gives the steady-state populations; viz.^{3c} $\bar{n}_i = (S_0)_i (\psi_0)_i$.

Finally, we note one cautionary comment: The transformation⁵ which takes A into M does not take (A + D) into (M + D) unless **D** is a scalar matrix; viz. $\mathbf{D} = \text{constant} \times I$. Thus, the eigenvalues of (A + D) and of (M + D) are, in general, slightly different from each other in the fall-off region, although they agree at both the high- and low-pressure limits. However, we have shown numerically that both matrices give identical results at the limits described in conjectures 2 and 3. Likewise, in the intermediate region where (A + D) and (M + D) give slightly different results, conjecture 1 holds for either. This imperfection is of little hindrance at the present time in our pursuit of a fuller understanding of the shapes of unimolecular fall-off curves.

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Photochemistry of Molybdenum(V) Tetraphenylporphyrin Studied by Laser Flash Photolysis. Light-Induced Homolysis of the Mo–O Bond of Oxoalkoxo- and Oxo(nitrito)molybdenum(V) Tetraphenylporphyrin

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Photolysis of oxoethoxomolybdenum(V) tetraphenylporphyrin ($O=Mo^{V}(TPP)OC_{2}H_{5}$) in a degassed mixture of 9:1 toluene-ethanol gives rise to the homolysis of the $Mo-OC_2H_5$ bond with the yield 0.03 to produce oxomolybdenum(IV) tetraphenylporphyrin (O-Mo^{IV}TPP) as a stable product. Oxo(nitrito)molybdenum(V) tetraphenylporphyrin (O-Mo^V (TP-P)ONO) in toluene also undergoes photochemical cleavage of the Mo-ONO bond with the yield 0.28 to give O-Mo^{IV}TPP and NO₂, which recombine to regenerate $O = Mo^{V}(TPP)ONO$. The quantum yield measurements in the temperature range 300-77 K have shown that the activation energies for the photocleavage of the $Mo-OC_2H_5$ and Mo-ONO bonds were 5.4 and 8.0 kcal mol⁻¹, respectively. The lowest excited state of $O = Mo^{V}(TPP)OC_{2}H_{5}$, presumably ascribable to the tripquartet state, is detected by the laser photolysis at 77 K. Because of the fact that the quantum yield for the photocleavage of the Mo-OC₂H₅ bond upon Q-band irradiation is very low in comparison with those obtained upon irradiation of the Soret and CT bands, it is concluded that the lowest excited state is not responsible for the photocleavage. The photoproduct O-Mo^{IV}TPP is found to react with oxygen, resulting in formation of the dioxygen adduct. The adduct gradually changes to the μ -oxo dimer [O=Mo^vTPP]₂O. The structure of the dioxygen adduct is discussed on the basis of optical and ESR measurements.

Introduction

There have been a number of studies on photochemistry of metalloporphyrins having various central metals.¹⁻⁵ For molybdenum porphyrins, two kinds of the photoreactions have been reported: (1) photodissociation of O_2 from diperoxomolybdenum(VI) porphyrin⁶ and (2) photoinduced homolytic cleavage of axial ligands of oxomolybdenum(V) tetraphenylporphyrin.^{7,8} However, the excited-state nature as well as the mechanisms on the photoreaction of molybdenum porphyrins has not yet been investigated in detail. The ESR studies of molybdenum(V) porphyrins have demonstrated that an unpaired electron is located in the $4d_{xy}$ orbital of the central Mo(V) atom.⁹ The unpaired electron interacts with the porphyrin ligand in the excited states, which may play a key role in photophysics and photochemistry of the molybdenum(V) porphyrins.

In the present work, we initially focused on the photochemistry of oxoethoxomolybdenum(V) tetraphenylporphyrin (O=Mo(T- PP)OC₂H₅) having $C_2H_5O^-$ as an axial ligand. During the course of this study, oxomolybdenum(IV) tetraphenylporphyrin (O= $Mo^{IV}TPP$), which is the stable photoproduct from O=Mo(TP-P)OC₂H₅ in degassed solutions, was found to react with molecular oxygen to give the oxygen adduct. The oxygen adduct of O= Mo^{IV}TPP spontaneously decomposes to yield the μ -oxo dimer $[O=Mo(TPP)]_2O$. Further, we found that $O=Mo^{IV}TPP$ reacts with NO in the presence of a small amount of oxygen to yield oxo(nitrito)molybdenum(IV) tetraphenylporphyrin (O=Mo^V(T-PP)ONO). The photochemistry of O=Mo^V(TPP)ONO is also investigated in detail.

Experimental Section

Reagent grade ethanol, methanol, and acetone were used as supplied. Benzene and toluene were distilled over P_2O_5 . Oxoethoxomolybdenum(V) tetraphenylporphyrin (O=Mo(TPP)O- C_2H_5) was synthesized and purified according to the procedures reported.^{10,11} Oxo(nitrito)molybdenum(V) tetraphenylporphyrin (O=Mo^V(TPP)ONO) was prepared by the anion-exchange method: Oxo(acetato)molybdenum(V) tetraphenylporphyrin in dichloromethane and an excess amount of NaNO₂ in water were mixed and rigorously stirred for several hours. After completion of the reaction, dichloromethane in the solution was evaporated under reduced pressure. The resulting solids were filtered and

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Figure 1. Absorption spectral change of 3.8×10^{-5} M O=Mo^V(TPP)-OC₂H₅ in a degassed mixture of 9:1 toluene-ethanol upon irradiation by the mercury lamp: (1) before irradiation; (2) after 2-min irradiation; (3) after 5-min irradiation; (4) after 15-min irradiation.

washed with distilled water to remove water-soluble impurities. After drying, the solids were dissolved in benzene. The benzene solution was filtered, and the filtrate was kept in the dark for several days. Dark green crystals of $O=Mo^V(TPP)ONO$ were obtained. Anal. Calcd for $O=Mo^V(TPP)ONO \cdot 2C_6H_6$: C, 72.56; H, 4.35; N, 7.55. Found: C, 72.44; H, 4.38; N, 7.47. The IR spectrum of $O=Mo^V(TPP)ONO$ in a KBr pellet exhibits $\nu(NO)$ at 1597 cm⁻¹.

