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Reversibility in the Formation of Oxo(peroxo)porphyrinatomolybdenums

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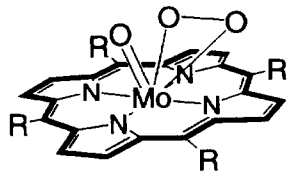
Reversibility in the formation reaction of a series of the oxo(peroxo)porphyrinatomolybdenums, [$Mo^{VI}O(tmp)(O_2)$] **1**, [$Mo^{VI}O(tdcpp)(O_2)$] **2**, [$Mo^{VI}O(ttp)(O_2)$] **3**, [$Mo^{VI}O(tdmpp)(O_2)$] **4**, and [$Mo^{VI}O(tpp)(O_2)$] **5**, was studied. In these dioxygen complexes with various porphyrin rings, two complexes, **2** and **4**, were newly prepared by the solid-state reactions of corresponding Mo(IV) complexes with O_2. All the complexes were characterized by IR, ^{1}H NMR, and UV-vis spectroscopic measurements. In the reaction of O_2 with [$Mo^{IV}O(tdcpp)$] **2r**, which has bulky substituents with an electron-withdrawal character, the association rate constant was determined to be 1.2×10^{-2} $dm^3\ mol^{-1}\ s^{-1}$ in toluene at 20 °C. The value of the rate constant is about one thirtieth of that for [$Mo^{IV}O(tmp)$] **1r**, which also has bulky substituents. The result indicates that the electronic effects of the porphyrin rings, which reflect on the redox potentials of the central molybdenum ion, are important in determining kinetic and thermodynamic stability of the dioxygen complexes. All the dioxygen complexes undergo deoxygenation upon photoirradiation to give corresponding [$Mo^{IV}O(por)$]. The redioxygenation profiles of [$Mo^{IV}O(por)$] in the dark were also significantly affected by the steric bulkiness of the porphyrin ligands. While the bulky porphyrin complexes of **1** and **2** gave full recovery of the dioxygen complexes in the dark, less bulky porphyrin complexes of **3**, **4**, and **5** undergo some side reactions to Mo(V) species. The rate and extent of the Mo(V) complex formations increase with decreasing steric bulkiness.

Molybdenum, one of the essential elements for life, takes various oxidation states from −II to VI; these states are closely correlated with the activities of metalloproteins such as xanthine oxidase and nitrogenase[1] and with its high catalytic activities for organic reactions.[2]

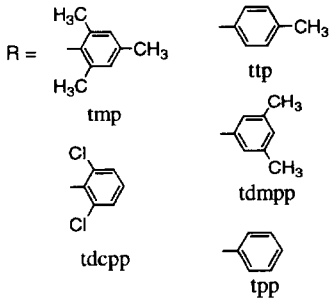
Porphyrinatomolybdenums show a strong affinity for dioxygen species in their higher-oxidation states.[3] A *trans*-diperoxo complex, [$Mo^{VI}(ttp)(O_2)_2$], is formed by the reaction of [$Mo^{V}O(ttp)(OMe)$] with H_2O_2,[4,5] and transformed to a *cis*-dioxo complex, [$Mo^{VI}(O)_2(ttp)$], by photoirradiation.[6] [$Mo^{V}O(tpp)(X)$] (X^- = Cl^-, Br^-, or NCS^-) undergoes the reaction with O_2^- at low temperatures to give a peroxomolybdenum(V) species of [$Mo^{V}O(tpp)(O_2)$]$^-$.[7]

We previously reported that an oxo(porphyrinato)molybdenum(IV), [$Mo^{IV}O(tmp)$], with bulky substituents, undergoes the reaction with molecular oxygen to afford a dioxygen adduct, [$Mo^{VI}O(tmp)(O_2)$], at room temperature.[8] The dioxygen complex liberates O_2 upon heating to give [$Mo^{IV}O(tmp)$]. The complex also liberates O_2 upon irradiation with visible light and is regenerated in the presence of dioxygen when visible light is excluded. This reversible dioxygenation was repeatedly observed both in solution[8] and in the solid state[9] under photochemical and thermal conditions. Structure determination by X-ray crystallography revealed that the dioxygen complex has oxo and peroxo ligands on the same side of the porphyrin plane and adopts an eclipsed orientation with respect to one of the pairs of *trans* N atoms of the pyrrole ring.[10] Even if porphyrin rings had no bulky substituents, the solid state reaction of [$Mo^{IV}O(por)$] (por = ttp, tpp) with O_2 gave the corresponding dioxygen complexes of [$Mo^{VI}O(por)(O_2)$].[11]

In order to understand the electronic and steric effects on the kinetic and thermodynamic stability of these oxo(peroxo)porphyrinatomolybdenums(VI), a series of dioxygen complexes with various porphyrin substituents as illustrated in Fig. 1 were prepared and characterized. In this paper, the effects of porphyrin substituents on the formation



[$Mo^{VI}O(por)(O_2)$]



[$Mo^{VI}O(tmp)(O_2)$] : **1** [$Mo^{VI}O(tdcpp)(O_2)$] : **2**

[$Mo^{VI}O(ttp)(O_2)$] : **3** [$Mo^{VI}O(tdmpp)(O_2)$] : **4**

[$Mo^{VI}O(tpp)(O_2)$] : **5**

Fig. 1. Oxo(peroxo)porphyrinatomolybdenums(VI).

of dioxygen complexes are discussed.

Experimental

Materials. 2,4,6-Trimethylbenzaldehyde, 2,6-dichlorobenzaldehyde, 3,5-dimethylbenzoic acid, and $[Mo(CO)_6]$ were purchased from Aldrich. A spectral grade of toluene used in the kinetic studies was purchased from Dojindo Laboratory. CH_2Cl_2 used in cyclic voltammetry was purchased from Nacalai Tesque and purified by distillation under Ar before use. Other agents and solvents were purchased from Wako and used as received. Pure oxygen (grade B, > 99.9%) was purchased from Nippon Sanso. $^{18}O_2$ was obtained from Cambridge Isotope Laboratories.

