

Reactions of Molybdenum(V)porphyrins with Phenol Derivatives Involving Parallel Inner and Outer Sphere Electron Transfer

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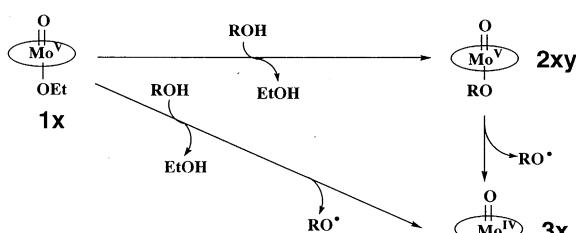
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Reactions of oxoethoxomolybdenum(V)porphyrins and substituted phenols were investigated by UV-vis absorption spectra. Ligand substitution or reduction of the metal center proceeded depending on the steric repulsion between the substituents of the phenols and the porphyrin skeletons. Proton transfer from the phenols to the axial ligand of the molybdenumporphyrin initiated the reactions. Parallel outer sphere and inner electron transfer proceeded parallel in the reduction of the molybdenum center.

Many studies concerning catalytic oxidation of hindered phenols have been made by using Schiff base complexes of cobalt¹ and metalloporphyrins.² Most of these studies have discussed the interaction between 4-position of the phenol derivatives and metal center. The authors studied reactions of substituted phenols with molybdenum(V)porphyrins and found that the oxidation of phenol proceeds by parallel outer and inner sphere one electron transfer from the phenol substrate to the molybdenum center.

This letter reports that the reaction of molybdenum(V)porphyrins with phenols gives a ligand-substituted complex or a complex with reduced metal center depending on the steric repulsion between phenol substrate and porphyrin skeleton and that outer sphere electron transfer takes place from phenolate ion to the metal center for the latter. We followed reactions of the oxoethoxomolybdenum(V)porphyrins, Mo^V(tpp)(O)(OEt), **1p**, and Mo^V(tmp)(O)(OEt), **1m**,³ with phenols in benzene by means of UV-vis absorption spectroscopy. Abbreviations of the complexes are shown in Scheme 1.

Scheme 1.



Abbreviations for complexes (1x, 2xy, 3x)

Equatorial ligand is represented by x where tpp and tmp are abbreviated as p and m.

Abbreviations for axial ligand, y.

Abbreviation	2xa	2xb	2xc
Axial ligand	-O-	-O-	-O-

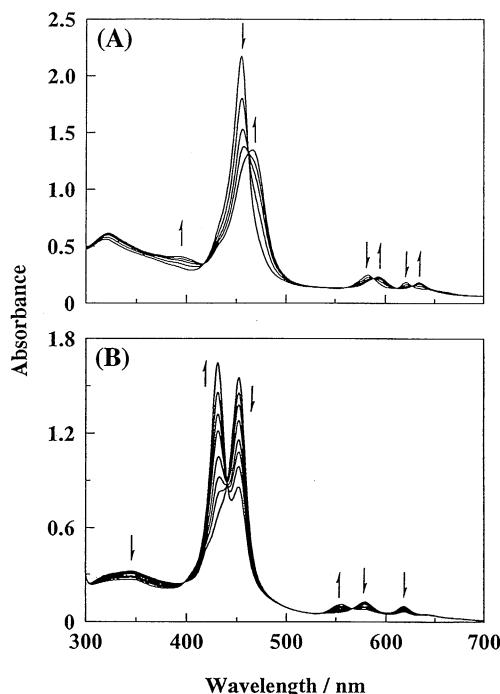


Figure 1. UV-vis absorption spectral changes in molybdenumporphyrin upon addition of phenol in benzene under nitrogen at 20.0 °C. (A) Absorption spectra of **1m** (1.11×10^{-5} mol dm⁻³) at 0.5, 5, 10, 15, and 25 min after addition of 10 eq. of phenol. (B) Absorption spectra of **1p** (1.06×10^{-5} mol dm⁻³) at 1, 5, 10, 20, 40, 60, 80, and 210 min after addition of 1000 eq. of 2,6-di-*t*-butyl-*p*-cresol.

Figure 1(A) shows the time course of UV-vis absorption spectral change in complex **1m** in benzene after addition of phenol (10 eq.). The intensities of the initial bands decreased and new bands appeared. The new bands were attributed to Mo^V(tmp)(O)(OPh), **2ma**. Isosbestic points indicate that only initial and final species exist in the reaction system. The ligand substitution was completed in 25 min. A similar ligand substitution was observed for **1p** and phenol.

Figure 1(B) shows the spectral change in **1p** upon addition of 2,6-di-*t*-butyl-*p*-cresol (1000 eq.) in the dark. The spectrum changed gradually with isosbestic points. New Soret and $\alpha\beta$ bands appeared and increased in their intensities, as the bands attributable to **1p** decreased. The new bands were attributable to those of Mo^V(O)(tpp), **3p**.⁴ Changes in the ESR spectrum under the same reaction conditions are shown in Figure 2. The signal due to Mo^V decreased in intensity⁵ and a new signal that was attributed to a phenoxy radical originating from 2,6-di-*t*-butyl-*p*-cresol appeared at $g = 2.006$. The complex **1m** showed a similar UV-vis spectral change in the reaction with 2,6-di-*t*-