A 250-W mercury lamp, USHIO USH-250 D, was a light source for steady light photolysis. For photochemical preparation of $O=Mo^{IV}TPP$, sunlight was used as a light source.

Optical absorption and ESR spectra were recorded on a Hitachi 330 spectrophotometer and JEOL JES FE 3AX X-band spectrometer, respectively.

Laser photolysis was performed with the use of a Nd:YAG laser (HY 500 from JK Lasers Ltd.) equipped with second- (532 nm), third- (355 nm), and fourth- (266 nm) harmonic generators. The detection system of the transient spectra was reported elsewhere.¹²

The quantum yields for the photoreaction were determined by the laser photolysis method, which has been described in detail in previous papers.^{2,3,5} A benzene solution of zinc(II) tetraphenylporphyrin was used as the standard solution for measurements of the photon numbers of a laser pulse. The yields were also measured with monochromatic light from a xenon lamp incorporated in a Hitachi MPF 4 spectrofluorimeter.

Sample solutions were degassed on a vacuum line.

Results

The absorption spectrum of $O=Mo^{V}(TPP)OC_{2}H_{5}$ in benzene exhibits major absorption peaks at 620 and 580 nm in the Q-band region and at 452 nm in the Soret band region. The molar absorption coefficients were obtained as 9.6×10^{3} , 1.5×10^{4} , and $1.83 \times 10^{5} \text{ M}^{-1} \text{ cm}^{-1}$ at 620, 580, and 452 nm, respectively.

Figure 1 shows the absorption spectral changes observed for a degassed 9:1 (v/v) mixture of toluene and ethanol containing 3.8×10^{-5} M O=Mo^V(TPP)OC₂H₅ upon irradiation with the mercury lamp. The absorption peaks of O=Mo^V(TPP)OC₂H₅ decrease in intensity with irradiation time, and a new peak appears at 553 nm. The initial green color of the solution turned redish orange at the end of the photoreaction. The photochemical reaction of O=Mo^V(TPP)OC₂H₅ is expressed as

$$O = Mo^{V}(TPP)OC_{2}H_{5} \xrightarrow{h_{\nu}} O = Mo^{IV}TPP + C_{2}H_{5}O^{\bullet}$$
(I)

Since the spectral changes exhibit isosbestic points until the end of the photoreaction, 1 mol of $O=Mo^V(TPP)OC_2H_5$ gives 1 mol of $O=Mo^{IV}TPP$ upon irradiation. No photochemical reaction was observed for the solution of $O=Mo^{IV}TPP$. The molar absorption coefficients of $O=Mo^{IV}TPP$ in the solution were de-

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Figure 2. Transient absorption spectrum observed for 3.8×10^{-5} M O=Mo^V(TPP)OC₂H₅ in a degassed mixture of 9:1 toluene-ethanol 50 ns after 355-nm laser pulsing.

TABLE I: Quantum Yields for Photodissociation of the Mo-OC₂H₅ Bond in Various Solvents

solvent	quantum yield ^a	solvent	quantum yield ^a
methylcyclohexane benzene toluene acetone	0.043 0.046 0.046 0.050	ethanol methanol toluene + 10% ethanol	0.006 0.006 0.03

^a Experimental errors are ±10%.

termined as 2.1×10^4 and 3.55×10^5 M⁻¹ cm⁻¹ at 553 and 430 nm, respectively.

Figure 2 shows the transient spectrum observed for $O=Mo^V$ -(TPP)OC₂H₅ in a mixture of 9:1 toluene-ethanol, at 50 ns after 355-nm laser pulsing. The spectrum, which exhibits no decay over a few milliseconds, is in good accord with the difference spectrum obtained by subtracting the spectrum of $O=Mo^V(TPP)OC_2H_5$ from that of $O=Mo^{IV}TPP$, indicating that $O=Mo^{IV}TPP$ is also produced by the laser photolysis of $O=Mo^V(TPP)OC_2H_5$. Because of the fact that the slow formation of $O=Mo^{IV}TPP$ cannot be observed, the $C_2H_5O^{\bullet}$ radical yielded from the photolysis of $O=Mo^V(TPP)OC_2H_5$.

The quantum yield for the formation of $O=Mo^{1V}TPP$ from $O=Mo^{V}(TPP)OC_{2}H_{5}$ in a mixture of 9:1 toluene-ethanol was determined as 0.03 by using the laser photolysis method. The 532-nm laser photolysis of $O=Mo^{V}(TPP)OC_{2}H_{5}$ gave the same transient as that obtained by 355-nm laser photolysis: The yield is 0.025, a value almost identical with that measured at 355 nm. Judging from the absorption spectrum of $O=Mo^{V}(TPP)OC_{2}H_{5}$ in benzene, we consider that 532- and 355-nm light pulses are absorbed by the Soret band and the charge-transfer band, respectively.^{12,13}

An earlier study on photochemistry of oxomethoxomolybdenum(V) tetraphenylporphyrin ($\bigcirc Mo^V(TPP)OCH_3)^7$ has shown that the Q-band irradiation does not give rise to the formation of $\bigcirc Mo^{IV}TPP$. We have reconfirmed that Q-band irradiation gives a lower quantum yield than Soret band irradiation: The quantum yield for the formation of $\bigcirc Mo^{IV}TPP$ from $\bigcirc Mo^V(TPP)OC_2H_5$ upon Q-band irradiation is less than 0.001.

