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Preparation, Characterization, and Reaction of Novel Dioxoruthenium(VI) Porphyrin Cation Radical Complexes

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Novel dioxoruthenium(VI) porphyrin cation radicals were prepared in the stoichiometric oxidation of Ru^{VI}TMP(O)$_2$ (**1**) and Ru^{VI}OEP(O)$_2$ (**2**) with phenoxathiin hexachloroantimonate. ^{2}H-NMR, UV–vis, and ESR were measured to determine the electronic structure of the oxidation products. The oxidation product (**3**) of **1** shows a broad Q band and a less intense and blue-shifted Soret band, suggestive of the porphyrin cation radical formation. Further, the single ESR signal for **3** at $g = 2.002$ at 77 K is a clear demonstration of one-electron oxidation of the porphyrin ring to form a free radical complex. The presence of two oxo ligands in **3** was confirmed in the reaction of **3** with Ph$_3$P under argon to give 2 mol equiv of Ph$_3$P=O. Very similar results were also obtained when **2** was oxidized under the same condition, and the oxidation product (**4**) was also assigned to be a dioxoruthenium(VI) porphyrin cation radical. The chemical shifts of **3** and **4** were determined by deuterium NMR using partially deuterated **3** and **4**. On the basis of paramagnetic shifts, the radical orbitals of **3** and **4** were determined to be A$_{1u}$. Further, oxidation reactions of diphenyl sulfide and some olefins were carried out with high valent ruthenium complexes (**1**–**4**), and the results show that **3** and **4** exhibit greater reactivity than **1** and **2**; however, the enhancement of the reactivities are less than those expected for the complexes bearing A$_{2u}$ radical orbitals.

Introduction

Biological utilization of higher valent iron–oxo species in the oxidative metabolisms by metalloenzymes such as P-450, peroxidase, catalase, and methane monooxygenase has received much attention.[1] While compound II (oxoferryl heme) of peroxidase plays an important role in biological system, one-electron oxidation of the porphyrin ring of compound II to form compound I causes a remarkable enhancement of its reactivity.[1,2] Though many efforts have been made to understand the structure and roles of those reactive intermediates by employing their model systems, difficulties in observing them remain in many cases due to their instability. For instance, synthetic models of compound I of peroxidase, i.e., oxoferryl porphyrin cation radicals, are only observable at low temperature.[3] However, a family of higher valent oxoruthenium complexes has been demonstrated to be relatively stable.[4,5] Further, ruthenium shares the same number of outer shell electrons with iron and forms porphyrin complexes with structures isoelectronic to those iron porphyrins. So far the most highly oxidized species are dioxoruthenium(VI) porphyrin complexes, which can oxidize many organic substrates.[5]

Recent model studies on oxoferryl porphyrin cation radical complexes by utilizing tetraphenylporphyrin (TPP) derivatives allow us to consider details of biological oxidative metabolism of many types of reactions including hydroxylation of unactivated alkanes;[6] however, the active sites of hemoproteins are composed of the iron protoporphyrin IX complex. In addition, the radical orbital (HOMO) of TPP derivatives has been generally attributed to A$_{2u}$[7] whereas those of protoporphyrin IX and OEP[8] have been shown to be A$_{1u}$.[7]

In this study, we have prepared novel porphyrin cation radical derivatives of dioxoruthenium(VI)–TMP, Ru^{VI}TMP(O)$_2$,[5a,b,9] and dioxoruthenium(VI)–OEP, Ru^{VI}OEP(O)$_2$.[5c,8] Further, their reactivities are compared with the corresponding dioxoruthenium(VI) porphyrins to examine the effect of one-electron oxidation of the porphyrin ring.

Experimental Section

Materials. Methylene chloride was refluxed with calcium hydride and distilled under argon just before use. Other solvents were used without further purification. Deuterated solvents, acetic acid-d_1, deuterium oxide,

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(8) OEP: octaethylporphyrin.

(9) TMP: 5,10,15,20-tetramesitylporphyrin.