Measurements. UV-vis spectra were recorded on a Hitachi spectrophotometer model 808 or on a Hitachi UV-3000 spectrophotometer. IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer. ^{1}H NMR spectra were measured with a JEOL EX270 FT-NMR spectrophotometer. FAB MS spectra and elemental analysis were carried out at the Center for Instrumental Analysis, Hokkaido University. ESR spectra were recorded on a JEOL JES-FE3X spectrometer. TPD (Temperature Programmed Desorption) mass spectra were measured in the range of room temperature to 200 °C with a temperature rising speed at 2—4 °C per min under 10^{-5} Torr (1 Torr = 133 Pa). The evolved gases were analyzed with an ANELVA AQA100R quadruple mass spectrometer. Cyclic voltammetry was performed with a BAS CV-50 voltammetric analyzer. The working and the counter electrodes for the cyclic voltammetry were a Pt disk and a Pt wire, respectively. The reference electrode was an Ag/AgCl, against which the half-wave potentials of Fc^+/Fc ($E_{1/2}(Fc^{+/o})$) (Fc = ferrocene) was 0.52 V. The sample solution in CH_2Cl_2 containing 0.1 mol dm^{-3} TBAP were deoxygenated by Ar stream. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} at room temperature. Kinetic measurements of the reversible dioxygenation of $[Mo^{IV}O(tdcpp)]$ **2r** in toluene were carried out using a Hitachi 808 spectrophotometer with thermostated cells. The change in absorbance at 430 nm was analyzed by the plot of $\ln((Abs_t - Abs_\infty)/(Abs_0 - Abs_\infty))$ vs. time, where Abs_∞ is the final absorbance, Abs_0 the initial absorbance, and Abs_t the absorbance at an appropriate time t. The concentration of O_2 was determined by the partial pressure of O_2 in the optical cell and the Ostwald's solubility coefficient (12.8×10^{-8} m^3) of O_2 in toluene at 20 °C.[8,12]

Preparation of Porphyrins. H_2tdmpp, H_2ttp, and H_2tpp were prepared by Alder's method.[13] H_2tmp and H_2tdcpp were synthesized by Lindsey's method.[14] 3,5-Dimethylbenzaldehyde was prepared from 3,5-dimethylbenzoic acid in two steps and used for the synthesis of H_2tdmpp, i.e., the benzoic acid was reduced to the corresponding benzyl alcohol using $LiAlH_4$, and the alcohol was converted to the benzaldehyde by using a pyridinium chlorochromate (PCC) as an oxidizing agent.[15] Those compounds were identified by ^{1}H NMR and UV-vis spectral measurements and elemental analysis.

Preparation of Dioxygen Complexes. $[Mo^{VI}O(tmp)(O_2)]$ **1** was prepared by the method of a previous report.[8] The elemental analysis was satisfactory and all the spectral data agreed well with the previous results.

$[Mo^{VI}O(tdcpp)(O_2)]$ 2. The mixed solvent of decaline (36 ml) and octane (9 ml) was bubbled with oxygen gas for 30 min; then were added H_2tdcpp (500 mg, 0.5 mmol) and $[Mo(CO)_6]$ (ca. 1 g). The mixture was refluxed for 6 h with vigorous stirring, during which time the Soret band of the free porphyrin disappeared. The solution was left to stand at room temperature and then filtered. The filtrate was chromatographed on a silica-gel column using CH_2Cl_2 as an eluent. After the first red band containing free porphyrin was passed through the column, the eluent was changed to CH_2Cl_2 containing 5% (v/v) ethanol.[16] The eluted green band was collected and evaporated in vacuo. The solid material obtained was dissolved in a small amount of CH_2Cl_2 and introduced into a schlenk tube connected to a vacuum line. The solution was again evaporated to dryness, then heated at 260 °C under 10^{-2} Torr.[17] The schlenk tube containing the purple solid material was opened in a glove bag with a dioxygen atmosphere and left to stand over a week in the dark. The resulting solid was dissolved again in a small amount of CH_2Cl_2 and chromatographed on silica gel using CH_2Cl_2 as an eluent. The second red band thus eluted was collected and evaporated to dryness. The material was dissolved in a small amount of CH_2Cl_2 followed by the addition of pentane to give a dark red precipitate. The powdery compound was washed with pentane and dried in a dioxygen atmosphere. Yield 57 mg (11%). Anal. Found: C, 51.84; H, 2.48; N, 5.33; Cl, 27.21%. Calcd for $C_{44}H_{20}Cl_8MoN_4O_3$: C, 51.19; H, 1.95; N, 5.43; Cl, 27.47%. UV-vis (toluene, 20 °C) λ_{max}/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 430 (162), 532 (9.81), 564 (14.2), 613 (2.48). ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 9.12 (AB quartet, 4H, β-pyrrole), 8.74 (s, 2H, β-pyrrole), 8.37 (s, 2H, β-pyrrole), 7.91—7.70 (m) (12H, *m,p*-2,6-dichlorophenyl). IR (KBr) ν 932 (ν_{O-O}), 918 cm^{-1} ($\nu_{Mo=O}$). FAB MS: m/z^+ = 1000 ($[MoO(tdcpp)]^+$).

$[Mo^{IV}O(tdcpp)]$ 2r. The complex was prepared by the pyrolysis of $[Mo^{V}O(tdcpp)(OEt)]$[16,17] or that of the dioxygen complex of **2**. UV-vis (toluene, 20 °C) λ_{max}/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 429 (432), 554 (20.8), 591 (5.31). ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 8.98 (s, 8H, β-pyrrole), 7.95—7.70 (m) (12H, *m,p*-2,6-dichlorophenyl). IR (KBr) ν 982 cm^{-1} ($\nu_{Mo=O}$).

