



# Kinetic and Catalytic Studies of High Valent Chromium (IV) Oxo Species with Tetrakis-2,3,4,5,6-pentafluorophenyl Porphyrin

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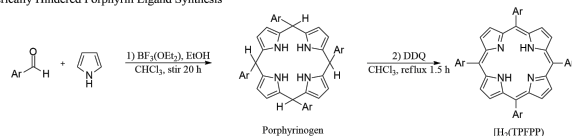
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## Introduction and Significance

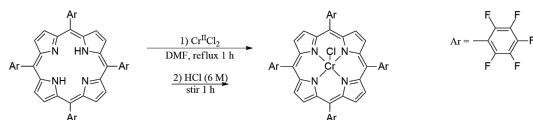
The cytochrome P450 enzyme superfamily is known to catalyze many oxidation reactions in nature. The reactions of synthetic biomimetic catalysts involve the formation of a high valent transition metal-oxo intermediate as the active oxygen atom transfer species. The highly electron withdrawing chromium (III) tetrakis-2,3,4,5,6-pentafluorophenyl porphyrin was first synthesized and characterized. Then, the complex was used to generate the high valent oxo intermediate using iodobenzene diacetate. Kinetic studies performed involved the oxidation of triphenylphosphine, thioanisole, and thioanisole derivatives. The oxidation was observed with UV-Vis by watching the decay of chromium (IV). The rate constants were then determined and a Hammett Correlation Plot was made. Furthermore, catalytic studies were performed to determine the solvent and light effect on the porphyrin's oxidation capability of thioanisole.

## Synthesis

Sterically Hindered Porphyrin Ligand Synthesis



Chromium Insertion



## UV-Vis Spectroscopy

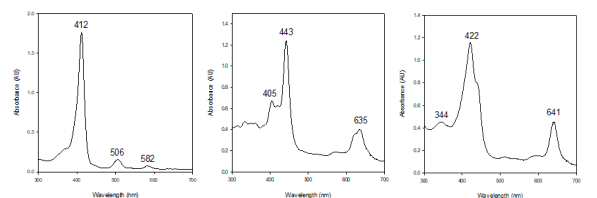


Figure 1. UV-vis spectrum of [H<sub>2</sub>(TPFPP)] (left) in CH<sub>2</sub>Cl<sub>2</sub>, [Cr<sup>III</sup>(TPFPP)Cl] (middle) in CH<sub>2</sub>Cl<sub>2</sub>, and [Cr<sup>V</sup>=O(TPFPP)] generated with 5 equivalence of PhI(OAc)<sub>2</sub> (right) in CH<sub>2</sub>Cl<sub>2</sub>.

## Solvent and Light Effect on Thioanisole Oxidation

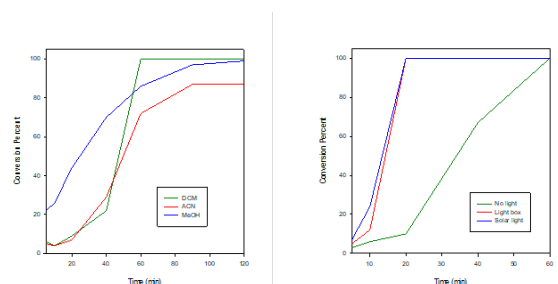


Figure 2. Top left is catalytic reaction profile for the solvent effect on the oxidation of thioanisole by [Cr<sup>V</sup>=O(TPFPP)] (0.5 μmol [Cr<sup>III</sup>(TPFPP)Cl], 0.5 mmol thioanisole, 0.1 mmol 1,2,3-trichlorobenzene, 0.5 mmol water, and 0.75 mmol PhI(OAc)<sub>2</sub>) where the 2 mL of solvent that the oxygen source was dissolved in was changed. Top right is catalytic reaction profile for the light effect on the oxidation of thioanisole by [Cr<sup>V</sup>=O(TPFPP)] using the same conditions except that the solvent was dichloromethane, and the reaction was either kept in the dark, in a Rayonet Reactor light box, or under a solar light generator. Conversion percent was determined by GC-MS analysis detecting the oxidized thioanisole.

## Kinetics Reaction Profile

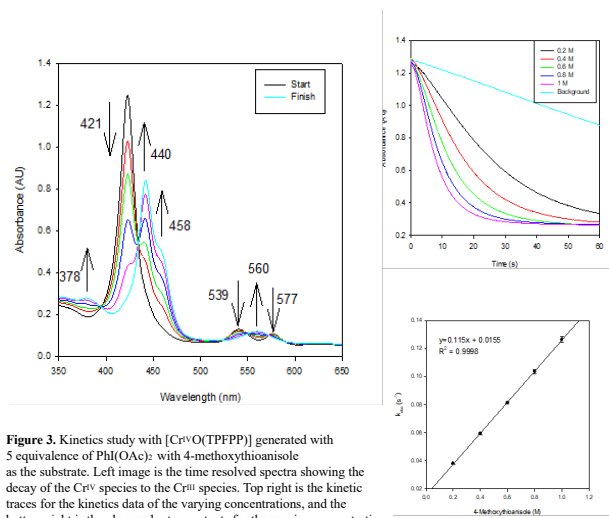


Figure 3. Kinetics study with [Cr<sup>V</sup>=O(TPFPP)] generated with 5 equivalence of PhI(OAc)<sub>2</sub> with 4-methoxythioanisole as the substrate. Left image is the time resolved spectra showing the decay of the Cr<sup>V</sup> species to the Cr<sup>III</sup> species. Top right is the kinetic traces for the kinetics data of the varying concentrations, and the bottom right is the observed rate constants for the varying concentrations. Kinetics data was obtained using a stop flow.

## Kinetic Data of Oxidation of Substituted Thioanisoles

Table 1. Observed rate constants for reactions of [Cr<sup>V</sup>=O(TPFPP)] generated with 5 equivalence of PhI(OAc)<sub>2</sub> with thioanisole and derivatives.

| Substrate            | k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> ) |
|----------------------|---|
| 4-methoxythioanisole | 0.115   |
| 4-methylthioanisole  | 0.0713  |
| Thioanisole          | 0.0137  |
| 4-fluorothioanisole  | 0.436   |
| 4-chlorothioanisole  | 0.0023  |

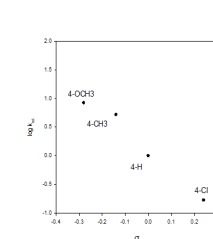


Figure 4. Hammett Correlation Plot of thioanisole and derivatives with 4-fluorothioanisole omitted because it was an outlier. This was the case with other complexes studied in our lab.

## Conclusion

- Typically, thioanisoles with more electron donating substituents at the para position are oxidized by [Cr<sup>V</sup>=O(TPFPP)] at a faster rate.
- It can be concluded from the Hammett Correlation Plot that a positive charge likely builds up or negative charges are lost in the transition state during the oxidation of thioanisoles.
- [Cr<sup>V</sup>=O(TPFPP)] oxidizes thioanisole most efficiently in dichloromethane under a light source.

## Acknowledgments

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