In Table I are listed the quantum yields for the formation of $O = Mo^{IV}TPP$ from $O = Mo^{V}(TPP)OC_2H_5$ in several solvents at room temperature, measured by 355-nm laser photolysis. The yields range from 0.006 to 0.05. Obviously, hydrocarbon solutions give higher quantum yields than alcohol solutions. No excited states of $O = Mo^{V}(TPP)OC_2H_5$ could be detected by laser photolysis at room temperature.

In order to study the photochemistry of $O=Mo^{V}(TPP)OC_{2}H_{5}$ at low temperatures, a mixture of 9:1 toluene-ethanol was used as a solvent which affords a transparent glassy solution even at



Figure 3. Quantum yields for the photodissociation of the Mo–OC₂H₅ bond of O–Mo^V(TPP)OC₂H₅ in the temperature range 200–320 K.

77 K. Figure 3 shows quantum yields for the formation of O= Mo^{IV}TPP from O=Mo^V(TPP)OC₂H₅ in a mixture of 9:1 toluene-ethanol, measured in the temperature range 320-77 K. The yield (Φ) asymptotically increases with an increase in temperature, indicating that there is an activation process for the photocleavage of the Mo-OC₂H₅ bond. With use of the quantum yield (Φ_r) of the reactive state responsible for the cleavage, the yield is formulated as

$$\Phi = \Phi_{\rm r} k_{\rm r} / (k_{\rm r} + k_{\rm d}) \tag{1}$$

where k_r and k_d are the rate constants for the cleavage of the Mo-OC₂H₅ bond and for the regeneration of O-Mo^V(TPP)O-C₂H₅ from the reactive state, respectively. On the assumption that only k_r is given by an Arrhenius expression

$$k_{\rm r} = k_{\rm r}^{0} \exp(-\Delta E/RT) \tag{2}$$

eq 1 is transformed to

$$\Phi = \Phi_{\rm r} / (1 + k_{\rm d} / k_{\rm r}^0 \exp(\Delta E / RT))$$
(3)

The quantum yield at an infinite temperature (Φ_{ω}) is formulated as

$$\Phi_{\infty} = \Phi_{\rm r} k_{\rm r}^{0} / (k_{\rm r}^{0} + k_{\rm d})$$
 (4)

From eqs 3 and 4, we obtain

$$\Phi_{\infty}/\Phi - 1 = k_{\rm d}(k_{\rm r}^{0} + k_{\rm d})^{-1}[\exp(\Delta E/RT) - 1]$$
 (5)

On the assumption that

$$\Delta E/R \gg T \tag{6}$$

eq 5 is transformed to

$$\Phi_{\infty}/\Phi - 1 = k_{\rm d}(k_{\rm r}^{0} + k_{\rm d})^{-1} \exp(\Delta E/RT)$$
(7)

From the plot of Φ at various temperatures, as shown in Figure 3, we can estimate $\Phi_{\infty} = 0.032$. The plot of $\ln (\Phi_{\infty}/\Phi - 1) \text{ vs } 1/T$ gave a straight line. The slope and intercept of the line give $\Delta E/R = 2.7 \times 10^3$ and $k_d (k_r^0 + k_d)^{-1} = 1.76 \times 10^{-5}$. The former value satisfies eq 6 in the temperature range studied. The latter value implies $k_r^0 \gg k_d$, indicating that $\Phi_{\infty} = \Phi_r k_r^0/(k_r^0 + k_d) = \Phi_r = 0.032$. The quantum yield (Φ) is, therefore, represented as

$$\Phi = 0.032[1 + 1.76 \times 10^{-5} \exp(2.7 \times 10^3/T)]^{-1} \quad (8)$$

It is noted that the yield of the reactive state is as small as $\Phi_r = 0.032$.

Low-temperature photolysis of $O=Mo^{v}(TPP)OC_{2}H_{5}$ in a mixture of 9:1 toluene ethanol at 77 K gave a transient spectrum which decays with a lifetime shorter than 100 ns. The same transient was observed for a methylcyclohexane solution of $O=Mo^{v}(TPP)OC_{2}H_{5}$ at 77 K.

Figure 4 shows the transient spectrum observed for a methylcyclohexane solution of $O=Mo^{V}(TPP)OC_{2}H_{5}$ at 77 K, 50 ns after 355-nm laser pulsing. The transient spectrum shows bleaching of $O=Mo^{V}(TPP)OC_{2}H_{5}$, and positive absorption appears in the wavelength ranges 460 nm < λ < 540 nm and λ >



Figure 4. Transient absorption spectrum observed for $O=Mo^{V}(TPP)O-C_{2}H_{5}$ in methylcyclohexane 50 ns after 355-nm laser pulsing at 77 K.

640 nm. Since (1) the transient spectrum is similar to the triplet-triplet absorption spectrum of usual metallotetraphenylporphyrins^{14,15} and (2) the decay of the transient is strictly expressed as single exponential function of time with a rate constant of $k = 6.4 \times 10^6 \text{ s}^{-1}$, we consider that the transient is ascribed to the lowest excited state of O=Mo^V(TPP)OC₂H₅. No residual absorption was detected after the decay of the transient. The photoreaction of O=Mo^V(TPP)OC₂H₅ is completely suppressed at 77 K.

The laser photolysis studies of $O = Mo^{IV}TPP$ in methylcyclohexane as well as in a mixture of 9:1 toluene-ethanol were carried out in the temperature range 293-77 K. No transient, however, was detected. It is suggested that the lifetime of the lowest excited state of $O = Mo^{IV}TPP$ is shorter than that of $O = Mo^V(TPP)O$ - C_2H_5 .

