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PHOTOREDUCTION OF MANGANESE(III), IRON(III), COBALT(III), AND MOLYBDENUM(V) TETRAPHENYLPORPHYRINS IN 2-METHYLTETRAHYDROFURAN

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The central metals in the metallotetraphenylporphyrins with axial halo or pseudohalo ligands, Mn^{III}(tpp)X (tpp = 5,10,15,20-tetraphenylporphinato; X = I, Br, Cl, OAc, NCS), Fe^{III}(tpp)Cl, Co^{III}(tpp)Cl, and Mo^{V}O(tpp)X (X = Br, Cl, F, NCS, N_3), in 2-methyltetrahydrofuran are photoreduced with visible light at room temperature to form Mn^{II}(tpp), Fe^{II}(tpp), Co^{II}(tpp), and Mo^{IV}O(tpp), respectively.

In spite of extensive studies on the photochemistry of porphyrins with interests in solar energy problems and photosensitizer for simple molecules which sometimes act as mediators in biochemical reactions, only a few studies have been reported on the photoreduction of the central metals of metalloporphyrins in pure aprotic solvents. Examples are provided by manganese etioporphyrins in pyridine in the sun light,1) molybdenum alkoxo tetraphenylporphyrin in benzene in the visible light,2) 1-(1-naphthyl)-2-(4-pyridyl)-ethylene complex of cobalt etioporphyrin in polar solvents,3) and rhodium and cobalt tetraphenylporphyrins in 2-methyltetrahydrofuran in the UV light.4) However there are no reports on the photoreduction of the central metals in the metalloporphyrins with halo or pseudohalo axial ligands in non-coordinating aprotic solvents by the irradiation of visible light.

In the present communication, the photochemical reactions of manganese(III), iron(III), cobalt(III), oxomolybdenum(V) tetraphenylporphyrins with axial halo or pseudohalo ligands in 2-methyltetrahydrofuran (MTHF) are studied by means of electronic and ESR spectral measurement.

Absorption spectra are recorded on a Hitachi 808 spectrophotometer and X-band ESR spectra on a JEOL JES FE1X spectrometer. MTHF, washed with aqueous sodium hydroxide and dried with calcium chloride, was purified by fractional distillation, stored on NaK alloy and again distilled in vacuo immediately before use. Sample solutions were all deaerated by repeated freeze-thaw cycles before photoirradiation. Photoirradiation was carried out at 25 °C with a 500W-xenon lamp with cutoff and interference filters. The path length of the optical quartz cell in a thermostated Pyrex glass vessel was 1, 5, or 10 mm. The metallotetraphenylporphyrins, Mn^{III}(tpp)X,5,6) Fe^{III}(tpp)Cl,5) Co^{III}(tpp)Cl,7) Mo^{V}O(tpp)X,8) Mn^{II}(tpp),9) Fe^{II}(tpp),9) Co^{II}(tpp),5) and Mo^{IV}O(tpp),10) were prepared according to the literatures. Quantum yield was measured by employing the Reinecke's salt as a standard actinometer.11)

The main three bands, Soret, β, and α bands, of the visible absorption spectrum of $\mathrm{Mo^{V}O(tpp)Cl}$ in MTHF at 25 °C are at 493, 623, and 670 nm respectively.12) The absorbances of these three bands were decreased with the appearance of new peaks at 427 and 555 nm as the solution was photoirradiated in the visible region (>440 nm). The spectral change exhibited isosbestic points at 401, 449, 538, and 569 nm. The absorption bands of the final complex were consistent with those of $\mathrm{Mo^{IV}O(tpp)}$ synthesized independently.