$[Mo^{VI}O(ttp)(O_2)]$ 3. H_2ttp (200 mg, 0.2 mmol) and an excess of $[Mo(CO)_6]$ (ca. 0.5 g) were added to the mixed solvent of 24 ml of decaline and 6 ml of octane, and the mixture was refluxed for 2 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was loaded on a silica-gel column and eluted with CH_2Cl_2 containing 0.4% of MeOH. The bands of the free bases and of an undefined green material were removed. Another green band containing $[Mo^{V}O(ttp)(OMe)]$ was collected by using 5% MeOH/CH_2Cl_2 as an eluent; the eluent was evaporated to dryness.[18] The solid of $[Mo^{V}O(ttp)(OMe)]$ was heated at 260 °C under reduced pressures (ca. 10^{-2} Torr) to give $[Mo^{IV}O(ttp)]$ **3r**.[17] The crude **3r** was ground in a mortar in a glove bag with oxygen gas and left to stand there in the dark for over two weeks. The resulting solid material was dissolved in CH_2Cl_2 and chromatographed with a silica-gel column using CH_2Cl_2 as an eluent. The second red band was collected and evaporated to dryness. The product was dissolved in a small amount of CH_2Cl_2 followed by the addition of pentane to obtain the dark red powdery compound; this was washed with pentane and dried in a dioxygen atmosphere. Yield 54 mg (33%). Anal. Found: C, 69.15; H, 4.77; N, 6.95%. Calcd for $C_{48}H_{36}MoN_4O_3$: C, 70.93; H, 4.46; N, 6.89%. UV-vis (CH_2Cl_2, 20 °C) λ_{max}/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 432 (179), 529 (11.6), 560 (13.0). ^{1}H NMR (CD_2Cl_2, 270 MHz) δ = 9.22 (AB quartet, 4H, β-pyrrole), 8.90 (s, 2H, β-pyrrole), 8.50 (s, 2H, β-pyrrole), 8.20—7.81 (br), 7.60, 7.57 (16H, *o,m*-tolyl), 2.66 (s, 6H, *p*-CH_3), 2.65 (s, 6H, *p*-CH_3). IR (KBr) ν 926 (ν_{O-O}), 910 cm^{-1} ($\nu_{Mo=O}$). FAB MS: m/z^+ = 782 ($[MoO(ttp)]^+$).

$[Mo^{VI}O(tdmpp)(O_2)]$ 4. This complex was prepared by the same method as that of **3** by using H_2tdmpp instead of H_2ttp. Yield 30 mg (17%). Anal. Found: C, 72.18; H, 5.60; N, 6.26%. Calcd for $C_{52}H_{44}MoN_4O_3$: C, 71.88; H, 5.10; N, 6.45%. UV-vis (toluene, 20 °C) λ_{max}/nm ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}): 432 (174), 530 (12.1), 562

(13.9). ^{1}H NMR (CD_2Cl_2, 270 MHz) δ = 9.23 (AB quartet, 4H, β-pyrrole), 8.91 (s, 2H, β-pyrrole), 8.50 (s, 2H, β-pyrrole), 7.97—7.56 (br), 7.43, 7.40 (12H, *o*-,*p*-3,5-dimethylphenyl), 2.59, 2.56, 2.52 (24H, *m*-CH_3). IR (KBr) ν 928 (ν_{O-O}), 912 cm^{-1} ($\nu_{Mo=O}$). FAB MS: m/z^+ = 838 ([MoO(tdmpp)]$^+$).

[Mo^{VI}O(tpp)(O$_2$)] 5. This complex was prepared by a similar method to that for **3** by using H_2tpp instead of H_2ttp. Yield 17 mg (11%). Anal. Found: C, 70.61; H, 4.23; N, 7.26%. Calcd for $C_{44}H_{28}MoN_4O_3$: C, 69.84; H, 3.73; N, 7.40%. UV-vis (CH_2Cl_2, 20 °C) λ_{max}/nm (ε/10^3 dm^3 mol^{-1} cm^{-1}), 430 (158), 528 (10.5), 560 (12.2). ^{1}H NMR (CD_2Cl_2, 270 MHz) δ = 9.22 (AB quartet, 4H, β-pyrrole), 8.90 (s, 2H, β-pyrrole), 8.50 (s, 2H, β-pyrrole), 8.0—7.8 (br), 7.80, 7.79 (20H, phenyl H). IR (KBr) ν 928 (ν_{O-O}), 910 cm^{-1} ($\nu_{Mo=O}$). FAB MS: m/z^+ = 726 ([MoO(tpp)]$^+$).

Results and Discussion

Preparation and Characterization of Dioxygen Complexes. While the dioxygen complex of [Mo^{VI}O(tmp)(O$_2$)] **1** having a bulky ligand was prepared by the reaction of [Mo^{IV}O(tmp)] **1r** with O_2 in solution, [Mo^{VI}O(tdcpp)(O$_2$)] **2** was obtained by the reaction of [Mo^{IV}O(tdcpp)] **2r** in the solid state with O_2. In the solution reaction, **2r** which has a bulky but more electron-withdrawing ligand gave some molybdenum(V) complexes in addition to **2**. This phenomenon can be explained by that the dioxygenation with O_2 proceeded so slowly that some side reactions occurred. In the cases of the less bulky complexes of [Mo^{VI}O(ttp)(O$_2$)] **3**, [Mo^{VI}O(tdmpp)(O$_2$)] **4**, and [Mo^{VI}O(tpp)(O$_2$)] **5**, [Mo^{IV}O(por)] in the solid state were left to stand in a dioxygen atmosphere over two weeks to obtain the corresponding dioxygen complexes. The oxo(peroxo)porphyrinatomolybdenums thus prepared were characterized by several spectral methods. All the isolated dioxygen complexes were quite stable at room temperature in the solid state in the dark.

