Transition-Metal Complexes of Pyrrole Pigments. XXII. Photoredox Behavior of Oxo(tetra-*p*-tolylporphinato)molybdenum(V) Complexes[†]

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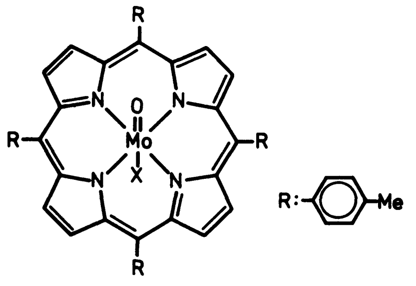
Photochemical reduction of oxomolybdenum(V) complexes of 5,10,15,20-tetra-*p*-tolylporphine, [$\mathrm{Mo^VO(X)(ttp)}$], was investigated under irradiation with the visible light in benzene, where X stands for an axial ligand placed trans to the oxo group. Irradiation of [$\mathrm{Mo^VO(X)(ttp)}$] resulted in a homolytic cleavage of the Mo–X bond to afford [$\mathrm{Mo^{IV}O(ttp)}$] and a radical species generated from the axial ligand (X). The reduction rate was controlled by the nature of the Mo–X bond, and a complex with less ionic character of the axial bond was more reactive in the homolysis process. The bulkiness of the axial alkoxo ligands may provide two different effects which are opposite to each other on the reactivity: (i) The repulsive interaction between an axial ligand and the equatorial ttp accelerates the homolysis of the Mo–X bond; (ii) the diffusion rate of the radical species, generated by the photochemical cleavage of the axial coordinate bond, from the coordination sphere is progressively retarded as the bulkiness of the alkoxo ligand increases. The second effect seems to be more pronounced for the present photochemical reaction. The photochemical reduction of [$\mathrm{Mo^VO(X)(ttp)}$] is essentially composed of two sequential steps, photochemical cleavage of the Mo–X bond and diffusion of the radical species from the coordination sphere. Reoxidation of [$\mathrm{Mo^{IV}O(ttp)}$] under aerobic irradiation conditions afforded [$\mathrm{Mo^VO(OH)(ttp)}$] and [$\mathrm{(Mo^VO(ttp))_2O}$] via the postulated intermediate formation of [$\mathrm{Mo^V(OO\cdot)(ttp)}$].

The redox chemistry of metalloporphyrins and the reaction behavior of their various axial ligands have attracted much attention in connection with the development of oxygen carriers, oxygenation catalysts, and photochemical catalysts. We have investigated the redox behavior of some molybdenum[1] and niobium[2] complexes of 5,10,15,20-tetraphenylporphine by means of electrochemical methods. The redox potentials for couples of $\mathrm{Mo^V/Mo^{IV}}$ and $\mathrm{Nb^V/Nb^{IV}}$ as observed for these porphine complexes have been found to vary depending upon the nature of axial ligands, and fall in the region between 0 and −0.8 V vs. SCE. We have found recently that irradiation of tri-*μ*-oxo-bis(5,10,15,20-tetra-*p*-tolylporphinato)niobium(V) in benzene with the visible light under aerobic conditions afforded two paramagnetic species at room temperature.[3] One of the paramagnetic species, which is ESR silent, oxidized heterocyclic bases, while the other species, which is detectable by ESR, oxidized olefins catalytically to afford the corresponding epoxides selectively. On the other hand, Ledon and his associates have reported that the photo-assisted reduction of molecular oxygen to hydrogen peroxide took place in the presence of methoxooxo(5,10,15,20-tetraphenylporphinato)molybdenum(V).[4] In order to clarify axial ligand effects on the photoreduction process, oxo(tetra-*p*-tolylporphinato)molybdenum(V) complexes with various axial ligands, [$\mathrm{Mo^VO(X)(ttp)}$] (X stands for an axial ligand placed trans to the oxo group), were employed and their photoreduction behavior was investigated from kinetic and structural viewpoints in this work. Reoxidation of the resulting oxomolybdenum(IV) species was also studied under aerobic conditions by spectroscopic means.



