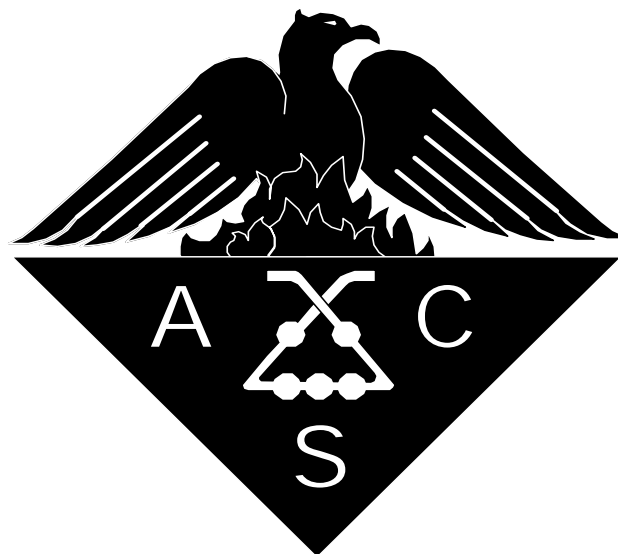


2009 Cleveland ACS Meeting-In-Miniature Program

Ohio Aerospace Institute
Cleveland, Ohio

March 18, 2009



Analytical Chemistry Session

Host: Dr. David Miller

2:50. Determination of mutagenic polycyclic aromatic hydrocarbons (PAHs) by *Vibrio fischeri*-based assay. Klaira Freeman,* Robert Wei, Department of Chemistry, Cleveland State University, Cleveland, OH 44115.

Polycyclic aromatic hydrocarbons (PAHs) are major urban contaminants, many of which have been shown to possess mutagenic properties. Various methods have been used to evaluate potential mutagenic and/or carcinogenic properties of the PAHs in humans, which include DNA strand breakage and comet assay, Ames test, and experiments on rodents. These tests are expensive and/or time consuming. A less expensive alternative is *Vibrio fischeri*, a bioluminescent marine bacterium commonly used in toxicology tests as part of the *Microtox* system. The goal of this study is to determine if *V. fischeri* is an effective means of differentiating mutagenic and nonmutagenic PAHs. This study examined three PAHs with mutagenic properties: and three with nonmutagenic. Six concentrations ranging from 0.1 ppm to 5 ppm were used. To determine their relative toxicity, *V. fischeri* were cultured in a complex growth medium. 1 mL aliquots of these cultures were then exposed to 0.5 mL PAH solution at pH 7.0. Inhibition of luminescence was then studied both short and long term.

3:10. Application of Liquid Chromatograph Tandem Mass Spectrometry to Breast Cancer Research

Kerri M. Smith**^a, Monaca Montano^b, Yan Xu^a, ^aDepartment of Chemistry, Cleveland State University, Cleveland Ohio, 44115, ^bDepartment of Pharmacology, Case Western Reserve University, Cleveland, Ohio, 44106.

Hexamethylene bisacetamide (HMBA), a polar basic compound, has recently been shown to have antineoplastic activity by inducing up-regulation of the antiproliferative breast cancer protein HEXIM1 (hexamethylene bisacetamide-inducible protein 1). Current tumorigenesis studies in mouse models demand a more sensitive method for the detection and quantification of HMBA than what is represented in the current literature. Our lab is working to develop and validate according the FDA Guidelines an LC-MS/MS method for the quantitative determination of HMBA in human and mouse plasma and mouse mammary tissue using heptamethylene bisacetamide (7MBA) as the internal standard. This presentation will discuss the results of the work.

3:30. Analytical Method Development for 6-Benzylthioinosine, A Novel Myeloid Differentiation-Inducing Agent

Lan Li^{a,**}, David N. Wald^b, William Tse^b, Yan Xu^a, ^aDepartment of Chemistry, Cleveland State University, Cleveland, Ohio 44115; ^bDepartment of Pathology, Case Western Reserve School of Medicine, Cleveland, Ohio 44106.

6-Benzylthioinosine (6BT) is a novel monocytic differentiation agent with apparent specificity on leukemic cells and low toxicity on non-malignant cells. 6BT is currently being investigated for treating acute myeloid leukemia (AML). Since AML is characterized as the arrest of differentiation of immature myeloid cells, a therapeutic strategy for AML was developed by inducing differentiation of leukemic cells. While the currently used agents are only useful for acute promyelocytic leukemia, a rare subtype of AML, 6BT exhibits not only high myeloid differentiation-inducing activity in a subset of leukemia cells but also specific

mechanisms of action. Therefore, 6BT is exploited as therapeutics for other AML subtypes. The analytical analysis of 6BT will enable the pharmacokinetic study of 6BT and facilitates the therapeutic development of 6BT. Our preliminary work shows that we can extract 6BT by liquid-liquid extraction from plasmas and detect it by the LC-MS/MS method developed. Two linear calibration curves (3-1000 ng/mL) were established by utilizing 2-amino-6-benzylthioinosine (2A6BT) as the internal standard. After validation, the methods developed showed high recovery, accuracy and precision. Our future work will focus on applying the established methods for the determination of 6BT in pharmacokinetic studies. The information obtained will facilitate the therapeutic development of 6BT.