The elemental analyses were consistent with their respective compositions, as described in the experimental section. FAB MS measurements gave the parent peak of [MoO(por)] units instead of the expected mass number of the dioxygen complexes. Previously it was reported that **1** liberates dioxygen gas upon heating and photoirradiation to give **1r**.[8] The dioxygen complexes of **2**—**5** also undergo gas evolution upon heating and photoirradiation (vide infra). To confirm that the gas evolved in the course of the pyrolysis of the dioxygen complexes in the solid state is O_2, TPD mass measurements were carried out for **2** and **3**. O_2 was detected from 40 to 120 °C with a maximum at 94 °C for **2**, and from 50 to 150 °C with a maximum at 121 °C for **3**. These results were comparable to the data in the system of **1**.[8] When the solid materials obtained by the pyrolysis for the TPD mass measurements were dissolved in toluene under Ar, each solution gave a UV-vis spectrum, typical of the oxomolybdenum(IV) complex of the corresponding porphyrin. This result confirmed that the dioxygen complexes of **2** and **3** liberate dioxygen to give Mo(IV) complexes by heating in the solid state as shown in Eq. 1.

$$[Mo^{VI}O(por)(O_2)]\ (solid) \xrightarrow{\Delta} [Mo^{IV}O(por)] + O_2 \qquad (1)$$

The pyrolyses of **4** and **5** also gave corresponding oxo(porphyrinato)molybdenums(IV).

The infrared spectral data of a series of oxo(peroxo)porphyrinatomolybdenums are summarized in Table 1. Each complex showed the characteristic Mo=O and O–O stretching bands at around 910 and 926 cm^{-1}, respectively. These assignments were confirmed by the isotopic shifts with its $^{18}O_2$ derivative in the systems of **2** and **3**. [Mo^{VI}O(por)(^{18}O$_2$)] (por = tdcpp, ttp), synthesized by the reaction of [Mo^{IV}O(por)] with $^{18}O_2$ in the dark, had no absorptions at around 926 cm^{-1} whereas a new absorption band appeared at around 870 cm^{-1}. Thus, the absorptions at around 926 cm^{-1} were assigned to the O–O stretches. The calculation by harmonic oscillator supported the assignment. The absorption bands around 910 cm^{-1} assigned to the stretch of Mo=O were in the range observed for other porphyrinatomolybdenums(VI) such as [Mo^{VI}(O)$_2$(ttp)].[6] The location of the O–O stretches at around 926 cm^{-1} indicates that in all the complexes O_2 is coordinated to the central molybdenum ion in a peroxide (O_2^{2-}) fashion.[19] These results are consistent with the structure obtained for **1**.[10]

^{1}H NMR spectra provided further information about the structure of these complexes in solution. The ^{1}H NMR spectrum of **3** in CD_2Cl_2 was exemplified in Fig. 2. The sharp signals and their observed regions indicated that the complexes are diamagnetic. This is consistent with the oxidation state VI of the central molybdenum ions with no d-electrons. The characteristic AB quartet signal and the two singlet signals at β-pyrrole protons observed for **3** were also found for **2**, **4**, and **5** as listed in Table 2. Thus, the isolated dioxygen complexes of **2**, **3**, **4**, and **5** have the same coordination sphere as that of **1**, i.e., all the complexes have a symmetry plane that passes though two *trans* N atoms of pyrrole and the single oxygen atom, and perpendicularly bisects the inter-oxygen bond of the peroxo ligand, as shown in Fig. 1.

Absorption maxima and molar absorptivities of a series of the oxo(peroxo)porphyrinatomolybdenums(VI) are summarized in Table 3. The spectra were measured in aprotic solvents in the dark. Each dioxygen complex has three characteristic absorption bands, at around 430 nm for the Soret band and at around 530 and 560 nm for Q-bands. Upon photoirradiation with visible light (Xe lamp), the dioxygen complexes in solution caused UV-vis spectral changes. The in-

Table 1. IR Stretching Data for Oxo(peroxo)porphyrinatomolybdenums (KBr Pellet)

Complexes	$\nu_{Mo=O}$/cm^{-1}	ν_{O-O}/cm^{-1}
1[a]	912	928
[Mo^{VI}O(tmp)(^{18}O$_2$)][a]	916	875
2	918	932
[Mo^{VI}O(tdcpp)(^{18}O$_2$)]	923	872
3[b]	910	926
[Mo^{VI}O(ttp)(^{18}O$_2$)][b]	916	870
4	912	928
5[b]	910	928

a) Ref. 8. b) Ref. 11.

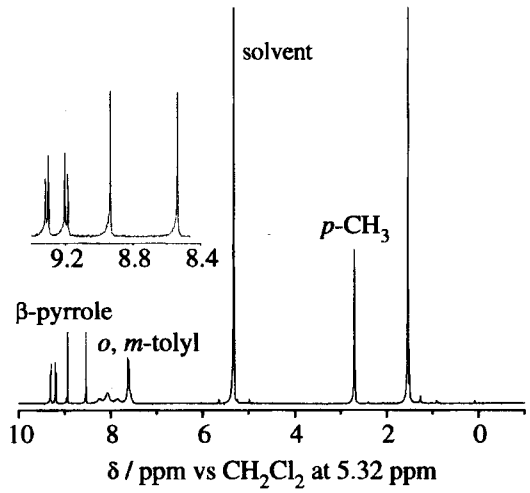


Fig. 2. ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 20 °C in the dark.

tensity of the Soret band at around 430 nm increased and new absorption maxima at around 555 and 590 nm appeared, with the disappearance of the two Q-bands at around 530 and 560 nm. The final spectrum agreed with that of the corresponding molybdenum(IV) complexes. As observed for **1**, the photoirradiation of the oxo(peroxo)porphyrinatomolybdenums(VI) in solution also caused the release of O_2, as shown in Eq. 2.[8]

$$[Mo^{VI}O(por)(O_2)]\ (soln.) \xrightarrow{h\nu} [Mo^{IV}O(por)] + O_2 \quad (2)$$