The steady light photolysis of $O = Mo^{V}(TPP)OC_{2}H_{5}$ was carried out in aerated solutions. In an aerated ethanol solution, the photoproduct $O = Mo^{IV}TPP$ is readily oxidized to regenerate $O = Mo^{V}(TPP)OC_{2}H_{5}$. According to the earlier work by Ledon et al.,⁷ regeneration of $O = Mo^{V}(TPP)OC_{2}H_{5}$ from $O = Mo^{IV}TPP$ is represented as

$$2O = Mo^{V}TPP + O_2 + 2C_2H_5OH \rightarrow$$

$$2O = Mo^{V}(TPP)OC_2H_5 + H_2O_2 (II)$$

Here 2 mol of $O=Mo^{IV}TPP$ reacts with 1 mol of O_2 to yield $O=Mo^V(TPP)OC_2H_5$ and H_2O_2 . It, therefore, is suggested that an oxygen adduct of $O=Mo^{IV}TPP$ may play an important role for the oxidation reaction.

Figure 5 shows the absorption spectra of $O = Mo^{IV}TPP$ in dry toluene before and after exposure to oxygen. When a toluene solution of 2.8×10^{-4} M $O = Mo^{IV}TPP$ is saturated with oxygen at 1 atm, the absorption peak at 532 nm markedly diminishes in intensity and broad absorption appears. However, after the oxygen-saturated solution is degassed on a vacuum line, the spectrum of the solution shows the regeneration of $O = Mo^{IV}TPP$ in ca. 60% yield, indicating that the species, which gives broad absorption, is probably ascribed to the oxygen adduct of $O = Mo^{IV}TPP$. Very recently, Tachibana and Imamura reported that $O = Mo^{IV}TPP$ forms the oxygen adduct.¹⁶ The oxygen adduct gradually changes to the μ -oxo dimer $[O = Mo^VTPP]_2O$, as will be shown later.

When a toluene solution containing 2.7×10^{-6} M O—Mo^{IV}TPP is exposed to oxygen at 1 atm, merely a small decrease in the absorbance of O—Mo^{IV}TPP is observed. Probably, the oxygen adduct tends to dissociate at low concentrations of O—Mo^{IV}TPP. It, therefore, is concluded that the oxygen adduct becomes the

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Figure 5. Absorption spectra of (A) 2.8×10^{-4} and (B) 2.7×10^{-6} M O=Mo^{IV}TPP in degassed and oxygen-saturated toluene: (a) degassed solution; (b) oxygen-saturated solution at 1 atm; (c) degassed solution of (b); (d) degassed solution; (e) oxygen-saturated solution at 1 atm.



Figure 6. ESR spectra observed at 77 K for 2.8×10^{-4} M O=Mo^{IV}TPP in oxygen-saturated toluene solution at 1 atm: (a) immediately after saturation of oxygen; (b) 20 min after saturation of oxygen; (c) 1 day after saturation of oxygen.

predominant species on going from low to high concentrations of $O=Mo^{IV}TPP$. From these results, we consider that the oxygen adduct is not a 1:1 complex of $O=Mo^{IV}TPP$ and O_2 . Presumably, 2 mol of $O=Mo^{IV}TPP$ and 1 mol of O_2 afford 1 mol of oxygen adduct.

An oxygen-saturated benzene solution of 2.8×10^{-4} M O= Mo^{1V}TPP was kept in the dark. A few days later, the solution affords black crystals. By optical and ESR measurements, the solids were identified as the μ -oxo dimer of O=Mo^{IV}TPP ([O=Mo^VTPP]₂O).^{9,10}

Figure 6 shows the ESR spectrum measured at 77 K for the toluene solution of 2.8×10^{-4} M O=Mo^{IV}TPP after saturation of oxygen at 1 atm. The sample solution, which was frozen in liquid nitrogen within 5 min after exposure to oxygen, exhibits two half-field ESR signals of the triplet species: a strong signal at 1610 G with a peak to peak width of ca. 50 G and a weak one at 1662 G with a peak to peak width of ca. 10 G. When the sample solution was kept at room temperature, the signal of the former gradually disappeared and the latter signal became strong. After 1 day, only the signal with the peak to peak width of ca. 10 G can be detected. We found that the signal having narrower



Figure 7. Absorption spectra of (A) 2.33×10^{-5} M O—Mo^V(TPP)ONO and (B) O—Mo^{IV}TPP in benzene.

width is identical with that of the μ -oxo dimer ([O=Mo^VTPP]₂O). This finding implies that the half-field signal at 1610 G is due to a precursor of [O=Mo^VTPP]₂O. On the basis of the absorption and ESR spectroscopic studies on oxidation of O=Mo^{IV}TPP in toluene, the precursor is ascribed to the oxygen adduct of O= Mo^{IV}TPP.

The spin Hamiltonian of the S = 1 state is represented by **H** = $\beta HgS + D(S_z^2 - 1/_3S^2) + E(S_x^2 - S_y^2)$, where the hyperfine interaction is neglected and the symboles have their usual meanings. The fine structure constants, D and E, were obtained as $D = 5.04 \times 10^{-2}$ cm⁻¹ and $|E| = 4.0 \times 10^{-3}$ cm⁻¹ for the oxygen adduct and $D = 3.35 \times 10^{-2}$ cm⁻¹ and $|E| = 7.6 \times 10^{-4}$ cm⁻¹ for $[O = M0^{V}TPP]_2O$.

As mentioned above, $O = Mo^{IV}TPP$ reacts with oxygen to form the oxygen adduct. Thus, it is expected that $O = Mo^{IV}TPP$ reacts with NO to give the NO adduct. However, no reaction between $O = Mo^{IV}TPP$ and NO was observed at both room temperature and 77 K.

During the course of this study on nitrosylation of O=Mo^{IV}-TPP, we found that O=Mo^{IV}TPP reacts with NO in the presence of O_2 to yield oxo(nitrito)molybdenum(V) tetraphenylporphyrin $(O=Mo^{V}(TPP)ONO)$. Isolation and purification of $O=Mo^{V}$ -(TPP)ONO were made as follows. A degassed benzene solution (500 cm³) with dissolved O=Mo^V(TPP)OC₂H₅ (300 mg) was exposed to sunlight for 3 days to prepare the benzene solution of O=Mo^{IV}TPP. The color of the solution turned from green to dark red as the photoreaction proceeds. The dark red solution was saturated with NO gas at 200 Torr on the vacuum line. Then, oxygen gas was introduced slowly into the solution until the color of the solution turned from dark red to dark green. It should be noted that excess oxygen reduces the yield of O=Mo^V(TPP)ONO. After excess NO gas and solvent were removed from the dark green solution on a vacuum line, the resulting solids were dissolved again in dry benzene. The benzene solution, which was allowed to stand for several days in the dark, gave dark green crystals of O=Mo^V(TPP)ONO in 30% yield. IR, ESR, and absorption spectra and chemica! analysis of the crystals were in precise agreement with those for O=Mo^V(TPP)ONO obtained by the anion-exchange method described previously.

