

Electrochemistry of *para*-Substituted Oxomolybdenum(V) Tetraphenylporphyrin Complexes

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Introduction

Metalloporphyrin complexes have been under investigation for many years [1]. The early interest in these complexes resulted from their presence in a variety of biological systems. Among these are hemoglobin [2, 3], the cytochromes [4], chlorophylls [5], and the oxygenases [6]. Transition metal tetraphenylporphyrin (TPP) complexes have been used to examine model biochemical reactions. Electron transfer reactions of iron porphyrins have been studied as cytochrome models [7]. Cobalt and iron TPP complexes [8] have been studied as synthetic dioxygen carriers. Although molybdenum is not found complexed by porphyrin type ligands in living systems, some important enzymes do contain Mo [9] (e.g. nitrogenase, nitrate reductase, xanthine oxidase, sulfite oxidase, etc.). In another area, Matsuda *et al.* [10] have examined the chemistry of oxomolybdenum TPP complexes as a step toward the preparation of one-dimensional electric conductors by stacking of planar metal complexes. Mo is useful in this regard since it has a number of readily accessible oxidation states.

In recent years, metalloporphyrins have come under study as light harvesting systems for solar energy conversion [11–13]. Metalloporphyrin complexes have intense absorptions in the visible region of the electromagnetic spectrum. In particular, Ledon and coworkers [13] have described the photo-assisted reduction of dioxygen to hydrogen peroxide catalyzed by OMo(V)(TPP)OCH_3 . When OMo(V)(TPP)OCH_3 was aerobically irradiated in the Soret region, a new absorbance was evolved, characteristic of OMo(IV)(TPP) . The original Mo(V) complex was completely restored in the dark. The formation of the OMo(IV)(TPP) complex by photohomolysis of the Mo–OCH₃ bond was confirmed by EPR spectroscopy and spin-trapping experiments.

Electrochemical studies have been used to examine the redox processes of *para*-substituted tetraphenyl-

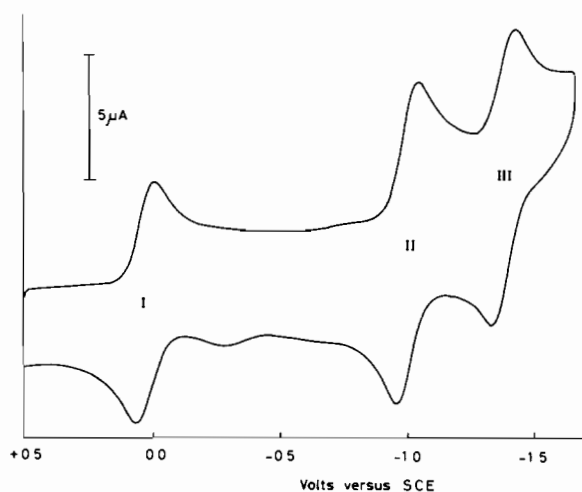


Fig. 1. Cyclic voltammogram for $\text{OMo(V)(}p\text{-H-TPP)NCS}$ in DMSO (scan rate = 100 mV/sec).

porphyrin ligands (*p*-X-TPP) as well as their metal complexes. Kadish and Morrison [14] have examined the effects of *para*-substituents on the free TPP ligands. Their results indicate that as the *para*-substituent becomes more electron-donating, the ligand reduction potentials shift in the cathodic direction. This shift indicates that for electron-donating groups, the reductions are more difficult to carry out. The opposite effect was observed for electron-withdrawing groups. Kadish and Morrison also obtained a linear correlation between $E_{1/2}$ and the Hammett σ_p parameter for the *para*-phenyl substituents. The electrochemistry of the metalloporphyrins is also interesting. Some metals are electrochemically inactive [15, 16] in metalloporphyrin complexes while others, such as Co [15–17], Mn [16, 18–20] Cr [16, 21], Fe [16, 22] and Mo [10, 16, 21] are redox active.

We have examined the electrochemistry of $\text{OMo(V)(}p\text{-X-TPP)NCS}$ to see how the $\text{Mo(V)} \rightarrow \text{Mo(IV)}$ reduction potential is affected by *para*-substituents on the TPP ligand. The results of this work are described here.