Electronic Effects of Porphyrin Ring. The dioxygen complex of **2** with bulky and electron-withdrawing substituents in toluene exhibited absorption bands at 430, 532, 564, and 613 nm (spectrum **A** in Fig. 3) immediately after dissolution under one atmospheric pressure (760 Torr) of dioxygen in the dark at 20 °C. The spectrum of **A** varied over 50 h to give the spectrum of **B**. The spectrum **B** showed no additional change after 50 h under the conditions. However, photoirradiation with visible light led to the spectrum **C**, which coincides with that of **2r**. Shading the light led to the regeneration of the spectrum **B**. When the solution was degassed immediately after the dissolution of the complex and photoirradiated, the spectrum **C** was obtained. No change in the spectrum was caused by successive irradiations.

The change between spectra **C** and **B** had isosbestic points at 415, 437, 540, 563, 587, and 598 nm, indicating that no side reactions are involved. The initial small change (**A**→**B**) in the dark indicated the establishment of the equilibrium. The extent of the change revealed that **2** and **2r** are ca. 80% and ca. 20%, respectively in the equilibrium state in toluene under 760 Torr of dioxygen.[20] The equilibrium constant ($K = [\mathbf{2}]/[\mathbf{2r}][O_2]$) thus obtained is 1090 dm^3 mol^{-1}. This result is contrast to the system of **1**, in which the equilibrium

Table 2. ^{1}H NMR Data for Oxo(peroxo)porphyrinatomolybdenums in CD_2Cl_2 at 20 °C

Complex	Chemical Shift δ/ppm		
	β-Pyrrole H	Phenyl protons	Phenyl substituents
1[a]	9.04 (AB q. (J = 5.7 Hz), 4H) 8.68 (s, 2H), 8.27 (s, 2H)	7.37, 7.33, 7.31, 7.23 (s each, 8H, *m*-mesityl)	2.61, 2.60 (s each, 12H, *p*-CH_3) 2.31, 1.97, 1.75, 1.56 (s each, 24H, *o*-CH_3)
2	9.12 (AB q. (J = 5.1 Hz), 4H) 8.74 (s, 2H), 8.37 (s, 2H)	7.91—7.70 (m) (12H, *m,p*-2,6-dichlorophenyl)	—
3[b]	9.22 (AB q. (J = 4.9 Hz), 4H) 8.90 (s, 2H), 8.50 (s, 2H)	8.20—7.81 (br), 7.60, 7.57 (16H, *o,m*-tolyl)	2.66, 2.65 (s each, 6H, *p*-CH_3)
4	9.23 (AB q. (J = 4.6 Hz), 4H) 8.91 (s, 2H), 8.50 (s, 2H)	7.97—7.56 (br), 7.43, 7.40 (12H, *o,p*-3,5-dimethyl-phenyl)	2.59, 2.56, 2.52 (24H, *m*-CH_3)
5[b]	9.22 (AB q. (J = 4.9 Hz), 4H) 8.90 (s, 2H), 8.49 (s, 2H)	8.0—7.8 (br), 7.80, 7.79 (20 H, phenyl H)	—

a) Ref. 8. b) Ref. 11. AB q.: AB quartet, s: singlet, m: multiplet, br: broad signal.

Table 3. UV-vis Spectral Data for Oxo(peroxo)porphyrinatomolybdenums at 20 °C

Complex	Solvent	Soret band λ_{max}/nm (ε/10^3 dm^3 mol^{-1} cm^{-1})	Q-band λ_{max}/nm (ε/10^3 dm^3 mol^{-1} cm^{-1})
1[a]	Toluene	430 (169)	531 (12.2), 563 (14.0)
2	Toluene	430 (162)	532 (9.81), 564 (14.2), 613 (2.48)
3[b]	CH_2Cl_2	432 (179)	529 (11.6), 560 (13.0)
4	Toluene	432 (174)	530 (12.1), 562 (13.9)
5[b]	CH_2Cl_2	430 (158)	528 (10.5), 560 (12.2)

a) Ref. 8. b) Ref. 11.

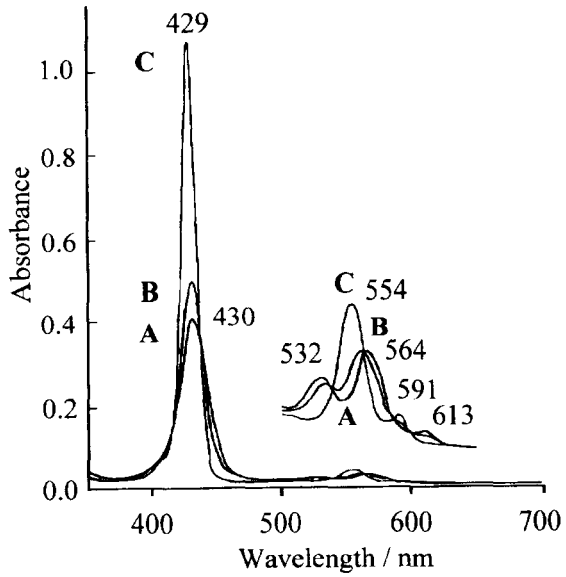


Fig. 3. UV-vis spectral change of **2** in toluene at 20 °C. **A** is the spectrum observed immediately after the dissolution of **2** in the dark under 760 Torr dioxygen partial pressure, **B** is after 50 h, and **C** obtained by photoirradiation with visible light.

lies nearly 100% to the formation of the dioxygen complex.[8]