Figure 7 shows the absorption spectra of 2.33×10^{-5} M O== Mo^{IV}TPP and O=Mo^V(TPP)ONO in benzene. The molar absorption coefficients of O=Mo^V(TPP)ONO are determined as 4.5×10^4 , 5.5×10^4 , 1.03×10^4 , and 8.6×10^3 M⁻¹ cm⁻¹ at the peak wavelengths, 340, 485, 611, and 655 nm, respectively. The absorption spectrum of O=Mo^V(TPP)ONO resembles that of oxochloromolybdenum(V) tetraphenylporphyrin.

Figure 8 shows the transient absorption spectrum observed for a degassed benzene solution of 1.2×10^{-5} M O=Mo^V(TPP)ONO at 50 ns after 355-nm laser pulsing. Since the transient spectrum is identical with the difference spectrum obtained by subtracting the spectrum of O=Mo^V(TPP)ONO from that of O=Mo^{IV}TPP, we concluded that the transient is ascribed to O=Mo^{IV}TPP produced by photolytic homolysis of the Mo-ONO bond:

 $O = Mo^{V}(TPP)ONO \xrightarrow{h\nu} O = Mo^{V}TPP + NO_{2}$ (III)

The transient spectrum uniformly decays in the whole wavelength



Figure 8. Transient absorption spectrum observed for a degassed benzene solution of 1.2×10^{-5} M O=Mo^{IV}TPP 50 ns after 355-nm laser pulsing.



Figure 9. Quantum yields for the formation of $O=Mo^{IV}TPP$ from $O=Mo^{V}(TPP)ONO$ in degassed toluene in the temperature range 200-300 K.

region studied according to second-order kinetics with a rate constant $8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The decay process of the transient is expressed by the recombination reaction between NO₂ and O=Mo^{IV}TPP:

$$O = Mo^{IV}TPP + NO_2 \rightarrow O = Mo^{V}(TPP)ONO \quad (IV)$$

No stable photoproducts were detected after the photolysis of $O=Mo^V(TPP)ONO$. The quantum yield for the formation of $O=Mo^{IV}TPP$ from $O=Mo^V(TPP)ONO$ is determined as 0.28 \pm 0.03 at 355 nm. The laser photolysis of $O=Mo^V(TPP)ONO$ at 532 nm also gave rise to the formation of $O=Mo^{IV}TPP$ with 0.3 \pm 0.03 yield, in agreement with that obtained by 355-nm laser photolysis.

In aerated solutions, $O = Mo^{IV}TPP$ produced by laser photolysis of $O = Mo^{V}(TPP)ONO$ decays according to second-order kinetics with a rate constant identical with that measured for the degassed solution. It is concluded that the rate for the reaction between O_2 and $O = Mo^{IV}TPP$ is much slower than that between NO_2 and $O = Mo^{IV}TPP$.

Figure 9 shows the quantum yields for the formation of $O=Mo^{IV}TPP$ from $O=Mo^{V}(TPP)ONO$ in toluene, represented as a function of temperature. The yield increases with an increase in temperature and tends to level off at higher temperatures. Analogous to the case of $O=Mo^{V}(TPP)OC_{2}H_{5}$, we assume that (1) the homolysis of the Mo-ONO bond occurs from a reactive state with an activation energy ΔE and (2) the reactive excited state regenerates the ground state $O=Mo^{V}(TPP)ONO$ without an activation energy. These assumptions lead to the expression of the quantum yield (Φ) identical with eq 3. According to the procedure used for analysis of the temperature-dependent quantum yields for the formation of $O=Mo^{IV}TPP$ from $O=Mo^{V}(TPP)$ - $OC_{2}H_{5}$, we find that the yield (Φ) for the formation of $O=Mo^{IV}TPP$ from $O=Mo^{V}(TPP)$ -ONO is expressed as

$$\Phi = 0.32[1 + 5.57 \times 10^{-7} (4.0 \times 10^3 / T)]$$
(9)

Equation 6 implies that (1) the yield of the reactive state is 0.32 and (2) the activation energy for the dissociation of the Mo-ONO bond from the reactive excited state is as large as 8 kcal mol⁻¹.

We could not detect any excited state of $O=Mo^{V}(TPP)ONO$ in toluene at a temperatures higher than 180 K. The low-temperature laser photolysis of $O=Mo^{V}(TPP)ONO$ in toluene at 77 K also gave no transients. The lifetime of the lowest excited state of $O=Mo^{V}(TPP)ONO$ is probably much shorter than the duration of the laser pulse (20 ns).

Discussion

The absorption spectrum of O—Mo^V(TPP)OC₂H₅ is composed of three major bands:^{12,13} the Q band (540 nm < λ < 650 nm), the Soret band (370 nm < λ < 470 nm), and probably the CT band (λ < 370 nm). The CT band originates from charge transfer from the porphyrin ligand to the central Mo(V) atom upon excitation. The Soret band is suggested to be the π,π^* transition mixed with a CT transition. At 532 nm, the absorption tail of the Soret band only slightly overlaps with that of the Q band. Thus, we consider that 355- and 532-nm laser pulses are principally absorbed by the CT band and the Soret band, respectively.

