

A Study on Molecular Oxygen Activation by an Iron (II) System using Linear Free Energy Relationships

Roshaan Surendhran, Alex D'Arpino, Bao Scisent, Suman Kr Dey and David C Lacy[†]
University at Buffalo, Department of Chemistry

ABSTRACT

A prominent challenge in the field of synthetic inorganic and organometallic chemistry is understanding small molecule activation. It is known that enzymes such as Tau-D and Cytochrome P450 perform oxygen activation in nature but not much is known about the mechanistic pathway by which this happens. The focus of this project is the activation of molecular oxygen. In an attempt to probe this mechanism, a series of p-substituted carbamoyl methyl tripodal ligands were synthesized.

These ligands were further reacted with iron (II) acetate to create functional models of molecular oxygen activating moieties. The iron (II) compounds were reacted with oxygen and the reaction was monitored using UV-Vis spectroscopy to gain some insight into the mechanism of the reaction. Using the values for the rate constant of this reaction a Hammett plot was generated and the results are shown here.

CONTACT

David C Lacy,
Assistant Professor
University at Buffalo
Email: dclacy@buffalo.edu
Website: davidclacy.wordpress.com

INTRODUCTION

Oxygen is imperative for life on Earth. It is involved in many of the most important chemical reactions and biological processes yet little is still understood about the mechanism by which this occurs. Of these processes, ones that involve enzymes like taurine α -ketoglutarate dioxygenase (TauD) and cytochrome P450 are of great interest to us¹.

PROJECT

A non-heme iron (II) model that can effectively mimic the oxygen activation functions of TauD can be used to study the mechanism. The model comprises of a family of ligands that vary only by the functional group. This will enable us to study the properties of the metal complex necessary to perform oxygen activation.

GOAL

The objective is to employ the Hammett relationship on the different iron complexes that have been synthesized. From the relationship that is developed with the kinetic data, we might be able to better understand the effect of the ligand on the reaction.

EXPERIMENTAL

The tris(N-carbamoylphenyl(methylamine)) ligand and its derivatives (H_3LPhX) were synthesized from nitrilotriacetic acid (NTA) using the procedure developed by Borovik et al². The compounds were characterized using H-NMR, C-NMR and FTIR. The iron complexes were made by deprotonating the ligand followed by metalation with iron (II) acetate. The product was isolated by recrystallization.

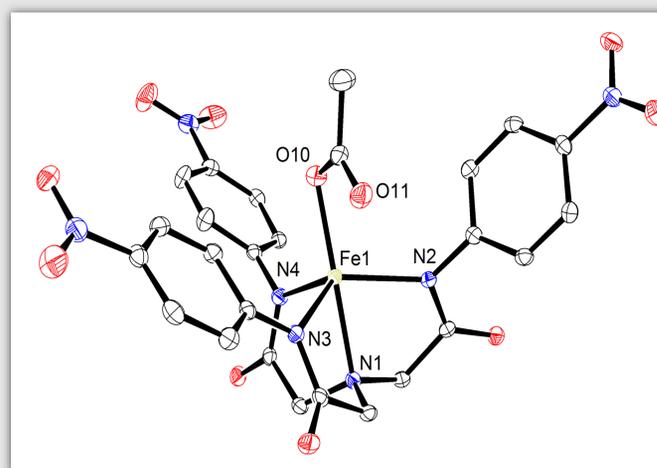
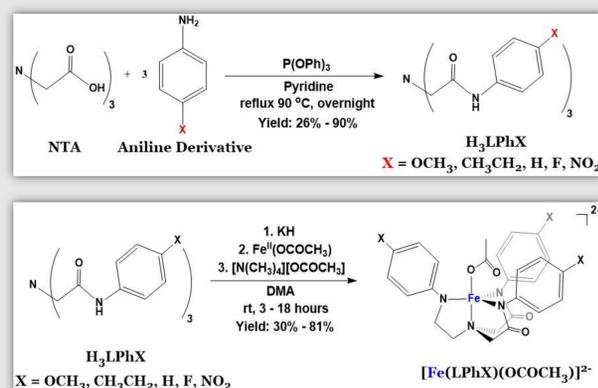


Figure 1. ORTEP plot of $[Fe(LPhNO_2)(OCOCH_3)]^{2-}$ with 50% ellipsoid probability.