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and sulfuric acid-d_2 were purchased from Aldrich and used without further purification. Phenoxathiin was purchased from Kanto Chemical Co. The salt phenoxathiin hexachloroantimonate was prepared by the published procedure.[10] Triphenylphosphine, pyrrole, mesitylene, and *m*-chloroperbenzoic acid (*m*CPBA) were obtained from Nacalai Tesque Inc., and mesitaldehyde was purchased from Aldrich. These reagents were used without further purification. OEPH$_2$ was prepared by the method of Inhoffen, Fuhrhop, and Brockmann.[11] TMPH$_2$ was prepared by the method of Wagner, Lawrence, and Lindsey.[12] Ru^{II}TMP(CO)(MeOH) and Ru^{II}OEP(CO)(MeOH) were synthesized by a literature method.[13] Ru^{VI}(OEP)(O)$_2$ (**2**) was prepared by the literature method.[5c]

Preparation of Ru^{VI}(TMP)(O)$_2$ (1). Ru^{VI}(TMP)(O)$_2$ (**1**) was prepared according to the method reported[5a,b] with some modification. To a CH$_2$Cl$_2$ solution (20 mL) of Ru^{II}TMP(CO)(MeOH) (100 mg) was added dropwise 200 mg of *m*CPBA in 50 mL of CH$_2$Cl$_2$. The solution was stirred for 10 min at room temperature and directly submitted to Al$_2$O$_3$-column chromatography without evaporation of the solvent. After the evaporation of the solvent, **1** was recrystallized from toluene/MeCN.

Deuterated Porphyrins. The meso positions of octaethylporphyrin were deuterated by using sulfonic acid-d_2.[14] Incorporation of deuterium was confirmed by ^{1}H-NMR (90% < D).

Mesitylene was treated twice with 10 M sulfuric acid-d_2 at 50 °C for 1 h, affording 60%-enriched mesitylene-d_3 as estimated by the ^{1}H-NMR spectrum.[15] Conversion of mesitylene-d_3 to mesitaldehyde-d_2 was accomplished by a literature method.[16] Pyrrole-d_5 was prepared by treatment with acetic acid-d_1 as described by Fajer et al.[17] Pyrrole-d_8 and meta-d_8 TMPH$_2$ were prepared from pyrrole-d_5 and mesitaldehyde-d_2 in the usual manner.[12]

One-Electron Oxidation of Ru(Por)(O)$_2$. Oxidation of **1** and **2** was performed in CH$_2$Cl$_2$ by adding a CH$_2$Cl$_2$ solution of phenoxathiin hexachloroantimonate[10] (1.2 equiv amount) under argon at –40 °C, to yield **3** and **4** quantitatively. The formation of **3** and **4** was monitored by UV–vis spectroscopy.

Preparation of ^{2}H-NMR and ESR Samples. A methylene chloride solution (20 mL) of **1** or **2** (0.4 mM) was added to 5 mL of CH$_2$Cl$_2$ solution containing 1.2 equiv of phenoxathiin hexachloroantimonate at –45 °C and stirred for 30 min under argon. By evaporation of most of the solvent, the solution was concentrated to 4 mL at –45 °C. The resulting solution was transferred to a NMR or ESR sample tube for further measurements.

Preparation of ^{31}P-NMR Samples. A methylene chloride solution (20 mL) of **3** or **4** (0.4 mM) was stirred with 5 equiv of Ph$_3$P at –45 °C for 30 min under argon. ^{31}P-NMR spectral measurements were performed at 23 °C after the solution was concentrated to 4 mM at room temperature.

Oxidation of Sulfide and Olefins with Dioxoruthenium Porphyrin Complexes. A dry methylene chloride solution of Ru porphyrin (0.4 mM) was stirred with 100-fold excess amounts of olefin at –45 °C for 10 h under argon. Similar oxidations were carried out with 300 equiv amounts of diphenyl sulfide for 3 h. The reactions were terminated by adding Ph$_3$P, and the oxidation products were analyzed by GLC.

Physical Measurements. UV–vis spectroscopic measurements were performed on a Hitachi 330 spectrophotometer, and a JEOL JES-3X instrument was used for ESR measurements. Deuterium NMR spectra at 46.1 MHz and ^{31}P-NMR spectra at 121.5 MHz were recorded on a Nicoret NT-300 spectrometer equipped with a Model 1280 computer system. Chemical shifts are referenced to tetramethylsilane (^{2}H-NMR) or H$_3$PO$_4$ (^{31}P-NMR), and downfield shifts are given a positive sign. GLC analysis was performed with a SHIMADZU GC-14A gas chromatograph.