[$\mathrm{Mo^VO(X)(ttp)}$] X: $\mathrm{OCH_3}$
$\mathrm{OC_2H_5}$
$\mathrm{OC_4H_9}$
$\mathrm{OCH_2C_6H_5}$
$\mathrm{OCOCH_3}$
Cl

Experimental

ESR spectra were recorded on a JEOL JES-ME-3 X-band spectrometer equipped with a 100-kHz field modulation unit; a standard $\mathrm{MgO/Mn^{II}}$ sample calibrated with a NMR magnetometer was employed for calibration of the magnetic field. Electronic and IR absorption spectra were measured with a Hitachi 340 recording spectrophotometer and a JASCO DS-403G grating spectrophotometer, respectively.

Materials. Benzene was purified by the standard method and distilled under nitrogen just before use. Nitrosobenzene of Tokyo Kasei Kogyo Co. was purified by sublimation at 38 °C under reduced pressure (930 Pa). 5,10,15,20-Tetra-*p*-tolylporphine, $\mathrm{H_2ttp}$, was prepared from pyrrole and *p*-tolualdehyde according to a procedure similar to that adopted for the synthesis of 5,10,15,20-tetraphenylporphine, $\mathrm{H_2tpp}$.[5,6] Oxomolybdenum(V) complexes of the former equatorial ligand with methoxo, ethoxo, chloro, and acetato moieties as the axial ligands were prepared in the light of reported procedures for the preparation of the corresponding complexes of the latter equatorial ligand.[1,7]

Methoxooxo(5,10,15,20-tetra-*p*-tolylporphinato)molybdenum-

[†] Contribution No. 816 from this Department.

(V), [Mo^{V}O(OCH$_3$)(ttp)]: Yield 47%; Vis$_{max}$ (benzene) 455, 583, and 623 nm; IR (KBr) 906 cm^{-1} (Mo=O). Found: C, 70.97; H, 4.42; N, 7.52%. Calcd for $C_{45}H_{31}N_4O_2Mo$: C, 71.52; H, 4.13; N, 7.42%.

Ethoxooxo(5,10,15,20-tetra-*p*-tolylporphinato)molybdenum(V), [Mo^{V}O(OC$_2$H$_5$)(ttp)]: Yield 54%; Vis$_{max}$ (benzene) 456, 580, and 620 nm; IR (KBr) 898 (Mo=O) and 519 cm^{-1} (Mo–O). Found: C, 72.70; H, 5.05; N, 6.78%. Calcd for $C_{50}H_{41}N_4O_2Mo$: C, 72.72; H, 5.00; N, 6.78%.

Chlorooxo(5,10,15,20-tetra-*p*-tolylporphinato)molybdenum(V), [Mo^{V}O(Cl)(ttp)]: Yield 61%; Vis$_{max}$ (benzene) 347, 422, 502, 630, and 677 nm; IR (KBr) 943 cm^{-1} (Mo=O). Found: C, 67.61; H, 4.37; N, 6.57%. Calcd for $C_{48}H_{36}ClN_4OMo \cdot HCl$: C, 68.00; H, 4.56; N, 6.43%.

Acetatooxo(5,10,15,20-tetra-*p*-tolylporphinato)molybdenum(V), [Mo^{V}O(OCOCH$_3$)(ttp)]: Yield 51%; Vis$_{max}$ (benzene) 409 sh, 482, 611, and 645 nm; IR (KBr) 914 and 947 cm^{-1} (Mo=O). Found: C, 69.48; H, 4.92; N, 6.33%. Calcd for $C_{50}H_{39}N_4O_3Mo \cdot CH_3CO_2H$: C, 69.41; H, 4.82; N, 6.23%.

Oxomolybdenum(V) complexes with butoxo and benzyloxo moieties as the axial ligands were prepared from [Mo^{V}O(Cl)(ttp)] according to the following procedure. An alcohol (1-butanol or benzyl alcohol; 20 mL) saturated with KOH was added to a dichloromethane solution (200 mL) containing [Mo^{V}O(Cl)(ttp)] (100 mg). After the mixture was evaporated to dryness in vacuo, the residue was extracted with dichloromethane. The extract was applied on a column of neutral aluminum oxide (Woelm, activity grade I) and eluted with dichloromethane containing the same alcohol species (1% v/v). The product fraction was evaporated to dryness in vacuo, and the residue was recrystallized from dichloromethane containing the same alcohol (ca. 1% v/v).