Crystal system	triclinic	Volume/ \AA^3	2144.57(10)
Space group	$P-1$	Final R indexes [all data]	$R_1 = 0.0609, wR_2 = 0.1045$
$a/\text{\AA}$	10.2009(3)	$Fe1-N1/\text{\AA}$	2.2309(18)
$b/\text{\AA}$	11.6975(3)	$Fe1-N2/\text{\AA}$	2.1643(18)
$c/\text{\AA}$	18.9343(5)	$Fe1-N3/\text{\AA}$	2.1499(19)
$\alpha/^\circ$	97.4707(9)	$Fe1-N4/\text{\AA}$	2.1639(18)
$\beta/^\circ$	96.4933(9)	$Fe1-O10/\text{\AA}$	2.1110(17)
$\gamma/^\circ$	104.4176(9)	$Fe1-O11/\text{\AA}$	2.4556(19)

Table 1: Crystal Data and bond lengths for $[Fe(LPhNO_2)(OCOCH_3)]^{2-}$

The synthesized complexes were reacted with excess oxygen in a controlled environment and the reaction was monitored by UV-Vis spectroscopy. An example spectrum for one of the complexes is shown below in figure 2.

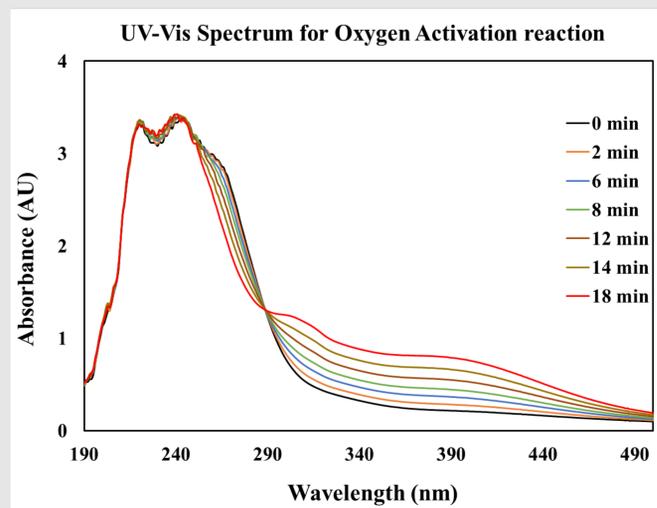
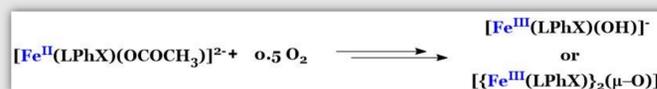


Figure 2. UV-Vis spectrum of the reaction of $[Fe(LPhCH_2CH_3)(OCOCH_3)]^{2-}$ with O_2

RESULTS AND DISCUSSION

From the UV-Vis spectrum, the pseudo first order rate constants for each reaction was calculated. These were then plotted against σ_x values obtained from literature. The relationship between the rate constant and σ_x is given by the Hammett relationship³.

$$\log\left(\frac{k_x}{k_H}\right) = \rho\sigma_x$$

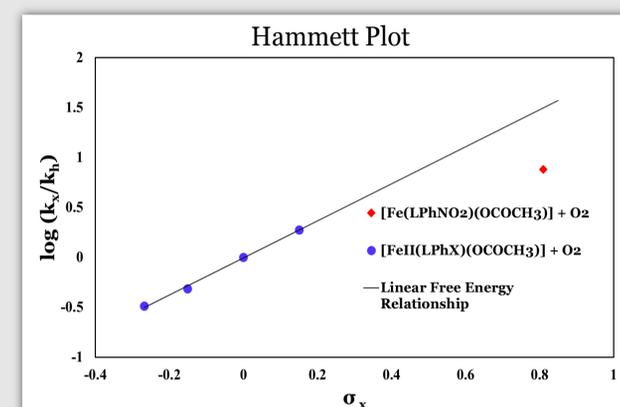


Figure 1. Hammett plot showing the Linear Free Energy Relationship.

From the plot, $\rho = 1.8708$. A value of $\rho > 1$ is indicative of a build-up of negative charge in the rate determining step of the reaction. As a consequence of this the linearity of the Hammett plot is not observed with strong electron withdrawing groups such as nitro substituents.

CONCLUSIONS

The major conclusion from this project is that we now have a system that will allow us to effectively study the kinetics of oxygen activation and through that infer the mechanism of the reaction.

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