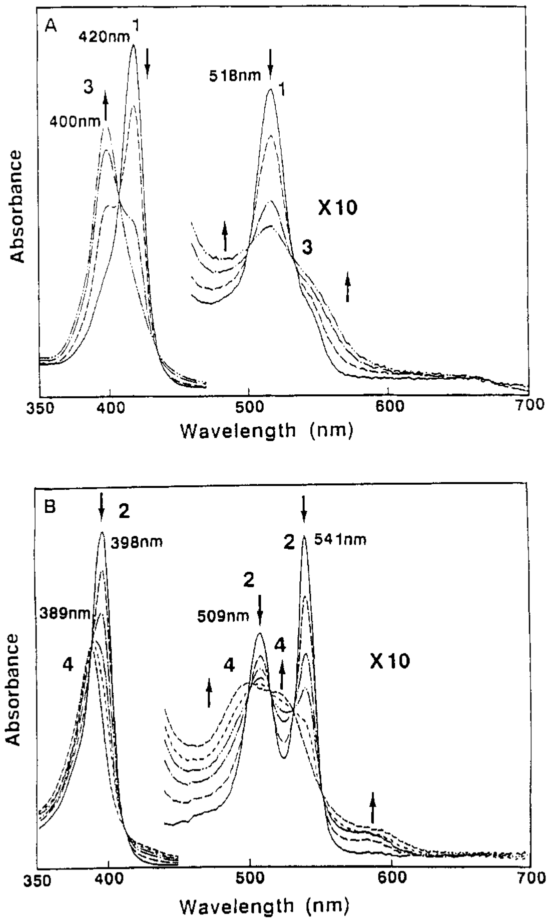

Figure 1. UV–vis spectral changes upon the titration of 1 × 10^{-5} M solution of Ru(TMP)(O)$_2$ (A) and Ru(OEP)(O)$_2$ (B) under anaerobic condition in CH$_2$Cl$_2$ at –40 °C with phenoxathiin hexachloroantimonate. Equivalents of phenoxathiin hexachloroantimonate present in the solutions are as follows: (A) (—) 0, (– –) 0.4, (– · –) 0.8, (– ·· –) 1.2; (B) (—) 0, (— —) 0.2, (– · –) 0.4, (– ·· –) 0.6, (- - -) 0.8, (– –) 1.0.

Results

Characterization of the Oxidation Products. Oxidation of Ru^{VI}TMP(O)$_2$ (**1**) and Ru^{VI}OEP(O)$_2$ (**2**) were carried out by introducing a small excess amount of phenoxathiin hexachloroantimonate in dry methylene chloride at –40 °C under argon to yield new complexes (**3**, **4**). The spectrophotometric titration of **1** (1 × 10^{-5} M) with aliquot addition of phenoxathiin hexachloroantimonate (total: 1.2 equiv) showed smooth conversion of **1** to **3** with isosbestic points in UV–vis spectra at 409, 436, 503, and 534 nm (Figure 1A). Very similar results were also obtained when Ru^{VI}OEP(O)$_2$ (**2**) was oxidized under the same conditions with isosbestic points at 389, 412, 500, 515, 531, and 552 nm (Figure 1B). A broadened Q band and less intense Soret band with blue shift are suggestive of the porphyrin cation radical formation.[18]

The oxidized products of **1** and **2** afforded ESR absorption at 77 K at g = 2.002 with a 13 G peak to peak width for **3** and g = 2.002 with an 8 G peak to peak width for **4** (Figure 2), indicative