Butoxooxo(5,10,15,20-tetra-*p*-tolylporphinato)molybdenum(V), [Mo^{V}O(OC$_4$H$_9$)(ttp)]: Yield 90%; Vis$_{max}$ (benzene) 455, 582, and 622 nm; IR (KBr) 905 cm^{-1} (Mo=O). Found: C, 73.14; H, 5.31; N, 6.56%. Calcd for $C_{52}H_{45}N_4O_2Mo$: C, 72.54; H, 5.29; N, 6.38%.

(Benzyloxo)oxo(5,10,15,20-tetra-*p*-tolylporphinato)molybdenum (V), [Mo^{V}O(OCH$_2$C$_6$H$_5$)(ttp)]: Yield 70%; Vis$_{max}$ (benzene) 458, 584, and 624 nm IR (KBr) 898 and 907 cm^{-1} (Mo=O). Found: C, 74.25; H, 5.20; N, 5.83%. Calcd for $C_{55}H_{43}N_4O_2Mo \cdot 1/4C_6H_5CH_2OH$: C, 74.50; H, 4.96; N, 6.12%.

Photoreduction Measurements. A benzene solution of [Mo^{V}O(X)(ttp)] (ca. 1×10^{-3} mol dm^{-3}) was sealed in a quartz tube (diameter, 5 mm) after evacuation of gas. The sample solution placed in an ESR cavity was irradiated with a 500-W tungsten lamp from a distance of 20 cm. ESR spectra were recorded under irradiation conditions. For detection of radical species, nitrosobenzene (ca. 5×10^{-2} mol dm^{-3}) was added to the sample solution to afford the corresponding spin adducts.

Benzene and [Mo^{V}O(X)(ttp)] were mixed in a spectrophotometric cell of 1-cm path length after both complex and solvent were degassed separately. The sample solution, containing ca. 4×10^{-6} mol dm^{-3} [Mo^{V}O(X)(ttp)], was irradiated with a 500-W tungsten lamp from a distance of 20 cm, and electronic absorption spectra were measured at appropriate time intervals.

Results and Discussion

Photoreduction of [Mo^{V}O(X)(ttp)]. The present oxomolybdenum(V) complexes, [Mo^{V}O(X)(ttp)], show characteristic ESR spectra in benzene, which consist of nine intense lines originated from the superhyperfine interaction of one d electron with four nitrogen nuclei of the equatorial ligand.[7] Although the ESR signals for the complexes with axial alkoxo ligands in benzene were subjected to change very slowly due to hydrolysis or dimerization of the complexes, the complexes dissolved in sufficiently dried and freshly distilled benzene remained stable without such decomposition for several hours in the dark at room temperature. The ESR signals for the present complexes except for [Mo^{V}O(Cl)(ttp)] underwent intensity decrease upon irradiation with the visible light under anaerobic conditions as shown in Fig. 1. The signals for the complexes with the alkoxo ligands disappeared in about 4 h and were recovered upon addition of alcohol species corresponding to the axial ligands under aerobic conditions, while the complexes remained ESR silent so long as anaerobic conditions were retained. These observations indicate that the irradiation results in reduction of the central metal atom along with elimination of the axial ligand as a radical species as shown by Eq. 1. The ESR signal for a benzene solution

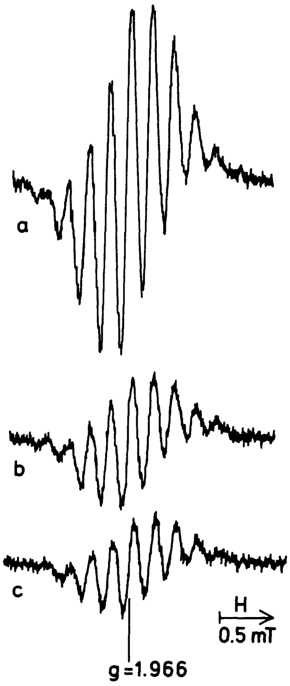
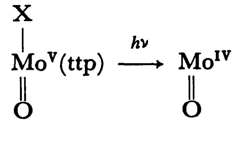


Fig. 1. ESR spectra for [Mo^{V}O(OCH$_3$)(ttp)] in benzene (ca. 1×10^{-3} mol dm^{-3}) under anaerobic conditions at room temperature: a, before irradiation; b, irradiated for 30 min; c, irradiated for 1 h.