The UV-vis spectral change gave kinetic data on the system of **2r**. To study the kinetics, the dioxygen complex **2** was dissolved in toluene under constant dioxygen pressures at 20 °C. The solution was left to stand for ca. 1 h after being stirred vigorously and then photoirradiated with visible light to give **2r**. The successive dioxygenation reaction in the dark to reach the equilibrium was followed by gauging the absorbance at 430 nm. The reaction obeyed a pseudo first-order rate law under a large excess of dioxygen ($[O_2] = (0.6—5.2)\times10^{-3}$ mol dm^{-3}; $[\mathbf{2r}] = (2.1—3.6)\times10^{-6}$ mol dm^{-3}). The pseudo first-order rate constants (k_{obs}) varied with the concentration of dioxygen. A plot of the rate constants (k_{obs}) vs. $[O_2]$ gave a straight line through an intercept, as shown in Fig. 4. The rate law (3) should be applied.

$$k_{obs} = k_1[O_2] + k_{-1}. \quad (3)$$

The second order rate constant for association, k_1, was determined from the slope to be 1.2×10^{-2} dm^3 mol^{-1} s^{-1} at 20 °C. The intercept gave the dissociation rate constant, k_{-1}, with the value of 1.6×10^{-5} s^{-1}. These rate constants gave an equilibrium constant of 750 dm^3 mol^{-1}. The constant was smaller than that obtained from the spectral change described above, i.e., the dioxygenation reactions of **2r** are so slow that some side reactions like decomposition to Mo(V) complexes might affect the rate constants, especially when the concentration of dioxygen is small.

The association rate constant for **2r** with O_2 is about one thirtieth of that for the reaction of **1r** with O_2 ($k_1 = 3.9\times10^{-1}$ dm^3 mol^{-1} s^{-1}, $k_{-1} < 7\times10^{-5}$ s^{-1} at 20 °C).[8] The difference in the two systems may be explained by the change in the redox potentials of oxo(porphyrinato)molybdenums(IV) be-

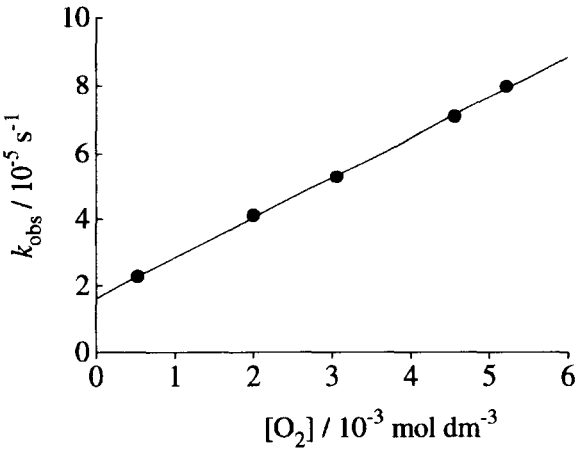


Fig. 4. A plot of the pseudo first-order rate constants vs. $[O_2]$ in toluene at 20 °C. $[\mathbf{2r}] = (2.1—3.6)\times10^{-6}$ mol dm^{-3}.

cause the coordination of O_2 should be accompanied by the change in the oxidation state of the molybdenum ion from Mo(IV) to Mo(VI). H_2tdcpp with the electron-withdrawing substituents should cause the decrease in electron-density of the central molybdenum ions.[21] **1r** gave the redox potential of Mo(V/IV) at 0.15 V vs. Ag/AgCl, whereas **2r** was oxidized at a more positive potential (0.33 V vs. Ag/AgCl) as listed in Table 4. It is thus reasonable that the tdcpp complex **2r** has a smaller formation equilibrium and the smaller association rate constant of the dioxygen complex as compared with the system of **1r**. The results clearly show that an electronic effect of the porphyrinato ligands must be an important factor controlling the kinetic and thermodynamic parameters of association rates of the dioxygen complex formation in these porphyrinatomolybdenum systems.

Steric Effect of Porphyrin Ring. The steric effects of porphyrin rings on the oxygenation profiles of the oxomolybdenum(IV) complexes were studied with UV-vis spectroscopy by following the redioxygenation reactions after the photoirradiation of the dioxygen complexes. In the case of the system of **1r**, the dioxygen complex of **1** was recovered quantitatively within 30 min, as shown in Fig. 5a. However, in the systems of [Mo^{IV}O(ttp)] **3r** and [Mo^{IV}O(tdmpp)] **4r** without bulky substituents, the redioxygenation reactions proceeded somewhat differently. The formation of the cor-

Table 4. Redox Potentials of Oxo(porphyrinato)molybdenums(IV) in CH_2Cl_2

Complexes	$E_{1/2}$/V[a] Mo(V/IV)	$E_{1/2}$/V[a] Ring oxidation
1r	0.15	1.53
2r	0.33	[b]
3r	0.15	1.48
4r	0.14	1.44
5r[c]	−0.01	1.45

a) $E_{1/2}$ is $(E_{pa}+E_{pc})/2$, E_{pa} and E_{pc} mean anodic and cathodic peak potentials, respectively. These values were referred to Ag/AgCl. b) Not observed. c) Ref. 3. These values are corrected by subtracting 0.03 V from those referred to SCE.

