) and 547 nm (ε= 1.8 x 10^4 M^{-1} cm^{-1}). Upon photolysis, the spectrum gradually changes with new peaks at 438, 566, and 606 nm and an isosbestic point at 557 nm. The photolysis of O_2Ti^{IV}(TPP) in both aerated and deaerated benzene yields the photoproduct. This indicates that atmospheric oxygen is not involved in the photoreaction. Irradiation of O_2Ti^{IV}(TPP) in toluene at 77 K gave the same photoproduct. The photoreaction seems to be unimolecular since diffusion is suppressed at 77 K.

The preparative photolysis of O_2Ti^{IV}(TPP) in benzene or in chloroform afforded $O{=}Ti^{IV}$(TPP)O with ca. 80% yield. It was found that solutions of the photoproduct slowly photodecomposed to yield $O{=}Ti^{IV}$(TPP) and an unidentified brown polymer.

The quantum yields, Φ, for the formation of the photoproduct from O_2Ti^{IV}(TPP) in benzene were found to be $\Phi < 10^{-3}$ 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 (20ns in duration) at 355nm. The transient spectrum observed at 50 ns after a pulse did not decay over a few ms. Since the transient spectrum and the difference spectrum, obtained by subtracting the spectrum of O_2Ti^{IV}(TPP) from that of the photoproduct, are in good agreement, the photoreaction of O_2Ti^{IV}(TPP) is concluded to occur within 50 ns after the pulse.

A solution of photoproduct, $O{=}Ti^{IV}$(TPP)O, in benzene was reacted with triphenylphosphine. The photoproduct in benzene was found to react with triphenylphosphine to quantitatively form oxotitanium(IV)tetraphenylporphyrin, $O{=}Ti^{IV}$(TPP), and triphenylphosphine oxide. 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 (Figure 1). The pseudo first order rate constant for the reaction was obtained to be $9.2 \times 10^{-4}\ s^{-1}$ at room temperature. This finding suggests that the photoproduct has an oxygen atom which is abstracted by triphenylphosphine.

The IR spectrum of O_2Ti^{IV}(TPP) shows a $v_{O\text{-}O}$ at 900 cm^{-1} in KBr. However the photoproduct displays no $v_{O\text{-}O}$ in the region of 900 cm^{-1}. This observation indicates that the oxygen-oxygen bond of O_2Ti^{IV}(TPP) is photodissociated in the photoproduct. The ^1H NMR spectrum of the photoproduct showed a strong temperature dependence.

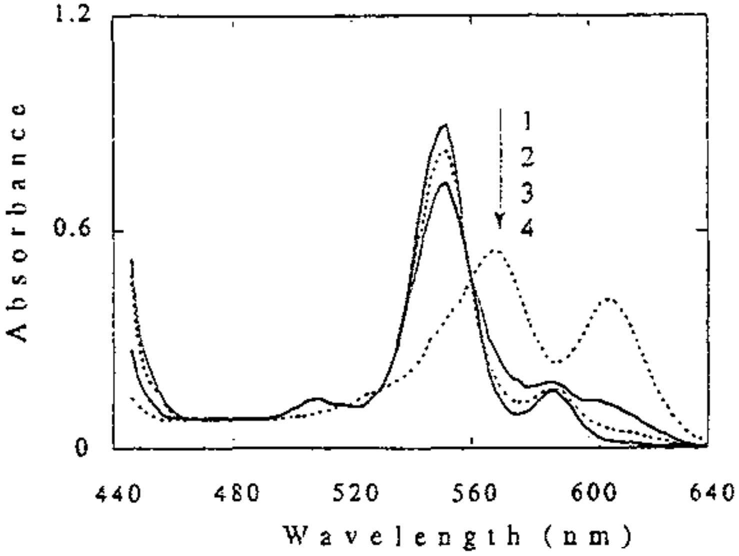


Figure 1. U.V./ Visible spectra of $O{=}Ti^{IV}(TPP)O$ (4.0×10^{-4} M) with added triphenyl phosphine (6.6×10^{-4} M) in benzene. Spectra taken at t=0 (1) 1 (2), 2.5 (3) and 12 h (4)

This behavior can be rationalized by a structure in which the porphyrin N-oxide is formed. The formation of porphyrin N-oxide would cause one of the pyrrole rings to bend out of plane and allow rotation of the phenyl rings. The photoproduct is therefore identified to be oxotitaniumtetraphenylporphyrin N-oxide (Figure 2(10)). The initial photochemical event of $O_2Ti^{IV}(TPP)$ is supposed to be 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 $O_2Ti^{IV}(TPP)$ (11). It is, therefore, suggested that the photochemical fission of the Ti-O bond does not give $O{=}Ti^{IV}(TPP)O$.

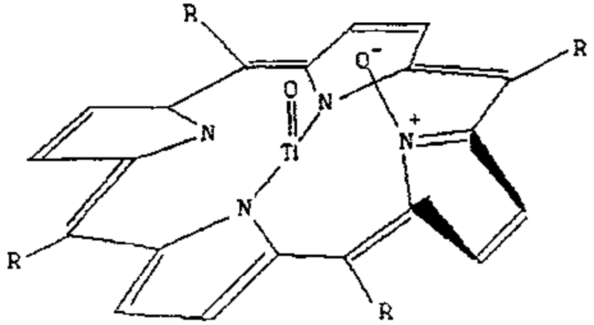
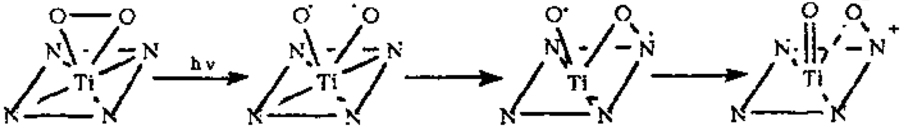


Figure 2 Schematic representation of the $O_2Ti(IV)$porphyrin photoproduct.