$$\overset{\displaystyle X}{\underset{\displaystyle O}{Mo^{V}(ttp)}} \xrightarrow{h\nu} \underset{\displaystyle O}{Mo^{IV}(ttp)} + X\cdot \qquad (1)$$

of [Mo^{V}O(X)(ttp)] also underwent intensity decay in the presence of nitrosobenzene as a spin-trapping agent upon anaerobic irradiation, but a new signal, which is

Table 1. Spin Hamiltonian Parameters for Spin Adducts of Nitrosobenzene and Radical Species Generated from [$Mo^VO(X)(ttp)$] in Benzene under Aerobic Irradiation at Room Temperature

Mother complex	g-Value	(Hyperfine splitting constants)[a]×10^4/T			
		A_N	$A_{o,p}$	A_m	A_β
[$Mo^VO(OCH_3)(ttp)$]	2.01	14.85	2.98	0.92	0.92
[$Mo^VO(OC_2H_5)(ttp)$]	2.00	15.61	3.04	1.04	0.56
[$Mo^VO(OC_4H_9)(ttp)$]	2.00	15.54	3.07	1.06	0.68
[$Mo^VO(OCH_2C_6H_5)(ttp)$]	2.00	15.66	3.40	1.07	0.53

a) Hyperfine splitting constants are defined as follows: A_N, due to the nitrogen nucleus of nitrosobenzene; $A_{o,p}$, due to the proton nuclei placed at ortho and para positions of the benzene moiety; A_m, due to the proton nuclei placed at meta positions of the benzene moiety; A_β, due to the proton nuclei placed at β-position of the alkoxo moiety.

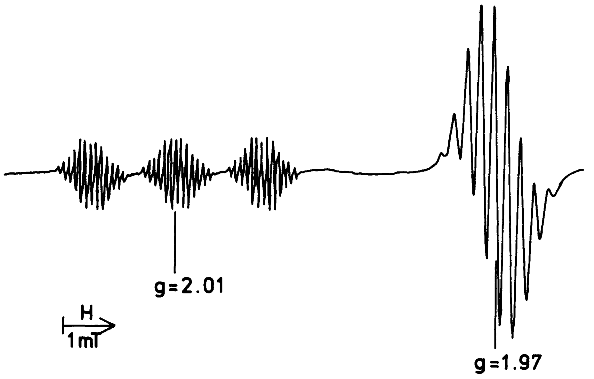
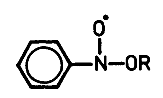


Fig. 2. ESR spectrum for [$Mo^VO(OCH_3)(ttp)$] in benzene (ca. 1×10^{-3} mol dm^{-3}) containing nitrosobenzene (ca. 5×10^{-2} mol dm^{-3}); irradiated for 30 min at room temperature.

attributed to the alkoxyl radical-nitrosobenzene adduct (**A**), appeared as shown in Fig. 2. Hyperfine splitting constants for several alkoxy adducts are listed in Table 1. The ESR behavior is in agreement with that observed during the photoreduction of methoxooxo(5,10,15,20-tetraphenylporphinato)molybdenum(V).[4]



A

The photoreduction of all the complexes other than [$Mo^VO(Cl)(ttp)$] was also examined by means of electronic spectroscopy as typically shown for [$Mo^VO(OC_2H_5)(ttp)$] in Fig. 3. The absorption bands at 456, 580, and 620 nm for the Mo^V species underwent intensity decay, and a new set of bands attributable to the Mo^{IV} species appeared at 434, 512(sh), 566, and 592 nm. The latter bands were further enhanced in their intensities along with the progress of photochemical reaction. Since isosbestic points were clearly observed at 396, 443, 535, 566, 598, and 648 nm, any additional reaction other than that given by Eq. 1 does not take place under the present conditions. Correlations between intensity of the Soret band and irradiation time are shown in Fig. 4. These correlations indicate that the photoreduction follows the first-order kinetics. Ledon et al. observed that the excitation of [Mo^VO-