Results and Discussion

The *p*-X-TPP ligands were synthesized from pyrrole and *p*-X-benzaldehydes using established synthetic procedures [23, 24]. The oxo-Mo(V) complexes were prepared from Mo(CO)_6 and *p*-X-TPP by modifications of procedures described by Ledon and Mentzen [25, 26], and Imamura *et al.* [27, 28]. For our complexes, the axial ligand employed was NCS^- . The NCS^- ligand bonds 'trans' to the oxo-

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TABLE I. Reduction Potentials for OMo(V)(*p*-X-TPP)NCS.^a

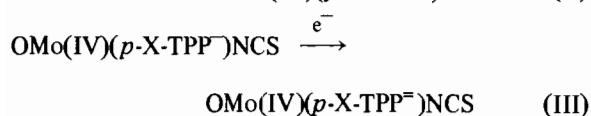
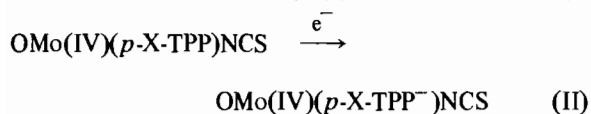
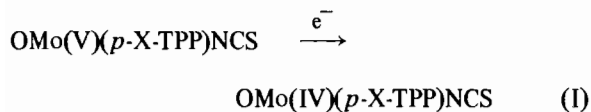
| OMo(V) (<i>p</i> -X-TPP)NCS | $E_{1/2}^b$ (Mo(V)) | $E_{1/2}^b$ (<i>p</i> -X-TPP (1st)) | $E_{1/2}^b$ (<i>p</i> -X-TPP (2nd)) |
|------------------------------|---------------------|--------------------------------------|--------------------------------------|
| X = CH ₃ O | 0.000 | -1.018 | -1.403 |
| CH ₃ | +0.013 | -1.008 | -1.391 |
| H | +0.030 | -0.988 | -1.363 |
| F | +0.045 | -0.957 | -1.319 |
| Cl | +0.065 | -0.940 | -1.294 |
| Br | +0.068 | -0.938 | -1.285 |

^a[OMo(V)(*p*-X-TPP)NCS] = $\sim 5 \times 10^{-4}$ M in DMSO with a glassy carbon working electrode and 0.05 M TBAP as supporting electrolyte
^bVolts versus SCE.

oxygen. This axial ligand allowed us to obtain analytically pure OMo(V)(*p*-X-TPP)NCS complexes after column chromatography on silica gel followed by recrystallization from CH₂Cl₂/hexane mixtures.

Cyclic voltammetry was used to examine the electrochemistry of the OMo(V)(*p*-X-TPP)NCS complexes. The experiments were carried out at ambient temperature with a homemade potentiostat using a conventional three electrode system. A glassy carbon electrode was used as the working electrode, and potentials are referenced to the saturated calomel electrode. Dimethylsulfoxide (DMSO) was dried over type 3A molecular sieves. Tetrabutylammonium perchlorate (TBAP; Fisher, Polarographic Grade) was used as the supporting electrolyte. OMo(V)(*p*-X-TPP)NCS concentrations were $\sim 5 \times 10^{-4}$ M with the supporting electrolyte present in ~ 100 -fold excess. The solutions were stirred and deaerated with N₂ for at least 20 minutes prior to each run. A blanket of N₂ was kept above the unstirred solution during the cyclic voltammetry run. The cyclic voltammogram for OMo(V)(*p*-H-TPP)NCS is shown in Fig. 1. This type of cyclic voltammogram is typical of what is observed for the entire series. Table I contains a compilation of the reduction potentials obtained from this work.

Three reversible reductions are observed in the range +0.5 to -1.5 V. They are assigned as follows:



The Mo(V)–Mo(IV) reduction was identified by comparison of the metalloporphyrin cyclic voltam-

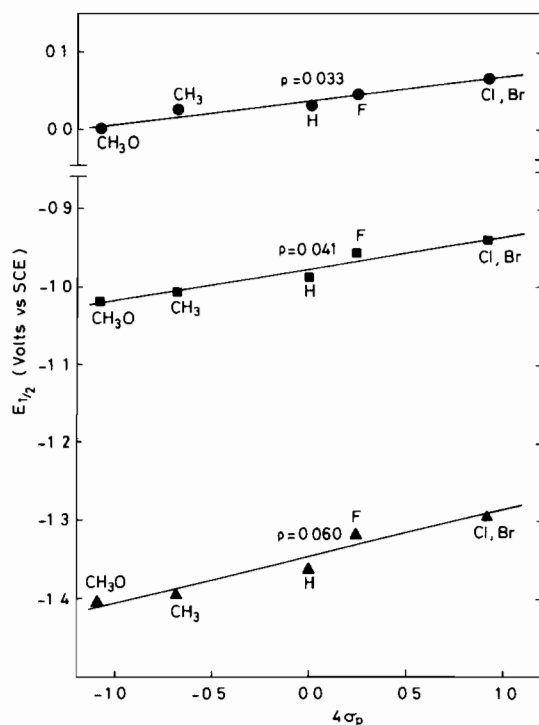


Fig. 2. $E_{1/2}$ versus $4\sigma_p$ for OMo(V)(*p*-X-TPP)NCS: X = CH₃O, CH₃, H, F, Cl, Br (● = Mo(V) → Mo(IV), reaction I; ■ = 1st ligand reduction, reaction II; ▲ = 2nd ligand reduction, reaction III).