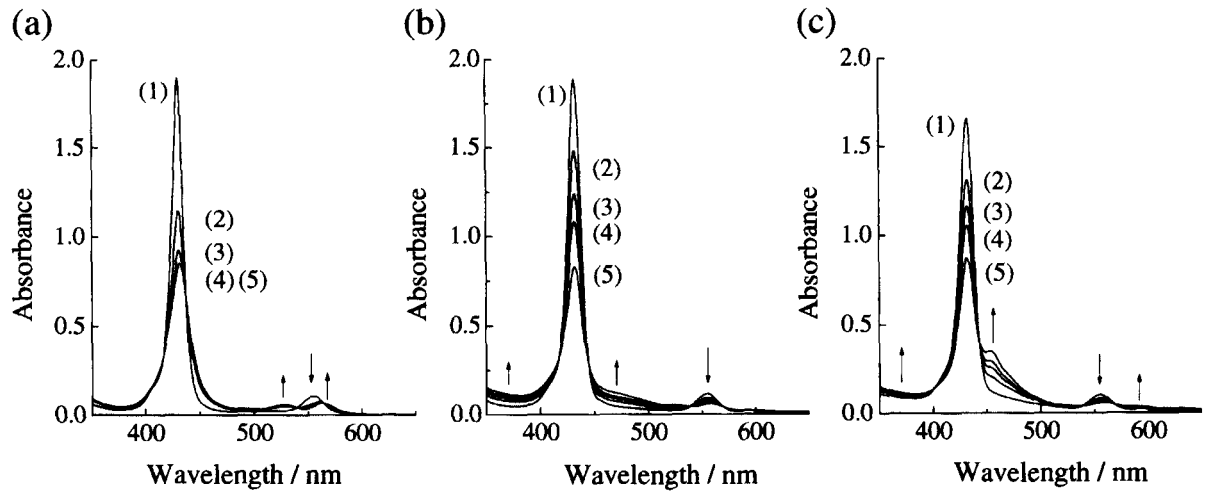
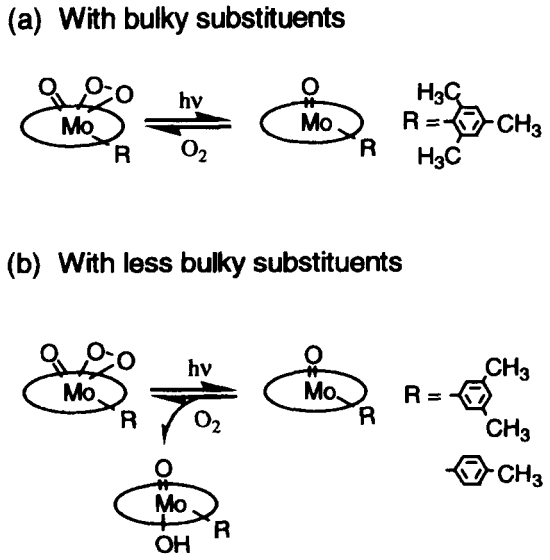


Fig. 5. UV-vis spectral changes by the reactions of [$Mo^{IV}O$(por)] with O_2 in toluene under 760 Torr dioxygen partial pressure at 20 °C. [$Mo^{IV}O$(por)] was formed by photoirradiation of [$Mo^{VI}O$(por)(O_2)]. a): the system of [$Mo^{IV}O$(tmp)] **1r**, b): [$Mo^{IV}O$(tdmpp)] **4r**, c): [$Mo^{IV}O$(ttp)] **3r**. Solid line (1): after photoirradiation for 1 min, (2): 10 min after shading the light, (3): 20 min, (4): 30 min, and (5): 60 min.

responding dioxygen complexes was not quantitative, as revealed by the incomplete recovery of the initial intensity in the Soret bands, and some extra absorption bands appeared, as shown in Figs. 5b and 5c. The spectral changes demonstrated that some side reactions took place with increasing the absorbance around 450 nm. The side reactions are more prominent in **3r**.

Although [$Mo^{IV}O$(por)] and [$Mo^{VI}O$(por)(O_2)] are ESR silent, the solutions of the dioxygenation systems of **3r**, **4r**, and **5r** gave the characteristic ESR signals of paramagnetic oxo(porphyrinato)molybdenums(V)[3] after repeated deoxygenation–oxygenation cycles with photoirradiation.[3] In the system of **1r** no ESR signal is observed under the same conditions. The intensity of the ESR signals, due to the byproducts, increased in the order of **3r** ≈ **5r**>**4r**. The results indicate that each [$Mo^{IV}O$(por)] formed from **3**, **4**, and **5** gives the corresponding Mo(V) complexes such as [$Mo^{V}O$(por)-(OH)] or [{$Mo^{V}O$(por)}$_2$(μ-O)] in the course of the dioxygenation reactions, and that the progress of the side reactions is largely affected by the steric hindrance of the porphyrin rings, as illustrated in Scheme 1. Namely, the reversibility of dioxygenation decreases with decreasing steric hindrance in the order of tmp>tdmpp>ttp≈tpp. From the results of these experiments, the reason why the dioxygen complexes of **3**, **4**, and **5** could not be synthesized in solution became obvious. Side reactions to go to Mo(V) complexes were preferable routes in solution if the porphyrins had no bulky substituents. These results were supported by the previous reports that [$Mo^{IV}O$(oep)] with a planar oep porphyrinato ligand afforded a paramagnetic μ-oxo dimer of [{$Mo^{V}O$(oep)}$_2$(μ-O)].[23] The reaction of [$Mo^{IV}O$(tpp)] with O_2 in solution also gave a corresponding μ-oxo dimer as the product.[24] The dioxygen complexes of **3**, **4**, and **5** once formed in the solid state were stable in the dark even in solution.

In order to obtain additional information on the reactivities of the Mo(IV) porphyrin complexes, we introduced methanol into these reaction systems. Oxo(porphyrinato)-



Scheme 1.

molybdenums(IV) undergo the reactions with methanol to give the corresponding methoxo(oxo)molybdenums(V), in which a methoxide ion is coordinated to the molybdenum ion with the *trans* position of the oxide ion.[3] Thus, the molybdenum(V) by-product is limited to [$Mo^{V}O$(por)-(OMe)] in the presence of methanol.