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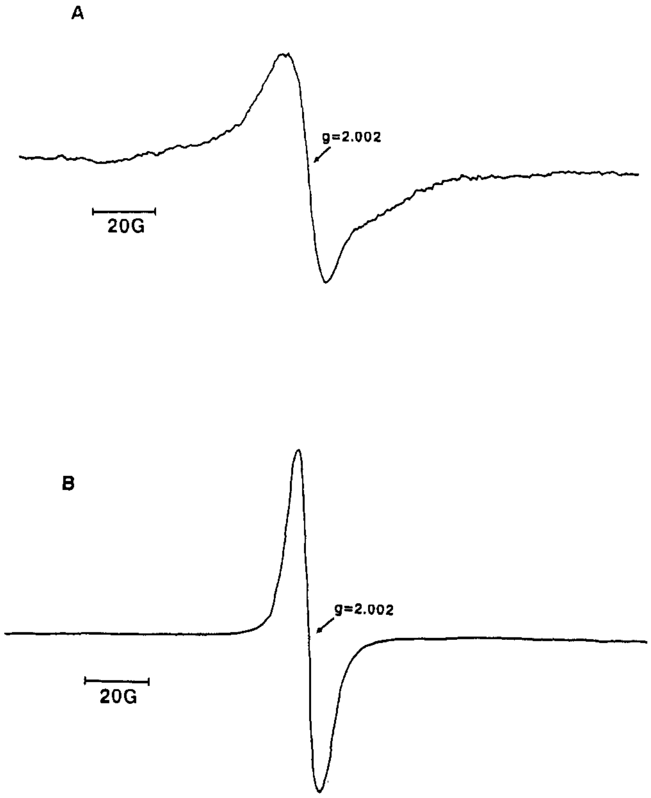

Figure 2. Frozen solution ESR spectra of 3 (A) and 4 (B) in methylene chloride at 77 K.

of free radical formation. The same spectra were also observed for the pyrrole and meta deuterated sample of 3. These results are a clear demonstration of one-electron oxidation of the porphyrin ring of 1 and 2 to form π-cation radical structures of 3 and 4 without any changes in the oxidation state of the central metal during the oxidation as diamagnetic Ru^{VI} with the low spin configuration (d^2, $S = 0$).[5a] Further, 2 equiv amounts of triphenylphosphine (Ph_3P) were oxidized by 3 and 4 under argon at −45 °C.[19] The stoichiometry of the triphenylphosphine oxide formed was confirmed by ^{31}P-NMR spectroscopy. These results suggested the presence of two oxo ligands in 3 and 4. Thus, the oxidation products of 1 and 2 by phenoxathiin hexachloroantimonate are assigned to be dioxoruthenium(VI) porphyrin cation radical complexes, $Ru^{VI}TMP^{\bullet+}(O)_2$ (3) and $Ru^{VI}OEP^{\bullet+}(O)_2$ (4). These cation radical complexes are only stable at −40 °C or below.

Oxidation of Sulfide and Olefins. Oxidation reactions of diphenylsulfide and some olefins were carried out with high valent ruthenium complexes (1–4), and results are summarized in Table I. Apparently, 3 and 4 exhibit greater reactivity than 1 and 2, respectively.

Determination of Radical Orbitals. In order to examine the radical orbitals of 3 and 4, NMR measurements of 3 and 4 were carried out at low temperature. It has been well known that deuterium NMR is often more suitable than proton NMR for the studies of paramagnetic species, because the deuterium spectrum does not experience unwanted broadening which is often encountered in the proton spectrum.[18g,h,i,20] Therefore, ^{2}H-NMR spectra of 3 (pyrrole-d_8, meta-d_8) and 4 (meso-d_4) were measured. The deuterium NMR spectrum of 3 at −40 °C is illustrated in Figure 3. The deuterium resonances are assigned as follows: pyrrole-D at −40.0 ppm, and meta-D at 8.5 ppm. These assignments were confirmed by disappearance of particular deuterium signal for the radical prepared either from pyrrole-d_8–1 or from meta-d_8–1. The deuterium resonance of meso-D of 4 appeared at 2.2 ppm at −40 °C (Figure 4). The chemical shifts of 1 and 2 are as follows: 1, pyrrole, 8.8 ppm, and meta, 7.3 ppm; 2, meso, 10.6 ppm. The isotropic ^{2}H-NMR hyperfine shift for the π-radical system is related through eqs 1 and 2 to

$$\left(\frac{\Delta H_{\mathrm{iso}}}{H}\right) = A^{\mathrm{D}}\frac{\gamma_e g\beta S(S+1)}{\gamma_{\mathrm{D}}\,3kT} \tag{1}$$

$$A^{\mathrm{D}} = Q\rho_{\mathrm{c}} \tag{2}$$

the π-electron spin density at the carbon to which the deuterium is attached. Here, eq 1 relates the observed isotropic shift ($\Delta H_{\mathrm{iso}}/H$) with the hyperfine coupling constant of the deuterium (A^{D}) (downfield deuterium shift corresponds to a positive value of A^{D}).[21] Equation 2 is the McConnel relation,[22] which connects A^{D} with the π-spin density on the carbon (ρ_{c}). With these equations, the observed hyperfine shifts of the β-pyrrole, meta, and meso D's are translated into π-spin densities at the β-pyrrole and meta carbons for 3 and meso carbons for 4, which are listed in Table II. Included in Table II for comparison are the MO-calculated values for metal-free A_{1u} and A_{2u} porphyrin π-cation radicals.