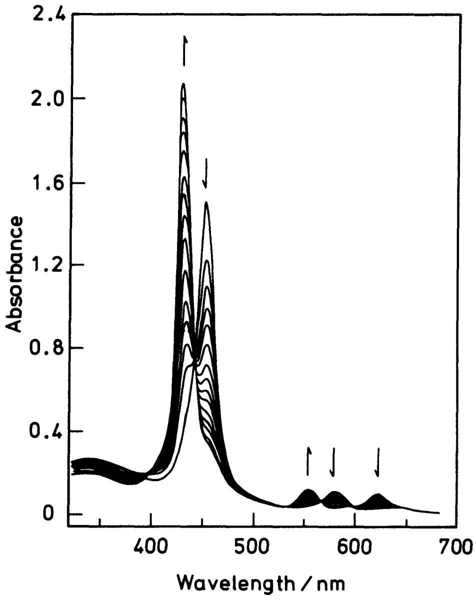


Fig. 3. Visible spectral change for [$Mo^VO(OC_2H_5)(ttp)$] in benzene (ca. 4×10^{-6} mol dm^{-3}) under irradiation at room temperature. Trends of spectral change with time are shown by arrows; measurements were carried out at 20 s intervals.

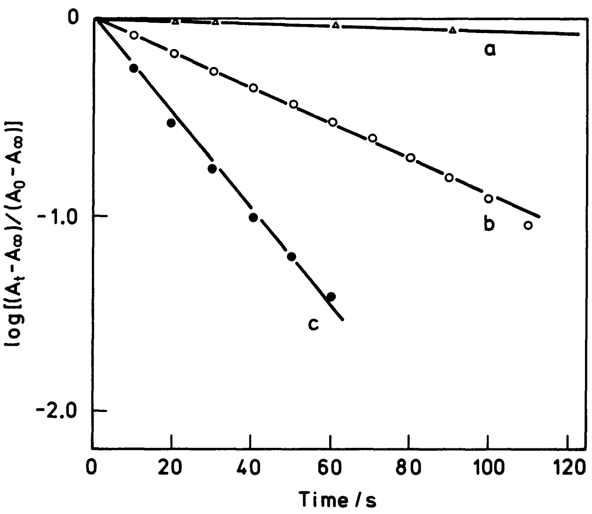


Fig. 4. First-order plots of Soret band intensity vs. irradiation time for [$Mo^VO(X)(ttp)$] in benzene at room temperature. Alkoxo moieties (X): a, $OCOCH_3$; b, $OCH_2C_6H_5$: c, OCH_3.

Table 2. Rate Constants of Photoreduction (*k*), Spectral Parameters, and Reduction Potentials for Molybdenum(V) Complexes

Complex	*k*[a]	Soret band[a]	IR (Mo=O)[b]	$E_{1/2}$(Mo)[c]
	s^{-1}	nm	cm^{-1}	V vs. SCE
[$Mo^VO(OCH_3)$(ttp)]	5.3×10^{-2}	455	906	−0.74
[$Mo^VO(OCOCH_3)$(ttp)]	4.1×10^{-4}	482	947, 914	−0.04
[$Mo^VO(Cl)$(ttp)]	No reaction	502	943	−0.06

a) Measured in benzene. b) KBr disc. c) Measured in dichloromethane for the corresponding tpp complexes, cited from Ref. 1.

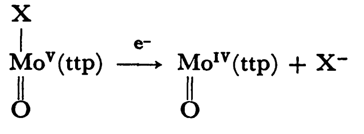
Table 3. Rate Constants of Photoreduction (*k*) and Spectral Parameters for Molybdenum(V) Complexes with Various Axial Alkoxo Ligands

Complex	*k*[a]	Soret band[a]	IR (Mo=O)[b]
	s^{-1}	nm	cm^{-1}
[$Mo^VO(OCH_3)$(ttp)]	5.3×10^{-2}	455	906
[$Mo^VO(OC_2H_5)$(ttp)]	5.6×10^{-2}	456	898
[$Mo^VO(OC_4H_9)$(ttp)]	2.3×10^{-2}	455	905
[$Mo^VO(OCH_2C_6H_5)$(ttp)]	1.3×10^{-2}	458	907, 898

a) Measured in benzene. b) KBr disc.