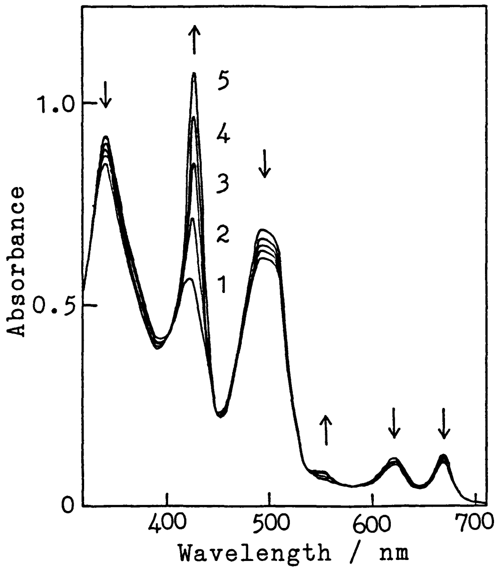

Fig. 1. Spectral change of $\mathrm{Mo^{V}O(tpp)Cl}$ in MTHF at 25 °C upon 489.5 nm-photoirradiation for (1) 0; (2) 20; (3) 40; (4) 60; (5) 80 min.

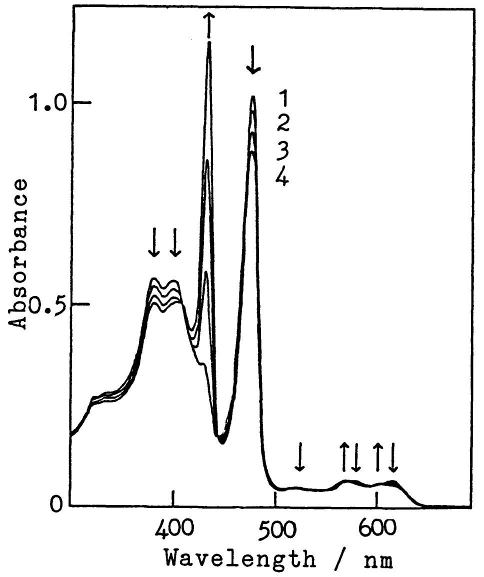

Fig. 2. Spectral change of $\mathrm{Mn^{III}(tpp)NCS}$ in MTHF at 25 °C upon 468.5 nm-photoirradiation for (1) 0.5; (2) 5.0; (3) 10; (4) 15 min.

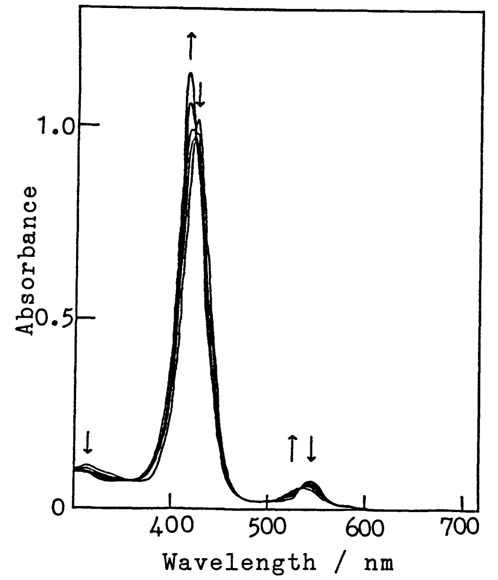

Fig. 3. Spectral change of $\mathrm{Co^{III}(tpp)Cl}$ in MTHF at 25 °C for 2 min upon 424 nm-photoirradiation.

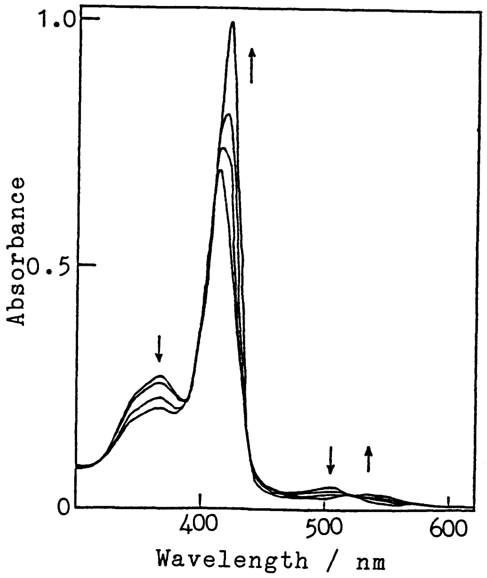

Fig. 4. Spectral change of $\mathrm{Fe^{III}(tpp)Cl}$ in MTHF at 25 °C for 1 h upon photoirradiation with 400-750 nm light.