The temperature dependence of the hyperfine-shifted deuterium resonances of 3 is illustrated in Figure 3 (inset) in the form of a Curie plot. Inspection of the figure shows that the usual Curie law behavior is seen for the β-pyrrole and meta deuterium resonances. These resonances have intercepts of 5.5 and 7.3 ppm at $1/T = 0$, within the diamagnetic shift region. These usual temperature dependences could be accounted for by 3 being a single spin state.

Discussion

Electronic State of Metalloporphyrin π-Cation Radicals. On the basis of the electrochemical oxidation of dioxoruthenium(VI) porphyrins, possible formation of the corresponding cation radicals as one-electron oxidation products was suggested.[5a,c] We have tried to prepare these products chemically and to characterize them with various spectroscopic measurements. Though one-electron oxidation of ruthenium(VI) porphyrin complexes is expected to yield either ruthenium(VII) or ruthenium(VI) porphyrin π-cation radical species, it is found in the present study that the one-electron oxidized products of $Ru^{VI}(Por)(O)_2$ are ruthenium(VI) porphyrin π-cation radicals, as evidenced by the UV–vis, ESR, and ^{31}P-NMR spectral data. This may be caused by the two oxo ligands which stabilize the metal d orbitals below the porphyrin π levels.

It has been well established that the salient feature of the A_{2u} porphyrin cation radical orbital is distribution of a substantial amount of positive spin density at the meso carbons and the pyrrole nitrogens, while the radical orbital in the A_{1u} state has nodes at these atoms (D_{4h} symmetry).[7] Accordingly, the isotropic hyperfine shift of the typical A_{2u} radical is expected to induce a large upfield contact shift for the meso deuteriums and a large downfield contact shift for the meta deuteriums, whereas meso deuteriums of the A_{1u} radical show a tiny shift. Generally, $(OEP^{\bullet+})M$ is an example of the A_{1u} radical and $(TPP^{\bullet+})M$ derivatives give the A_{2u} radicals. Observation of the chemical shift of the meso-D signal of 4 at 2.2 ppm is in good agreement with the radical orbital being A_{1u}. While a large upfield hyperfine shift of the β-pyrrole-D signal (8.8 ppm to −40.0 ppm) was observed upon the oxidation of 1, the meta-D signal of 3 did not shift very much (7.3 ppm to 8.5 ppm). On the basis of contact shifts, spin densities at the β-pyrrole and meta carbons for 3 and

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Table I. Oxidation of Diphenyl Sulfide and Olefins by Ruthenium Porphyrin Complexes at –45 °C[a]

	$TMPRu(O)_2$ (**1**)	$TMPRu(O)_2^{\bullet+}$ (**3**)	$OEPRu(O)_2$ (**2**)	$OEPRu(O)_2^{\bullet+}$ (**4**)
diphenyl sulfide[b]	13[d]	31 (Ph_2SO:$Ph_2S(O)_2$ = 25:3)	26 (22:2)	28 (18:5)
norbornene[c]	19[e]	28[e]	*f*	27[e]
trans-stilbene[c]	*f*	*f*	*f*	11[g]
cis-stilbene[c]	4 (trans:cis = 2:2)	9 (7:2)	1 (...)[g]	52 (35:17)

[a] Yields based on porphyrins (%). [b] Reaction time is 3 h. [c] Reaction time is 10 h. [d] Only Ph_2SO was obtained. [e] Norbornene oxide. [f] <1%. [g] Only trans epoxide was obtained.