Photolysis of $O = Mo^V(TPP)OC_2H_5$ in a degassed mixture of 9:1 toluene-ethanol gives $O = Mo^{1/V}TPP$ as stable product with a quantum yield of ca. 0.03 upon both 355- and 532-nm irradiation. On the other hand, irradiation of the Q band of $O = Mo^V(TPP)OC_2H_5$ gives a low quantum yield: $\Phi < 0.001$. Since the Q band scarcely has the CT character, this result indicates that the photoreaction occurs effectively when the absorption bands having the CT character is excited. Because of the fact that the yields obtained with the excitation of both the CT and the Soret bands are identical, it is suggested that the excitation energy of the CT band efficiently transformed to that of the Soret band by a fast internal conversion process.

The quantum yields for the photodissociation of the Mo–OC₂H₅ bond are markedly dependent on the nature of the solvent: $\Phi \simeq$ 0.05 in benzene, toluene, methylcyclohexane, and acetone but Φ = 0.006 in ethanol and methanol. Evidently, alcoholic solvents give lower quantum yields than other solvents. In particular, the acetone solution affords a higher quantum yield than the ethanol solution. Taking account of the close similarity of the dielectric constants of acetone ($\epsilon = 20.7$) and ethanol ($\epsilon = 24.3$),¹⁷ we consider that the dielectric constant does not play an important role in photodissociation of the Mo–OC₂H₅ bond. It seems that the OH group of alcohols causes efficient deactivation of the excited states of O=Mo^V(TPP)OC₂H₅ by forming the hydrogen bond like C₂H₅OH···O=Mo^V(TPP)OC₂H₅.

Low-temperature photolysis reveals that $O=Mo^{V}(TPP)OC_{2}H_{5}$ has a lowest excited state with a lifetime as short as 156 ns in methylcyclohexane at 77 K. Since the central Mo(V) atom in $O=Mo^{V}(TPP)OC_{2}H_{5}$ has an unpaired electron in the d_{xv} orbital, it is assumed that, as in the case of copper porphyrins,¹⁸ the lowest excited state is the tripquartet state (4T) which is in thermal equilibrium with the tripdoublet state (²T), closely lying higher in energy than ⁴T. Both the ⁴T and ²T states originate from the weak interaction between the ligand excited triplet state and an odd electron on the central Mo(V) atom. Because of the weak interaction, the ⁴T and ²T states probably have absorption spectra which resemble the triplet-triplet absorption spectrum of the usual metallotetraphenylporphyrins.¹⁹ From these considerations, the transient observed for $O = Mo^{V}(TPP)OC_{2}H_{5}$ after laser pulsing at 77 K can be assigned to the lowest excited ⁴T state. The nature of the ⁴T state of $O=Mo^{V}(TPP)OC_{2}H_{5}$ is summarized as follows: (1) The lifetime in ethanol is shorter than that in methylcyclohexane, and (2) the yield of the ⁴T state in ethanol is, although not quantitative, smaller than that in methylcyclohexane.

The present study has shown that the photodissociation of the $Mo-OC_2H_5$ bond in $O-Mo^V(TPP)OC_2H_5$ takes place effectively upon excitation of the Soret and CT bands. However Q-band excitation gives very low quantum yield. It, therefore, is postulated that the lowest excited ⁴T or the ²T state of $O-Mo^V(TPP)OC_2H_5$,

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which is located below the Q band in energy, is not responsible for the photodissociation of the $Mo-OC_2H_5$ bond.

For the dissociation of the Mo–OC₂H₅ bond, an electron should be transferred from the anion ligand (C₂H₅O⁻) to the central Mo(V) atom in O=Mo^V(TPP)OC₂H₅. Excitation of the Soret band gives rise to the dissociation of the Mo–OC₂H₅ bond. Since, as mentioned above, the Soret band is considered to have charge-transfer character, excitation of the Soret band may increase the electron affinity of the excited porphyrin ligand:

$$O = Mo^{V}(TPP)OC_{2}H_{5} \xrightarrow{h\nu} [O = Mo^{V\delta^{-}}(TPP^{\delta^{+}})OC_{2}H_{5}]^{*} \quad (V)$$

Because of the increased electron affinity, the TPP ligand can abstract an electron from the axial anion ($^{-}OC_{2}H_{3}$):

$$[O = Mo^{V\delta} (TPP^{\delta})OC_2H_5]^* \rightarrow [O = Mo^V TPP^{\bullet} OC_2H_5]$$
(VI)

An excess electron in the TPP ligand of $[O=Mo^VTPP^{-} OC_2H_5]$ is readily transferred to the central metal, Mo(V), leading to the formation of the complex $[O=Mo^{IV}TPPP \cdots OC_2H_5]$, in which the central Mo(IV) atom is suggested to interact with OC_2H_5 by a weak charge-transfer interaction. The complex dissociates with the activation energy to yield $O=Mo^{IV}TPP$ and OC_2H_5

 $[O = Mo^{V}TPP \cdots OC_{2}H_{5}] \rightarrow [O = Mo^{V}TPP \cdots OC_{2}H_{5}] (VII)$

followed by

 $[O = Mo^{IV}TPP \dots OC_2H_5] \rightarrow O = Mo^{IV}TPP + OC_2H_5 \quad (VIII)$

The quantum yield measurements at various temperatures for the photodissociation of the Mo- OC_2H_5 bond have established that (1) the yield of the reactive state is as small as 0.032 and (2) the activation energy, which is necessary for the dissociation, is ca. 5.4 kcal mol⁻¹. We assume that the reactive state is ascribed to $[O=Mo^VTPP^{-}\cdots OC_2H_5]$. This assumption gives an interpretation for the low quantum yield of the reactive state: the process (VI) is competitive with the fast internal conversion of the excited state ($[O=Mo^{V\delta-}(TPP^{\delta-})OC_2H_5]^*$. Since $[O=Mo^{IV}TPP\cdots OC_2H_5]$ regenerates $O=Mo^V(TPP)C_2H_5$ by electron backtransfer from the central Mo(IV) atom to OC_2H_5 , the activation energy is considered to be necessary for the dissociation process (VIII) in order to overcome the recombination reaction between $O=Mo^{IV}TPP$ and OC_2H_5 in $[O=Mo^{IV}TPP\cdots OC_2H_5]$.