The intensity of ESR signal ($\overline{g}$ = 1.967) due to Mo(V)(d^1) coupled with the four nitrogens of the tpp ligand[12)] decreased with the progress of the photoreduction, indicating also the formation of ESR-silent $Mo^{IV}O$(tpp). The one-electron photoreduction does not proceed by the photoirradiation in the Q band region but at the Soret band.[13)] Photoreduction was also confirmed for the other complexes in the title by the photoirradiation at the Soret band. The products in these reaction systems were all confirmed by the consistency of the electronic and/or the ESR spectra between the initial and the final complexes which were all synthesized independently.

When the $Mo^{V}O$(tpp)X (X = Cl, Br, N_3) solution containing phenyl-N-tert-butylnitrone (PBN) was photoirradiated in the visible region (440-750 nm) at room temperature, the ESR signal ($\overline{g}$ = 2.006, A_N = 14.7 G, A_H = 3.3 G) due to PBN radical appeared. The result indicates that the photoreactions of these complexes may proceed via the homolytic cleavage of the M-X bond followed by the reaction of the radical X· with the solvent MTHF.

$$M^{III,V}(tpp)X \xrightarrow[\text{in MTHF}]{h\nu\ (>400\ nm)} M^{II,IV}(tpp) + X\cdot \quad (X = Cl, Br, N_3) \qquad (1)$$

$$X\cdot + MTHF \longrightarrow MTHF\cdot + HX \qquad (2)$$

On the other hand the PBN radical was not observed in the photoreactions of $Mo^{V}O$(tpp)NCS and Mn^{III}(tpp)X (X = I, NCS). We think that I· and SCN· radicals produced by the photoirradiation may be scavenged efficiently by the dimerization of the radicals without abstraction of a hydrogen atom from MTHF.[14)]

Table 1. Quantum yield of the photoreduction in MTHF at 25 °C

Complex	Soret band nm	Excitation band nm	Quantum yield
Mn^{III}(tpp)I	498	498	1 x 10^{-4}
Mn^{III}(tpp)Br	483	481	3 x 10^{-6}
Mn^{III}(tpp)Cl	475	468.5	2 x 10^{-6}
Mn^{III}(tpp)OAc	467	468.5	≈ 1 x 10^{-7}
Mn^{III}(tpp)NCS	475	468.5	2 x 10^{-4}
Fe^{III}(tpp)Cl	416	418	8 x 10^{-6}
Co^{III}(tpp)Cl	424	424	6.7 x 10^{-3}
$Mo^{V}O$(tpp)Br	508	509	1.2 x 10^{-4}
$Mo^{V}O$(tpp)Cl	493	489.5	1.6 x 10^{-4}
$Mo^{V}O$(tpp)F	463	463	3 x 10^{-5}
$Mo^{V}O$(tpp)NCS	492	489.5	1.4 x 10^{-4}
$Mo^{V}O(tpp)N_3$	487	489.5	1.0 x 10^{-3}

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13) The photoirradiation of $Mo^{V}O(tpp)Cl$ with the light of Q band for 2 h did not cause the photoreduction.

14) The ESR measurements for the reaction systems of $Mn^{III}(tpp)OAc$, $Fe^{III}(tpp)Cl$, and $Mo^{V}O(tpp)F$ containing PBN gave no affirmative answer to the production of PBN radical because of the low quantum yields of these complexes. In the photoreduction of $Co^{III}(tpp)Cl$, the ESR signals due to PBN radical and some organic radical showing seven lines ($\bar{g}$ = 2.006) were observed. The detailed mechanisms of all these photoreactions are as yet unknown but will be the subject of our future studies.

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