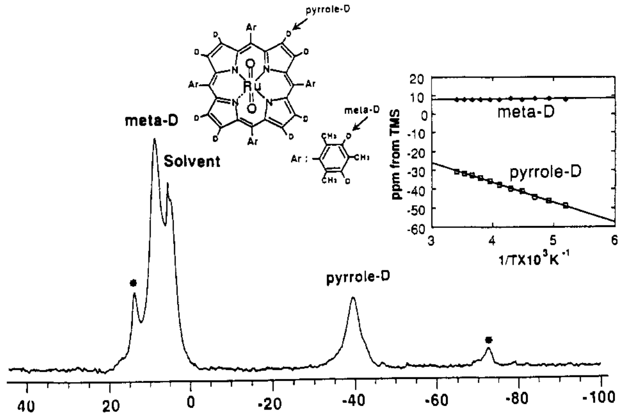

Figure 3. ^{2}H-NMR spectrum of **3**-d_{16} (β-pyrrole-d_8 and meta-d_8) at –40 °C in methylene chloride. The peaks marked with an asterisk come from the decomposed product. Inset: temperature dependence of the ^{2}H-NMR spectra of **3**.

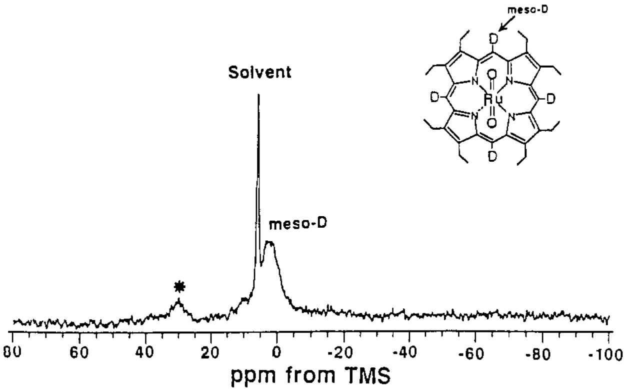

Figure 4. ^{2}H-NMR spectrum of **4** (meso-d_4) at –40 °C in methylene chloride. The peak marked with an asterisk results from the decomposed product.

Table II. Deuterium Isotropic Shifts and Spin Densities on β-Pyrrole, Meta, and Meso Carbons (ρ_c) for Dioxoruthenium(VI) Porphyrin π-Cation Radical Complexes

compound	deuterium position	deuterium isotropic shift/ppm	$\rho_{c(exp)}$[a]	$\rho_{c(calc)}$[b] A_{1u}	$\rho_{c(calc)}$[b] A_{2u}
$Ru^{VI}TMP^{\bullet+}(O)_2$	β-pyrrole	–48.8	0.0229	0.0262	0.0134
	meta	1.2	–0.0005	≈0	–0.0240
$Ru^{VI}OEP^{\bullet+}(O)_2$	meso	–8.4	0.0039	0.0012	0.1932

[a] Spin densities are obtained through eqs 1 and 2; T = 233K. [b] The values are obtained from ref 18f.

that at the meso carbons for **4** are readily calculated based on eqs 1 and 2. By comparison with theoretical values, the radical orbitals of **3** and **4** are concluded to be A_{1u}. On the other hand, the line width of ESR signal for **3** is broader than that of **4**, suggesting that **3** may have an A_{2u}-like radical orbital because of possible hyperfine coupling of pyrrole nitrogen with meta and pyrrole protons. Thus, ESR spectra of **3** (meta-d_8) and **3** (pyrrole-d_8) were measured at 77 K. Introduction of deuterium did not cause any appreciable spectral changes including the line width (13 G peak to peak width), indicating that the slightly broadened ESR signal of **3** was not caused by hyperfine coupling with the β-pyrrole proton and the meta proton. Although metal hyperfine coupling may contribute to the ESR line broadening for the A_{2u} radical state, this is ruled out by the very small hyperfine shift for the meta deuterium characteristic of the A_{1u} radical state. These results indicate the radical orbital of **3** to be A_{1u}, while the ESR signal is broadened possibly due to short electron spin relaxation.

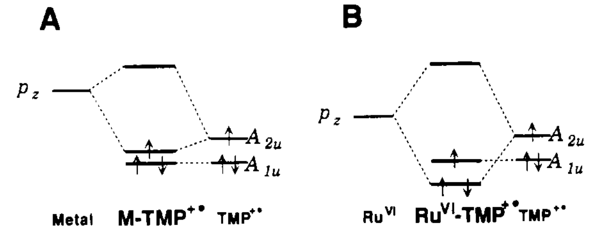

Figure 5. Orbital correlation diagram for the general M-TMP$^{\bullet+}$ (A) and $Ru^{VI}TMP^{\bullet+}(O)_2$ (B).