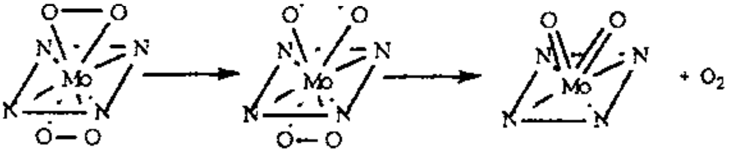
The photochemistry for the formation of the photoproduct, $O{=}Ti^{IV}(TPP)O$, is described below (Scheme 1).



Scheme 1

The oxygen-oxygen bond in $O_2Ti^{IV}(TPP)$ is initially photodissociated, followed by intramolecular oxygen atom transfer to yield $O{=}Ti^{IV}(TPP)O$. Since, $O{=}Ti^{IV}(TPP)O$ has an oxygen bound to the pyrrole nitrogen; an oxygen atom can then be readily abstracted by triphenyphosphine leading to the formation of $O{=}Ti^{IV}(TPP)$ and triphenylphosphine oxide.

It has been reported that $O_4Mo^{VI}TPP$ in both aerated and degassed benzene undergoes photoreaction to give $O_2Mo^{VI}TPP$ and dioxygen (11). The quantum yields for the photodissociation of dioxygen were determined to be 0.054 ± 0.005 at excitation wavelengths shorter than 450 nm (Figure 3). No photoreaction was observed upon excitation of the Q-band, as was the case of $O_2Ti^{IV}(TPP)$. No photoproducts were observed that could be assigned to an intramolecular oxygen transfer product. As in the case of $O_2Ti^{IV}(TPP)$, the initial photochemical event is presumed to be the fission of one of the oxygen-oxygen bonds in $O_4Mo^{VI}TPP$ leading to the facile dissociation of dioxygen (Scheme 2).



Scheme 2

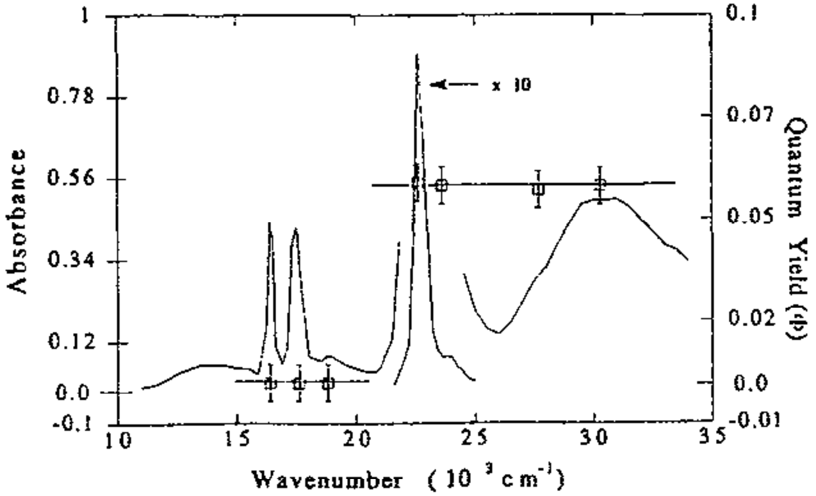


Figure 3. Absorption spectrum of $O_4Mo^{VI}TPP$ and the quantum yield (Φ) for the formation of the photoproduct, $O_2Mo^{VI}TPP$, in benzene solution.

Cobalt(II)tetraphenylporphyrin, $Co^{II}(TPP)$, forms a superoxo dioxygen adduct, O_2-$Co^{II}(TPP)$, in 2-methyltetrahydrofuran at 77 K (7). Low temperature laser flash photolysis studies were carried out in oxygen saturated solutions. The transient spectrum, obtained with excitation at both 355 and 532 nm, is in good agreement with the difference spectrum, obtained by subtracting the spectrum of O_2-$Co^{II}(TPP)$ from $Co^{II}(TPP)$. This result implies that the O_2-$Co^{II}(TPP)$ photodissociates O_2 upon laser irradiation with either the second, 532 nm or the third, 355 nm, harmonic of a Nd-YAG laser. This observation indicates that dioxygen dissociation occurs as a wavelength independent process.

D. CONCLUSION

Peroxotitanium(IV)tetraphenylporphyrin has been shown to preferentially cleave the oxygen-oxygen upon irradiation to yield a porphyrin N-oxide product. Both Ti(IV) and Mo(IV)tetraphenylporphyrin dioxygen complexes exhibited wavelength dependent photochemistry. Though the Mo complex does not form the N-oxoporphyrin product, the photoproduct can be rationalized by a reaction scheme in which the oxygen-oxygen bond is cleaved. In comparison, the cobalt(II)tetraphenylporphyrin dioxygen complex releases dioxygen upon irradiation. From these results, we believe that the primary photochemical process in these metalloperoxoporphyrins is to activate the coordinated dioxygen.

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