

CHEMISTRY SEMINAR

Biophysical Characterization of Metal Binding to de novo Due Ferri proteins

By Ethan Clare '25 Chemistry

11:30 a.m.

November 17, 2022

Mara Auditorium
Masters Hall Rm 110

Abstract:

Uncontrolled hydrolysis is the ultimate enemy when trying to work around the unwanted aqueous chemistry of abundant metals like titanium and vanadium. These metals, often used in industrial settings, are not seen much in biological environments because of their propensity to undergo this uncontrolled hydrolysis. However, nature has found ways around unwanted hydrolysis in many metals, including stabilizing iron. Using this as a model, a metalloprotein system has been developed that stabilized Ti and V in an aqueous setting, thus functionalizing them to cleave DNA. The Due Ferri single chain (DFsc) protein system has two iron binding sites and is modeled from natural proteins. The family encompasses many different proteins with unique modifications to the binding site. The main focus of this project is biophysically characterizing the metal binding of the DFsc proteins with tyrosine added to the active site (DY, DFY, G4Y) to better understand the structure function relationships in these enzymes. Furthermore, we are curious if the substitution of tyrosine improves metal stabilization and the binding interactions of the DF variants compared to proteins without tyrosine. We focused on titanium, vanadium, and zinc binding to the proteins, and were able to monitor the secondary structural of the protein associated with metal binding with circular dichroism spectroscopy. We expect to see 2 equivalents of metal binding to protein. Strong binding results with zinc and DY, DFY, and G4Y were observed, with some hopeful trials with titanium and vanadium, indicating that the tyrosine addition may be an important factor in stabilizing metal-protein interactions in the DFsc system.

CHEMISTRY SEMINAR

Selective oxidations of secondary alcohols using (tetraphenylcyclopentadienone)iron tricarbonyl as a catalyst

By Nicolle Elahian López '24 Chemistry

11:30 a.m.

November 17, 2022

Mara Auditorium
Masters Hall Room 110

Abstract:

Alcohol oxidations are important chemical reactions that have widespread use in everything from biochemistry to fine chemicals to pharmaceuticals. Recent explorations have been focused on the discovery of more environmentally friendly reactions by using catalysts from earth-abundant metals. Our group is interested in applying (cyclopentadienone)iron carbonyl compounds as catalysts in sustainable alcohol oxidations and carbonyl reductions, and we found evidence in one of our previous studies suggesting that some of our catalysts could selectively oxidize secondary alcohols in the presence of primary alcohols. Selective oxidations remove the need for protecting groups and lead to more efficient syntheses, as they can afford the desired product in one step (Figure 1). The goal of this project was to test the ability of (tetraphenylcyclopentadienone)iron tricarbonyl compounds (1) to catalyze the selective oxidation of secondary alcohols over primary alcohols using two different hydrogen acceptors: acetone and furfural. Acetone was used because it has a low oxidation potential; therefore, secondary alcohol oxidation is thermodynamically favored as opposed to primary alcohol oxidation. On the other hand, furfural has a higher oxidation potential, which is why only one equivalent was used to avoid over-oxidation. In competition experiments with both primary and secondary alcohols, reactions using furfural occurred with greater secondary alcohol oxidation selectivity compared to reactions using acetone. Oxidations with aliphatic primary alcohols displayed greater selectivity than those with benzylic primary alcohols. Trends in the selective oxidations of secondary alcohols of diols were less clear and were likely affected by alcohol steric hindrance and competing reactions.

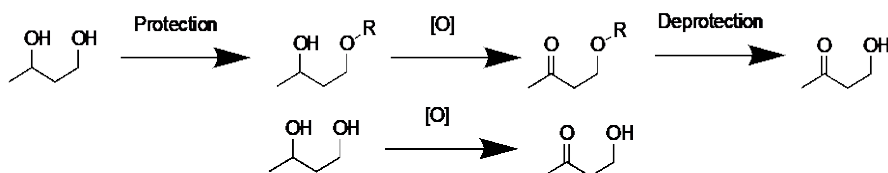
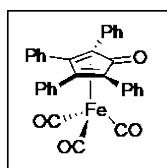


Figure 1. Syntheses using traditional, unselective alcohol oxidations (top) require protection and deprotection, increasing the number of steps. Selective alcohol oxidations can decrease the total number of steps (bottom).



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CHEMISTRY SEMINAR

Title: Effects of Alcohols and Glycine on Propane Hydrate Formation Kinetics

By Vy Tran '25 Chemistry

11:30 a.m.

November 17, 2022

Mara Auditorium
Masters Hall Rm 110

Abstract:

Clathrate hydrates are non-stoichiometric molecules with a gas or liquid molecule trapped inside a water cage. The shape of the water cage varies based on the size of the trapped molecule. Some common shapes of the cage are 5^{12} , $5^{12}6^2$, and $5^{12}6^4$. Larger structures such as S-I, S-II, and H are formed when cages combine in different ways. Clathrate hydrates form at low temperatures and high pressures. It has been shown in previous literature that the formation kinetics of hydrates are influenced by the presence of certain compounds such as alcohols, amino acids, surfactants, etc. The purpose of this study is to examine the effects of traces of alcohols and amino acids on formation kinetics of propane hydrates from ice particles. By spraying ultrapure water or a solution of ultrapure water with different concentrations of interested dopants into liquid nitrogen and pushing ice through a strainer, relatively spherical ice particles with diameter less than $180\ \mu\text{m}$ were obtained to form hydrates. Hydrates were formed by introducing propane gas into a cell containing ice particles at -15°C to -20°C with an initial pressure difference of 15 psi or 30 psi. Temperatures inside the cell were measured by three temperature probes with different lengths to account for the temperature variation within the cell. The pressure inside the cell was monitored with a pressure transducer. It was observed that 1% and 5% volume methanol catalyzed the reaction. 1% and 5% volume ethanol did not catalyze the reaction but made the formation period longer. However, the data collected were not very consistent, possibly due to the differences in the ice layer surface between runs. In future work, we plan to do more runs with similar conditions so as to get a better sense of the effects, as well as work on other amino acids and surfactants.