3:50. Effect of Cholesterol Levels in Lipid Membranes on Enzymatic and Redox Activity of Nitric Oxide Synthase

Noufissa Zanati,* Jean Boutros, John Moran, Mekki Bayachou, Department of Chemistry, Cleveland State University, 2399 Euclid Avenue, Cleveland, Ohio 44115-2214.

Cholesterol is a major risk factor for coronary heart disease that leads to myocardial infarction. The long-term goal of this investigation is to study the effects of increased cholesterol levels on the activity of membrane-bound proteins and enzymes that are critical in the functioning of the cardiovascular system. Specifically, in this project, the focus is on the enzyme nitric oxide synthase (NOS), which, in the endothelium, plays an important role of maintaining blood pressure. We use both enzymatic activity and electrochemical methods to assess the effect of increased cholesterol levels in phosphatidylcholine (PC) films on the function and redox activity of this enzyme in the PC/cholesterol environment. Enzyme full turnover measurements as a function of cholesterol content in the PC films allowed us to establish the effect of cholesterol on NOS function. On the other hand, we used cyclic voltammetry to measure changes in the transport properties of NOS oxygenase in the lipid/cholesterol film. Redox and enzymatic activity of NOS in the phospholipid film as a function of increased cholesterol will be discussed based on the kinetics and thermodynamics of electron transfer in the membrane-like films. The effect on enzyme full turnover will be discussed in the context of the hypothesized dynamic modulation of NOS function with increased levels of cholesterol.

4:10. Enhanced nitric oxide sensing on multi-walled carbon nanotubes decorated with ruthenium nanoparticles.

Pubudu Peiris** and Mekki Bayachou, Department of Chemistry, Cleveland State University, 2399 Euclid Avenue, Cleveland OH 44115. Nitric oxide (NO) is an important intercellular messenger that acts in many tissues to regulate a diverse range of physiological, pathological and pharmacological processes. Thus, from a biochemical as well as medical perspective, it is important to quantify the details of NO production in real-time under normal and pathological conditions. However, it is difficult to detect this analyte due to its short lifetime.

In this work we describe an electrochemical sensor for NO detection by ruthenium-nanoparticles-decorated multi-walled carbon nanotubes on microelectrodes. The acid treated MWCNTs are decorated with Ru nanoparticles by chemical reduction of the corresponding metal salts using ethylene glycol as reducing agent. These composite materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), energy dispersive x-ray spectroscopy (EDX), and Raman spectroscopy.

The fabricated NO sensor exhibit excellent catalytic behavior towards NO oxidation was assessed by cyclic voltammetry and amperometry. The presence of carbon nanotubes in

conjugation with ruthenium nanoparticles produces an electrocatalytic effect which counts for the superior performance of these improved NO sensors. The work will show how the sensor can be used to quantify NO at the level of live collection of cells, and live single cells.

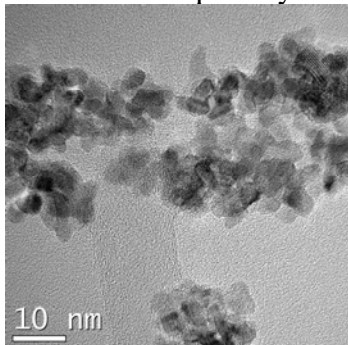


Figure 1. Typical TEM image of Ru nanoparticles decorated MWCNT

4:30 Measurement of Nitric Oxide Released From Cells and NOS-Modified Liposomes

Reshani Perera**, Pubudu Peiris and Mekki Bayachou, Department of Chemistry, Cleveland State University, 2399 Euclid Avenue, Cleveland OH 44115.

Nitric oxide (NO) is synthesized by nitric oxide synthases (NOS) to carry a number of physiological functions, including in the cardiovascular, neuronal and immune systems. Understanding its biological role requires the measurement of NO *in situ* in real time in selective, sensitive, and quantitative manner. Its short half-life in biological systems is a potential barrier for its direct determination.