mogram with that of the free ligand. The CV waves are observed to shift in the anodic direction as the para-substituent on the TPP ligand is changed from CH₃O to Br. Figure 2 shows a plot $E_{1/2}$ versus four times the Hammett σ_p parameter for the ligand *para*-substituents. The σ_p value for a substituent group was originally derived from its ability to affect the dissociation of *para*-substituted benzoic acids. However, in more general terms, the σ_p value reflects the ability of a group to donate electron density to a π -electron system. Relative to hydrogen, which is

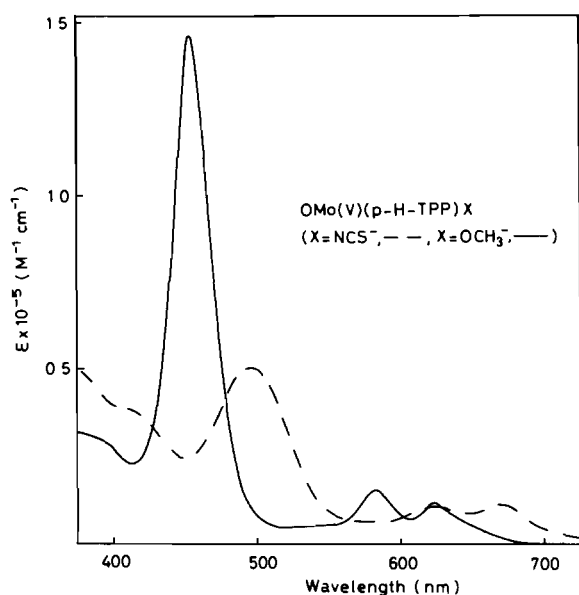


Fig. 3. Visible spectra for $\text{OMo(V)}(p\text{-H-TPP})\text{NCS}$ (---) and $\text{OMo(V)}(p\text{-H-TPP})\text{OCH}_3$ (—) in CH_2Cl_2 .

assigned a value of zero, groups which are more electron donating than hydrogen are assigned negative values and groups which are less electron donating are assigned positive values. A factor of four is used in this work because there are four substituent groups, one on each phenyl ring of the TPP ligand. It is satisfying to note the linear relationship between $E_{1/2}$ and $4\sigma_p$. The rho values show that the shifts in ligand reduction potentials are larger for each substituent when compared to the Mo reduction. In addition, the second ligand reduction is affected to a larger degree than the first ligand reduction. The rho value (0.033) for the metal reduction for the Mo complexes described here is similar to those reported for Mn(III) [20] and Co(III) [17] reductions. This is an interesting result since the Mo orbital associated with the redox process is the non-bonding d_{xy} orbital. Whereas for the Mn(III) and Co(III) complexes, the metal orbitals associated with the reduction are of appropriate symmetry to interact in a π -type fashion with the π -molecular orbitals of the TPP ligand. One would expect a larger rho value for Co and Mn when compared to Mo. The Mo and ligand reduction potentials are being controlled in a predictable fashion by the ligand substituents. As the para-substituent becomes more electron-withdrawing, the reduction potentials shift in the anodic (positive) direction. As the reduction potential of a chemical species is made more positive its reduction becomes easier. Reduction potentials shifted in the cathodic direction are more difficult to carry out.

It was mentioned above that the $\text{OMo(V)}(p\text{-H-TPP})\text{OCH}_3$ complex was reduced to the OMo(IV)

species when the molecule was irradiated in the Soret region of the visible spectrum. At the same time, the $\text{CH}_3\text{O}^\bullet$ radical was formed. Other alkoxide groups can be used in place of the methoxide axial ligand. UV-visible spectroscopy shows that in DMSO the NCS^- axial ligand is not displaced. However, the $\text{OMo(V)}(p\text{-X-TPP})\text{NCS}$ complexes can be converted instantaneously to the $\text{OMo(V)}(p\text{-X-TPP})\text{OCH}_3$ derivative in solution. The conversion is carried out by adding an excess of NaOCH_3 in methanol to either a DMSO or CH_2Cl_2 solution of $\text{OMo(V)}(p\text{-X-TPP})\text{NCS}$. The spectral results showing this conversion are presented in Fig. 3.

Although axial ligands can be used to alter the Mo reduction potential, only alkoxide type axial ligands have been used in the photoassisted reduction of Mo(V) to Mo(IV) described above. The results of this work show very clearly that the Mo(V) reduction potential in the TPP complexes can be 'fine-tuned' via the para-substituents on the TPP ligand. The $\text{OMo(V)}(p\text{-Br-TPP})$ complex should be the most efficient of the series described here for the photocatalyzed production of H_2O_2 from O_2 since it is the most easily reduced complex of the series.

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