(OCH_3)(tpp)] was effective exclusively with the Soret band energy for the photoreduction.[4] Since the Soret bands of [$Mo^VO(X)$(ttp)] and [$Mo^{IV}O$(ttp)] do not show significant overlap between them (Fig. 3), light quanta absorbed by the former Mo^V species must be exclusively used for the photoreduction even after generation of the latter Mo^{IV} species. This may provide the reason why the clear first-order kinetics (Fig. 4) was observed for the present photochemical reaction.

Rate constants for the photoreduction are listed in Table 2 along with reduction potentials and Mo=O stretching frequencies for the oxomolybdenum(V) complexes having various axial ligands. The bonding mode of the axial coordinate bond, Mo–X, varies in a wide range as controlled by the electronegativity of axial ligand X. The covalent character decreases as goes downwards for the complexes listed in Table 2. The axial coordinate bond in [$Mo^VO(Cl)$(ttp)] must be highly ionic in the light of structural determination of [$Mo^VO(Cl)$(tpp)] by means of the single-crystal X-ray diffraction measurements.[8] The axial bonding character is reflected on the Soret band energy, the Mo=O stretching frequency, and the reduction potential for an electrochemical process given by Eq. 2.

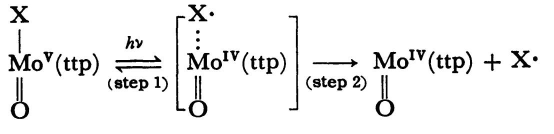


$$\overset{\displaystyle X}{\underset{\displaystyle O}{Mo^V}}(\mathrm{ttp}) \xrightarrow{e^-} \underset{\displaystyle O}{Mo^{IV}}(\mathrm{ttp}) + X^- \qquad (2)$$

On the basis of the data listed in Table 2, a complex with less ionic character of the axial coordinate bond is more reactive in the photoreduction process. The Soret band is plausibly assigned to a charge-transfer transition from the porphine ligand to the metal.[9] Then, the excited electron seems to occupy ultimately an antibonding orbital localized in the Mo–X bond for complexes having a highly covalent axial bond, and consequently the axial coordinate bond is destabilized. The excited state is plausibly represented for the case of the axial coordination with large ionic character as {[$Mo^{IV}O(ttp^+)]^+\cdots\cdots X^-$} which is regarded as a charge transfer complex, while the excited state for the covalent axial coordination may be given as {[$Mo^{III}O$(ttp^+)]$\cdots\cdots X\cdot$}. As a result, the electrostatic attraction between X^- and [$Mo^{IV}O(ttp^+)]^+$ is operative in the former case, while no such interaction would be expected in the latter. Therefore, a less electronegative axial ligand more readily undergoes the homolytic cleavage upon irradiation with the visible light.

Rate constants for the complexes with various axial alkoxo ligands are listed in Table 3 along with relevant spectral parameters. The rate of photoreduction decreases in the following order with respect to the alkoxo ligands: $OCH_3 \cong OC_2H_5 > OC_4H_9 > OCH_2C_6H_5$. In the light of the Soret band energies and the stretching frequencies of the Mo=O bond, there are no significant differences in the axial bonding character among these complexes. Therefore, differences in the reactivity must come from stereochemical origin. The bulkiness of the axial alkoxo ligand may provide two different effects which are opposite to each other on the reactivity. First, the repulsive interaction between an axial ligand, OR, and the equatorial one, ttp, accelerates the homolysis of the coordinate bond. Second, the diffusion rate of the radical species, generated by the photochemical cleavage of the axial coordinate bond, from the coordination sphere is progressively retarded as the bulkiness of the alkoxo ligand increases. The slow diffusion is in favor of recombination of the radical species and the reduced central metal. The second effect seems to be more pronounced for the present photochemical reaction in the light of the kinetic data given in Table 3.

On the basis of the above discussion, the present photochemical reduction of [Mo^{V}O(X)(ttp)] is essentially composed of two sequential steps, photochemical cleavage of the axial coordinate bond and diffusion of the radical species from the coordination sphere as shown by Eq. 3. The overall reaction rate for the complexes with smaller axial ligands is primarily controlled by the first step which is enhanced as the axial coordinate bond becomes more covalent, while the second step becomes the rate-determining one for the reaction of the complexes with more bulky axial ligands.