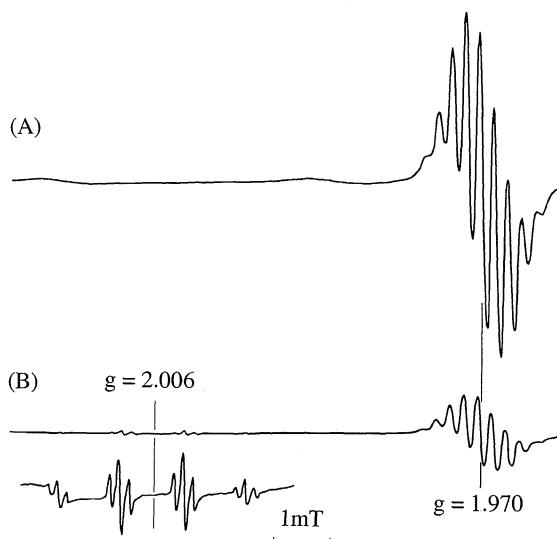


Figure 2. ESR spectra of (A) **1p**, and (B) after addition of excess amount of 2,6-di-*t*-butyl-*p*-cresol, in benzene under nitrogen.

butyl-*p*-cresol.

The complexes, **1p** and **1m** differed in their reaction behavior with a phenol having moderately bulky groups at 2 and 6 positions. The reaction of **1p** with 2,4,6-trimethylphenol at 20 °C gave a stable hexacoordinate complex, **2pc**, whose structure was similar to that of Mo^V(tpp)(O)(OPh), **2pa**, which was formed via the ligand substitution. On the other hand, reduction and coordination proceeded competitively at higher temperature for the reaction system of **1m** and 2,4,6-trimethylphenol. The reaction was divided into two stages. In the early stage (0 to 180 min after the addition of the phenol), an increase in quantity of both **2mc** and **3m** was observed. In the later stage (3 to over 20 h) complex **2mc** that was formed in the early stage was slowly transformed to **3m**. The reduction of **2mc** proceeded very slowly so that about 50 % of **2mc** was still left un-reduced after 20 h. These observations suggest that **3m** is formed by two distinct reaction paths. Complex **3m** is formed both directly by the reaction of **1m** and 2,4,6-trimethylphenol and *via* **2mc**.

The redox potentials of Mo^V/Mo^{IV} were observed at -1.05 and -1.15 V vs. Ag/AgNO₃ for **1p** and **1m**, respectively. Complex **1p** might be, therefore, more readily reduced by 2,4,6-trimethylphenol than **1m**. The difference in the reaction behavior between **1p** and **1m** was ascribed to the disturbance of the coordination bond formation due to the steric repulsion.

The reaction is summarized in Scheme 1. A substituted or unsubstituted phenol transfers a proton to the ethoxy ligand of complex **1** to cleave the Mo-OEt bond. If the steric repulsion is small, complex **2** is formed from **1** by the ligand substitution. With the large steric repulsion, on the other hand, the molybdenum center is reduced by an outer sphere one electron transfer. The ligand substitution and the reduction of molybdenum center take place competitively in the case of the moderate repulsion. In the last case, reduction of molybdenum center proceeds also by the thermolysis of complex **2** (inner sphere electron transfer).

It is emphasized that the first step is influenced only by the acidity of phenol derivatives and basicity of the axial ligand of the complex. For example, the complex [Mo^V(tmp)(O)⁺(ClO₄)⁻] is not subject to ligand substitution nor reduction by phenol derivatives, even though the complex has the most positive Mo^V/Mo^{IV} redox potential. This is attributable to the extremely weak basicity of ClO₄⁻ and excludes the possibility that the reaction is promoted by coordination of the phenol molecule to the vacant sixth coordination site prior to a proton transfer.⁶ The above observations indicate that the elimination of ethoxy group was initiated by a proton transfer.⁷

The second step depends on the steric repulsion. In the case of **1p** and unsubstituted phenol, coordination bond formation proceeds more effectively than the outer sphere electron transfer so that only the product of ligand substitution is obtained. With the moderate steric repulsion the bond formation between the anion and cation in the ion pair is slightly disturbed and, consequently, the reduction and ligand substitution proceed competitively as seen in the early stage of **1m** and 2,4,6-trimethylphenol. The rate of ligand substitution for **1m** and 2,4,6-trimethylphenol is smaller than that observed for **1p**. Bond formation between metal center and 2,6-di-*t*-butyl-*p*-cresolate is hindered and, therefore, **1p** or **1m** is only reduced by addition of 2,6-di-*t*-butyl-*p*-cresol.

As mentioned above, the reactions of phenols and oxoethoxomolybdenum porphyrins are initiated by the proton transfer. The whole reaction is highly dependent on the repulsive interaction between the substituents of phenols and porphyrin ligands. Under the moderate extent of the repulsion, the reduction of the molybdenum center proceeds by both outer and inner sphere one electron transfers.

References and Notes

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- 3 tpp and tmp denote 5,10,15,20-tetraphenylporphyrin and -tetramesitylporphyrin dianions, respectively.
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- 7 The reaction of the complex **1** and *p*-substituted thiophenols results in the formation of 1 eq. of the complex **3**, 0.5 eq. of diphenyldisulfides, and 1 eq. of ethanol. The logarithmic initial rate constant is linearly correlated with pK_a of the *p*-substituted thiophenol. The rate increases in the order of Br->Cl->H->CH₃-, indicating that a proton transfer is a rate-determining step of the reaction to the complex **3**.