Photolysis of O=Mo(TPP)ONO in benzene and toluene leads to formation of $O=Mo^{IV}TPP$ and NO_2 with 0.3 yield at room temperature, independent of the excitation wavelengths 355 and 532 nm. In analogy to the case of $O=Mo^V(TPP)OC_2H_5$, electron transfer from NO_2^- to the central Mo(V) atom is necessary for the homolysis of the Mo-O bond in $O=Mo^V(TPP)ONO$. Since light is initially absorbed by the porphyrin ligand, it seems that an electron from NO_2^- is captured by the porphyrin ligand, leading to the reactive state [$O=Mo^VTPP^-...^ONO$]. Electron transfer from TPP⁻⁻ to the central Mo(V) atom gives rise to the formation of [$O=Mo^{IV}TPP...^ONO$], which dissociates with the activation energy to yield $O=Mo^{IV}TPP$ and NO_2 . The complex [$O=Mo^{IV}TPPP...^ONO$] undergoes electron back-transfer from the central Mo(IV) atom to ONO to regenerate $O=Mo^V(TPP)ONO$.

The activation energy for the dissociation of the Mo-ONO bond is larger than that of the Mo-OC₂H₅ bond. The bond dissociation in the complex is, as mentioned above, in competition with the electron back-transfer that regenerates $O = Mo^V(TPP)OC_2H_5$ or $O = Mo^V(TPP)ONO$. Since the electron affinity of NO₂ (≥ 2.1 eV) is larger than that of OC₂H₅ (1.8 eV), electron back-transfer in [$O = Mo^{IV}TPPP \cdots OOC_2H_5$]. In other words, the dissociation of OC₂H₅ from [$O = Mo^{IV}TPPP \cdots OC_2H_5$] occurs more easily than that of NO₂ from [$O = Mo^{IV}TPPP \cdots ONC_3$]. Therefore, the activation energy of the former is necessarily larger than that of the latter in order to overcome electron back-transfer.

ESR studies have confirmed that the oxygen adduct of O= Mo^{IV}TPP is in the triplet state: $D = 5.04 \times 10^{-2}$ cm⁻¹ and $E = 4.0 \times 10^{-3}$ cm⁻¹. On the other hand, the μ -oxo dimer [O= Mo^VTPP]₂O in toluene gives $D = 3.35 \times 10^{-2}$ cm⁻¹ and E = 7.6 × 10⁻⁴ cm⁻¹. It has been suggested that the fine-structure constant (D) of the μ -oxo dimer resulted from the magnetic dipole-dipole interaction between the two unpaired electrons located at the two central Mo atoms.⁹ The distance between the two electrons estimated by the use of $D = g^2 \beta^2 / R^3$ is ca. 3.9 Å in the crystal of the μ -oxo dimer.⁹ The value of 3.9 Å is in good agreement with the distance between the two Mo atoms in the μ -oxo dimer obtained from the X-ray crystal structure determination.²⁰ In the present study, we obtained R = 3.7 Å as a distance between the two unpaired electrons on the Mo atoms of the μ -oxo dimer in toluene with the use of $D = g^2 \beta^2 / R^{3.21}$

It has been considered that the *D* value is a measure of the distance between two unpaired electrons. The fact that the *D* value of the oxygen adduct of $O=Mo^{IV}TPP$ is larger than that of the μ -oxo dimer [$O=Mo^{V}TPP$]₂O suggests that the distance between the two Mo atoms in the oxygen adduct is shorter than that in the μ -oxo dimer.

Iron(II) porphyrins (Fe^{II}P) are known to react with oxygen to yield the μ -oxo dimer of iron(III) porphyrin ([Fe^{III}P]₂O).²² The reaction intermediate, which leads to the formation of [Fe^{III}P]₂O, is considered to be the dioxygen adduct ([Fe^{III}P]₂O₂).²³ We initially considered that the dioxygen adduct of O=Mo^{IV}TPP is also formulated as [O=Mo^VTPP]₂O₂. A probable structure for [O=Mo^VTPP]₂O₂ is the μ -peroxo-bridged dimer of O=Mo^VTPP, in which an unpaired electron is located in the central Mo(V) atom of each O=Mo^VTPP. The distance between the two unpaired electrons in the μ -superoxo-bridged dimer is expected to be larger than that in the μ -oxo dimer. However, as mentioned above, the distance estimated from the D value of the oxygen adduct of O=Mo^{IV}TPP is smaller than that of [O=Mo^VTPP]₂O. We, therefore, assumed that the structure of the dioxygen adduct is as follows:



Here the dianion of dioxygen is sandwiched between the two porphyrin planes. This structure predicts that, in agreement with the consideration on the basis of the fine-structure constants Dand E, (1) the distance between the two Mo(V) atoms is shorter than that of $[O=Mo^{V}TPP]_2O$ and (2) because of the low symmetry of the molecule (C_2), the E value of the dioxygen adduct is larger than that of $[O=Mo^{V}TPP]_2O$, which is expected to be approximately axial symmetry.

In benzene, the dioxygen adduct $[O=Mo^{V}TPP^{+}]_{2}O_{2}^{2^{-}}$ changes to $[O=Mo^{V}TPP]_{2}O$. The formation of $[O=Mo^{V}TPPP]_{2}O$ is represented by

 $2O = Mo^{1V}TPP + O_2 \rightleftharpoons [O = Mo^{V}TPP^+]O_2^{2-}$

 $[O = Mo^{V}TPPP^{+}]O_{2}^{2-} \rightleftharpoons 2O = Mo^{V}(TPP)O^{+}$

 $O = Mo^{V}(TPP)O^{\bullet} + O = Mo^{V}TPP \rightarrow [O = Mo^{V}TPP]_{2}O$

In aerated ethanol, O=Mo^{IV}TPP is readily oxidized to regenerate O=Mo^V(TPP)OC₂H₅, presumably owing to

 $[O=Mo^{V}TPP^{+}]O_{2}^{2-} + 2C_{2}H_{5}OH \rightarrow 2O=Mo^{V}(TPP)OC_{2}H_{5} + H_{2}O_{2}$

The formation of H_2O_2 has already been detected for the aerated

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methanol solution of $O = Mo^{IV}TPP$.