$$\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{X}}{|}}{\text{Mo}^{\text{V}}(\text{ttp})}} \underset{(\text{step 1})}{\overset{h\nu}{\rightleftharpoons}} \left[\underset{\underset{\text{O}}{\|}}{\overset{\overset{\text{X}\cdot}{\vdots}}{\text{Mo}^{\text{IV}}(\text{ttp})}}\right] \xrightarrow[(\text{step 2})]{} \underset{\underset{\text{O}}{\|}}{\text{Mo}^{\text{IV}}(\text{ttp})} + \text{X}\cdot \qquad (3)$$

Reoxidation of [Mo^{IV}O(ttp)]. The photochemically reduced complex, [Mo^{IV}O(ttp)], was reoxidized under aerobic conditions in benzene to afford the starting complexes when the corresponding alcohols were added. The reoxidation process showed the second-order dependence on the molybdenum complex for all cases investigated here, and is in accord with the earlier work for [Mo^{IV}O(tpp)] in the presence of methanol.[4]

The fate of [Mo^{V}O(X)(ttp)] in benzene under aerobic irradiation conditions was monitored by electronic spectroscopy in the absence of an alcohol. The aerobic irradiation with the visible light resulted in appearance of absorption bands attributable to [Mo^{IV}O(ttp)]. The intensity increase of these bands, however, was found to level off within an hour at a lower level relative to that observed under anaerobic conditions; about 80% of the original complex was reduced. The observation indicates that the reoxidation of [Mo^{IV}O(ttp)] takes place by molecular oxygen under aerobic conditions. In a few hours under aerobic irradiation conditions, the absorption bands attributable to [Mo^{IV}O(ttp)] began to decrease in their intensities along with appearance of a new absorption band at 484 nm and precipitation of a dark crystalline material. The crystalline solid was slightly soluble in benzene and dichloromethane and exhibited electronic absorption spectra shown in Fig. 5. The absorption spectrum observed in benzene is identical with that for the μ-oxo dimer, [{Mo^{V}O(ttp)}$_2$O], while that in dichloromethane is identical with that for [Mo^{V}O(OH)(ttp)].[10] The ESR spectrum observed for the crystalline solid is shown in Fig. 6; $D=940\times10^{-4}\,\text{cm}^{-1}$, $E\cong0$. Consequently, this material is confirmed to be the μ-oxo dimer and hydrolyzed readily by a trace amount of water present in dichloromethane to afford [Mo^{V}O(OH)(ttp)]. Two fractions were recovered from the mother solution, obtained from the aerobic photochemical reaction of [Mo^{V}O(X)(ttp)] in benzene, by column chromatography [aluminum oxide (Woelm), activity grade III; eluant, dichloromethane]. The first fraction was identified as [Mo^{V}O(OH)(ttp)], while the second fraction was not identified with known species; the latter showing a Soret band at 484 nm. However, we may plausibly assign the peroxo complex, [Mo^{V}O(OO$\cdot$)(ttp)], to this species on the following grounds. (i) The absorption due to [Mo^{IV}O(ttp)] decreased in its intensity along with appearance of the 484-nm band (vide supra). (ii) Imamura et al. reported that [Mo^{V}O(X)(tpp)] is reduced via its reaction with KO$_2$.[12] They assigned [Mo^{V}O(OO$\cdot$)(tpp)] to an intermediate showing a Soret band in the 480—490-nm range. (iii) Ledon et al. proposed that the reoxidation of [Mo^{IV}O(tpp)] takes place via intermediate formation of [Mo(O$_2$)(OO$\cdot$)(tpp)] in a benzene-methanol mixture.[4] However, they did not identify the intermediate. (iv) [Nb^{IV}O(ttp)], which was generated from [{Nb^{V}(ttp)}$_2$O$_3$] under photochemical conditions, was reoxidized by the atmospheric oxygen to afford [Nb^{V}O(OO$\cdot$)(ttp)].[3]

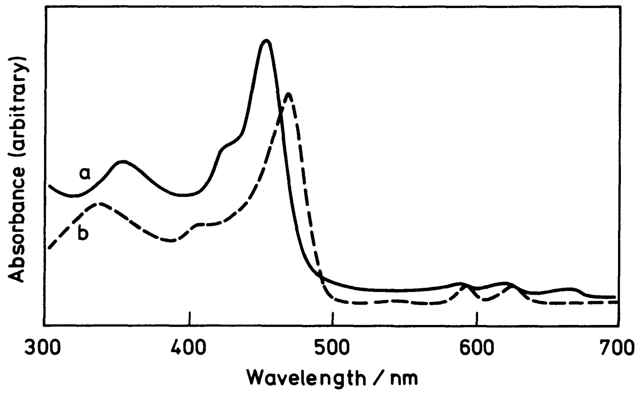


Fig. 5. Visible absorption spectra for the precipitated complex developed during reoxidation of [Mo^{IV}O(ttp)] in benzene without alcohols; measured in benzene (a) and dichloromethane (b).