The A_{2u} orbital of $(TMP^{\bullet+})M$ is able to interact with the p_z orbital of the central metal by utilizing a large spin density on the pyrrole nitrogen. Stabilization of A_{2u} by the interaction is usually small because of a large energy gap between p_z and A_{2u} (Figure 5A). In the case of **3**, the energy level of the p_z orbital might be much lower than usual due to its extremely high oxidation state. These effects could stabilize the A_{2u} orbital and make the A_{1u} orbital to be HOMO (Figure 5B).

Oxidation of Substrates. Interest in the hydrocarbon oxidation has stimulated a major effort to model the oxygen activation and transfer reactions characteristic of cytochrome P-450. Model studies have implicated the active intermediacy of an oxoiron(IV) porphyrin π-cation radical complexes in the catalytic cycle of P-450.[3,23–25] For example, though $O{=}Fe^{IV}TMP$ does not react with various olefins, $O{=}Fe^{IV}TMP^{\bullet+}$ readily oxidizes them.[3,23] The greater reactivities of $O{=}Fe^{IV}TMP^{\bullet+}$ as compared with $O{=}Fe^{IV}TMP$ would be caused by a A_{2u} radical orbital, which interacts with the central metal. Further, the oxo ligand may have more positive charge by forming a porphyrin π-cation radical, and it could result in the enhancement of electrophilic reactivities.

The oxidation reactions of sulfide and some olefins with **2** and **4** were examined to estimate the effect of A_{1u} radical on the reactivities. While similar reactivity was observed in the oxidation of sulfide, enhancement for the epoxidation of olefins is evident (Table I). However, in the case of $O{=}Fe^{IV}TMP$ and $O{=}Fe^{IV}TMP^{\bullet+}$, a much greater increase of reactivities upon the formation of the porphyrin π-cation radical was reported.[23,26] These differences could be attributed to their radical orbitals, A_{1u} and A_{2u}, as discussed above. Owing to the interaction of the porphyrin radical and oxo orbitals via metal orbitals, A_{1u} radicals are expected to be less effective than A_{2u} radicals.

According to the NMR study, the radical orbital of **3** has been assigned to A_{1u} even though TMP is the ligand. Thus, the

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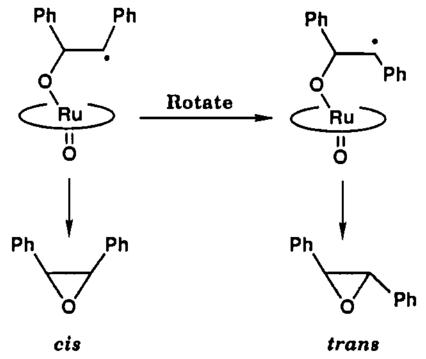
oxidations of diphenyl sulfide by **1** and **3** were also examined. In these reactions, one-electron oxidation from the porphyrin ring did not enhance the reactivity very much. Further, the reactivity of **3** for epoxidation of norbornene and *cis*-stilbene is slightly greater than that of **1** (Table I). Apparently, the oxidation of the porphyrin ring of **1** failed to increase the reactivity, indicating the radical orbital to be A_{1u} rather than A_{2u}. In addition, cis–trans conversion during the oxidation of *cis*-stilbene suggests radical intermediate formation in the reactions promoted both by dioxoruthenium(VI) porphyrin complexes and by the corresponding cation radicals (Scheme I).[5c,27]

In conclusion, novel dioxoruthenium(VI) porphyrin cation radicals were prepared in the stoichiometric oxidation of $Ru^{VI}TMP(O)_2$ (**1**) and $Ru^{VI}OEP(O)_2$ (**2**) with phenoxathiin hexachloroantimonate. The radical orbitals of **3** and **4** were determined to be A_{1u} on the basis of deuterium isotropic shifts. Further, oxidation reactions of diphenyl sulfide and some olefins were carried out with high valent ruthenium complexes (**1**–**4**), and the results show that **3** and **4** exhibit greater reactivity than **1** and **2**, however, the enhancement of the reactivities are less than those expected for the complexes bearing A_{2u} radical orbitals.

Scheme I



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