Figure 6a shows a UV-vis spectral change of **1r** after photoirradiation in 1% (v/v) MeOH/toluene in the presence of dioxygen. In neat toluene, the dioxygen complex of **1** was formed, whereas in the presence of MeOH, the extra absorbance around 450 nm increased slowly, indicating the formation of a small amount of [$Mo^{V}O$(tmp)(OMe)]. On the other hand, in less hindered porphyrin systems, the corresponding methoxo(oxo)molybdenums(V) were formed immediately after the photoirradiation, as shown in Fig. 6c for the reaction system of **3r**. On repeating the cycle of photoirradiation and shading the light of the solution, [$Mo^{V}O$(ttp)-

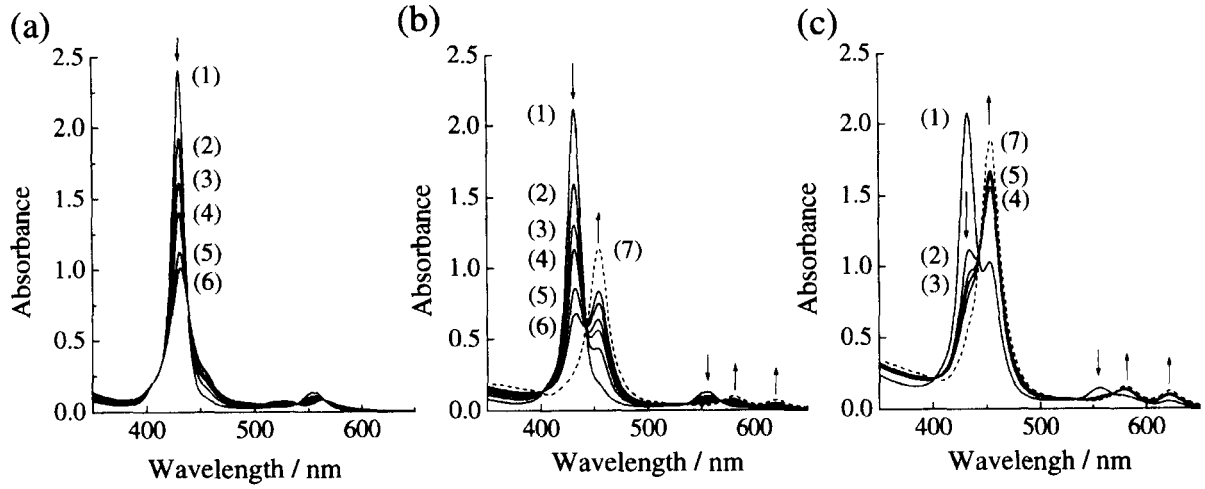


Fig. 6. UV-vis spectral changes by the reactions of [$Mo^{IV}O$(por)] with methanol in 1% MeOH/toluene (v/v) in air at 20 °C. [$Mo^{IV}O$-(por)] was formed by photoirradiation of [$Mo^{VI}O$(por)(O_2)]. a): [$Mo^{IV}O$(tmp)] **1r**, b): [$Mo^{IV}O$(tdmpp)] **4r**, c): [$Mo^{IV}O$(ttp)] **3r**. Solid line (1): after photoirradiation for 1 min, (2): 10 min after shading the light, (3): 20 min, (4): 30 min, (5): 60 min, and (6) 120 min. Dashed line (7) after repeated photoirradiation and shading the light.

(OMe)] produced absorption maxima at around 450, 580, and 620 nm. In the case of **4r**, which has more bulky substituents in comparison with **3r**, the spectral changes after photoirradiation indicated that the formation of [$Mo^{V}O$(tdmpp)(OMe)] is more difficult than for the system of **3r**, as shown in Fig. 6b. Since there are no significant differences in the redox potentials of **1r**, **4r**, and **3r** as listed in Table 4, these reactions are unlikely to be controlled by the redox properties of the central molybdenum ions. These results certified also that the steric hindrances of porphyrin rings reflect on the reactivity of the *trans* position of the oxide ion in the Mo(IV) complexes as well as on the reversibility of dioxygenation.

Conclusion

A series of oxo(peroxo)porphyrinatomolybdenums(VI) including new dioxygen complexes, **1**—**5**, were prepared and characterized. The complexes **2**, **3**, **4**, and **5**, which have various substituents were successfully prepared by the reactions of oxo(porphyrinato)molybdenums(IV) with O_2 in the solid state. The electron-withdrawing substituents of the porphyrin rings are unfavorable for the formation of the dioxygen complexes, i.e., an association rate constant in the reaction of [$Mo^{IV}O$(tdcpp)] **2r** (1.2×10^{-2} $dm^3\,mol^{-1}\,s^{-1}$) with O_2 is about one thirtieth of the system of [$Mo^{IV}O$(tmp)] **1r** (3.9×10^{-1} $dm^3\,mol^{-1}\,s^{-1}$). The spectral data indicated that the steric bulkiness of the porphyrin ring affects the reversibility of the formation of the dioxygen complexes, i.e., the reversibility is decreased with decreasing steric hindrance.

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5 Abbreviations: tmp = 5, 10, 15, 20- tetramesitylporphyrinato ligand; tdcpp = 5, 10, 15, 20- tetrakis(2, 6- dichlorophenyl)-porphyrinato ligand; ttp = 5,10,15,20-tetra(*p*-tolyl)porphyrinato ligand; tdmpp = 5,10,15,20-tetrakis(3,5-dimetylphenyl)porphyrinato ligand; tpp = 5,10,15,20-tetraphenylporphyrinato ligand; oep = 2, 3,7,8,12,13,17,18-octaethylporphyrinato ligand; por = general porphyrinato ligand; TBAP = tetrabutylammonium perchlorate.

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16 Data for [$Mo^{V}O$(tdcpp)(OEt)]. Anal. Found: C, 52.24; H, 2.88; N, 5.54; Cl, 27.47%. Calcd for $C_{46}H_{25}Cl_8MoN_4O_2$: C, 52.85; H, 2.41; N, 5.36; Cl, 27.13%. UV-vis (toluene, 20 °C) λ_{max}/nm ($\varepsilon/10^3$ $dm^3\,mol^{-1}\,cm^{-1}$) 451 (154), 577 (19.7), 610 (3.30).

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