We found that O=Mo^{IV}TPP in benzene in the presence of NO and a small amount of O_2 gives $O=MO^V(TPP)ONO$ as a stable product. It is likely that O=Mo^V(TPP)ONO is produced by either (1) the reaction between $O = Mo^{IV}TPP$ and NO₂ or (2) the addition reaction of NO to $O = Mo^{V}(TPP)^{+}O^{-}$.

Conclusion

On the basis of the present studies, we conclude that (1) O= Mo^v(TPP)OC₂H₅ and O=Mo^v(TPP)ONO undergo photodissociation of the Mo-O bond to yield Ó-Mo^{IV}TPP, (2) the low quantum yield for photodissociation of O==Mo^V(TPP)OC₂H₅ in ethanol is ascribed to the formation of the hydrogen bond, C₂- $H_5OH \rightarrow O = MO^{V}(TPP)OC_2H_5$, which is suggested to cause the efficient deactivation of the excited states, (3) the lowest excited state, ⁴T, is not responsible for the photodissociation of O=

 $Mo^{V}(TPP)OC_{2}H_{5}$, and (4) from the excitation wavelength dependence of the quantum yields, the charge-transfer character of the excitation bands is essential to the photodissociation of the Mo-O bond.

In addition to those mentioned above, we found that O= Mo^{IV}TPP reacts with oxygen to give the dioxygen adduct, which thermally decomposes to give the μ -oxo dimer [O=Mo^VTPP]₂O. From optical and ESR studies, the dioxygen adduct is assumed to have the structure $[O=Mo^{V}TPP^{+}]O_{2}^{2-}$ in which O_{2}^{2-} is sandwiched between the two porphyrin planes.

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Registry No. O=Mo(TPP)OC₂H₅, 65404-71-9; O=Mo^V(TPP)ON-O, 136882-00-3; O=Mo^{IV}TPP, 33519-60-7; O₂, 7782-44-7; [O=Mo(T-PP)]₂O, 61747-27-1; [O=Mo^VTPP⁺]₂O₂²⁻, 136910-93-5.

Electronic Energy Transfer in Anisotropic Systems. 4. Energy Migration in Two **Dimensions and Molecular Reorientation**

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The effect of molecular reorientation and energy migration on the steady-state and time-resolved fluorescence anisotropies is investigated. The energy migration takes place between isotropically oriented donors in a two-dimensional disordered system. The donor molecules are 2,5,8,11-tetra-tert-butylperylene (TBPe) which are solubilized in the hydrophobic part of unilamellar vesicles. The vesicles are prepared with 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) in a glycerol-water solution. At low number density of TBPe the fluorescence anisotropies are solely due to the reorientation of TBPe. The rotational motion of TBPe can be described as that of an oblate ellipsoid in a solvent. At high number densities of TBPe an additional depolarization, due to electronic energy migration, is observed. The fluorescence relaxation is single exponential at all temperatures (240 and 320 K) and concentrations studied. The order parameter of TBPe in the DOPC could be determined at temperatures above 260 K and was found to be small and constant. The time-resolved fluorescence anisotropies measured, at high and low number densities of TBPe, were analyzed globally. The analytical model used is based on the two-particle (tp) approximation of energy migration in a two-dimensional system. It was shown that the effect of vesicle curvature is negligible. The model contains only one unknown parameter, namely, a factor K which is modulated by molecular reorientations. In the so-called "dynamic" and "static" limits, i.e., for very fast or slow rotational rates, the tp model predicts the values of $K_{dyn} = 0.874$ and $K_{\text{stat}} = 0.740$, respectively. From experiments we find that the values of K agree reasonably with K_{stat} at temperatures between 260 and 320 K, while it surprisingly approaches the value of K_{dvn} at lower temperatures. The steady-state anisotropy was calculated by using the tp model. A good agreement with the experimental anisotropy was obtained for $K = K_{stat}$ at temperatures above 260 K. The increase of K observed at lower temperatures coincides with the phase transition of DOPC in the range 240-260 K. Thereby, TBPe molecules probably reorient and/or become spatially or orientationally correlated.

Introduction

Energy migration between fluorescent molecules, often referred to as donor-donor transfer, is most conveniently monitored in fluorescence depolarization experiments. In such studies the time-resolved and steady-state fluorescence anisotropies [denoted r(t) and r_s , respectively] are usually determined. The fluorescence anisotropy reports changes of the orientational distribution of the excited molecules during the fluorescence lifetime. If the molecules undergo rotational motions, this will change the orientational distribution and thereby contribute to the decay of r(t) and the value of r_s . Migration of electronic energy between the molecules also leads to a change of the orientational distribution of the excited molecules. However, the influences of rotational motions and energy migration on r(t) and r_s are not independent processes. The probability of energy migration depends on the relative orientation of the interacting molecules which actually changes by molecular rotations. For this reason experimental studies of energy migration are usually performed with fluorescent molecules at low temperatures, or when dissolved in vitreous solvents, or for short-living fluorophores where contributions from the rotational rates are small or negligible.¹⁻⁶ Even under these simplifying conditions the theoretical modeling of the fluorescence anisotropy is not trivial, and only approximate models are available. A more accurate handling, which also allows for studying systems having a spatial and/or an orientational anisotropy, can be activated by using Monte Carlo simulations where the interactions are explicitly considered.7,8

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