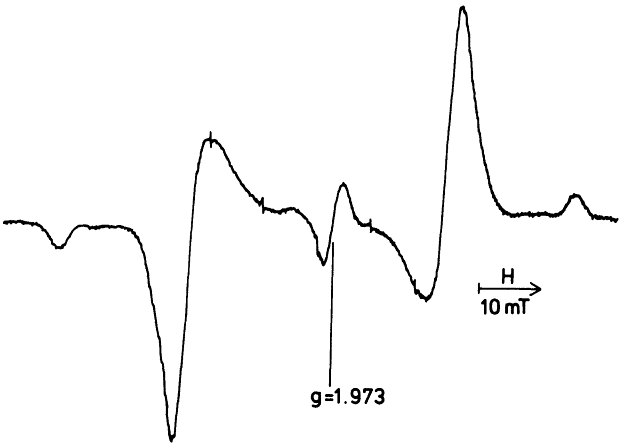
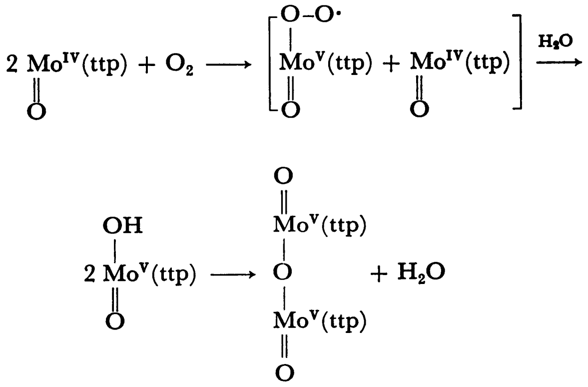


Fig. 6. ESR spectrum for the precipitated complex developed during reoxidation of [Mo^{IV}O(ttp)]; in solid state at room temperature.

In addition to the above conclusion, [Mo^{V}O(OH)-

(tpp)] has been found to undergo dehydration to afford $[\{\mathrm{Mo^{V}O(tpp)}\}_2\mathrm{O}]$ as precipitates in benzene.[11] Therefore, the reoxidation pathway for $[\mathrm{Mo^{IV}O(ttp)}]$ in benzene without an alcohol may be represented by Eq. 4 with participation of a trace amount of water from the open atmosphere.



$$2\,\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{Mo^{IV}(ttp)}} + \mathrm{O_2} \longrightarrow \left[\overset{\mathrm{O{-}O\cdot}}{\overset{|}{\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{Mo^{V}(ttp)}}}} + \underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{Mo^{IV}(ttp)}}\right] \xrightarrow{\mathrm{H_2O}}$$

$$2\,\overset{\mathrm{OH}}{\overset{|}{\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{Mo^{V}(ttp)}}}} \longrightarrow \begin{matrix} \mathrm{O} \\ \| \\ \mathrm{Mo^{V}(ttp)} \\ | \\ \mathrm{O} \\ | \\ \mathrm{Mo^{V}(ttp)} \\ \| \\ \mathrm{O} \end{matrix} + \mathrm{H_2O}$$

(4)

We have reported recently that tri-μ-oxo-bis(5,10,15,20-tetra-*p*-tolylporphinato)niobium(V) is capable of catalyzing the epoxidation of olefins by the atmospheric oxygen under irradiation with the visible light.[3] Since the catalytically active species in this reaction was confirmed to be $[\mathrm{Nb^{V}O(OO\cdot)(ttp)}]$, the peroxo molybdenum species, $[\mathrm{Mo^{V}O(OO\cdot)(ttp)}]$, which is likely formed under the present conditions, is also expected to act as an effective catalyst for the selective epoxidation of olefins in a similar manner.

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