We developed an electrochemical sensor for NO detection by electropolymerization of 3,4-ethylenedioxythiophene (EDOT) on 7- and 30- μm carbon fiber electrode (CFE) combined with ruthenium nanoparticles as catalytic sites for NO. We show that this “third generation” modified sensor has high sensitivity (more than 100 times than bare CFE), and excellent linearity on a wide range, including low concentrations (sub-nanomolar) of NO. Our modified microelectrodes offer the potential to measure small amounts of NO. We show that these sensors can be used in NO measurement at single cells (stimulate mouse embryonic fibroblast cells and human umbilical vein endothelial cells). We also used the sensor to measure NO released from NOS-loaded Lipid vesicles as model systems to understand NO release from cells. Understanding NO release from these artificial vesicles would also facilitate the development of anti-thrombotic vehicles for controlled release of NO.

Physical/Analytical Chemistry Session

Host: Dr. Mekki Bayachou

2:30 Structural Consequences of Pi-Electron Delocalization with Increased Length of Polyenes

Norman C. Craig, Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074.

Semiexperimental equilibrium structures, determined from high-resolution molecular spectroscopy and supplementary quantum chemical calculations, are available for *s-trans*-1,3-butadiene and for the C_6 backbone of *cis*-1,3,5-hexatriene. Quantum chemical calculations for *trans*-hexatriene and for the three isomers of octatetraene have been done at the B3LYP/cc-pVTZ level. A high-level ab initio calculation for the 90° -twisted structure of butadiene

provides localized bond lengths for C–C(sp²–sp²) and C=C bonds for comparison. The growing body of evidence shows that increasing the length of polyenes causes greater pi-electron delocalization as reflected in structural changes.

2:50. Structural Effects of Fluorine Substitution in the Isomers of 1,4-Difluorobutadiene

Deacon J. Nemchick* and Norman C. Craig, Department of Chemistry, Oberlin College, Oberlin, OH 44074.

Substitution by fluorine, the most electronegative element, has a large influence on the bond lengths in C₃ and C₄ ring systems. Does a similarly large influence occur in 1,4-difluorobutadiene? To answer this question, we have embarked on determining the semi-experimental equilibrium structures for the three isomers of 1,4-difluorobutadiene. Some rotational constants are available, and progress has been made in preparing the needed set isotopomers. Results of exploratory quantum chemical calculations will be reported.

3:10. Electric Fields with Fractional Charges are the Catalysts for Chemical Reactions

Ralph A. Gardner-Chavis, Associate Emeritus Professor, Department of Chemistry, Cleveland State University, Cleveland OH 44115.

Electric fields with fractional charges are illustrated by data in the Atomic Energy Level, AEL, tables from NIST. These tables present the energy states that electrons may occupy upon being excited from a bound state. For example, the first state above the ground state of the chromium atom is at 7,593.16 cm⁻¹. The first state for the chromium positive ion is at 11,961.81 cm⁻¹. The first four states for the chromium double positive ion are at 62.22, 183.16, 356.55 and 576.08 cm⁻¹. **States this close to the ground state will be occupied for a fraction of time, producing an electric field with a fractional charge.** Of the thousands of positive ions tabulated in the AEL tables only about one hundred have these low-lying states and almost all are known to function as catalysts. Each such ion has a different set of these low-lying states, thus each ion presents an electric field with a different charge to prepare the chemical reactants for the catalytic event. The appropriate ion to catalyze a chemical reaction has the field with the fractional charge which when imparted to the two reactants, changes the frequencies of the fields of the reactants at the sites of reaction so that they match harmonically, i.e. the ratio of the frequencies is a power of two. When the reactants meet in the field, because the frequencies of the electric fields now match, resonance occurs. It is during resonance that electrons are exchanged and chemical bonds are broken and made in the direction to satisfy the Free Energy constraint. The two examples present the catalytic reaction to destroy nitric oxide in automobile exhaust and the difference in reaction between zinc carbonic anhydrase and the cobalt and cadmium homologues.

3:30. Will Nitrogen-Treated Graphite Work as an Electrocatalyst in a Fuel Cell Oxygen Cathode?

Kiera A. Kurak* and Alfred B. Anderson, Department of Chemistry, Case Western Reserve University, 10600 Euclid Avenue, Cleveland OH 44106.

Nitrogen-treated graphite electrodes catalyze the four-electron electroreduction of O₂ to water in acid at potentials of < 0.70V. We have used the linear Gibbs energy relationship to predict the reversible potentials for forming intermediates during O₂ reduction in acid over graphene with two N atoms substituting for adjacent edge CH groups. Using bond strengths from VASP slab-band density functional calculations, it is predicted that one edge N has H

bonded to it as potentials below 1.70V. The first reduction step (predicted $U^0 = 0.89\text{V}$) forms OOH that dissociates and O bonds strongly to N with OH weakly associated. The OH abstracts H from NH, forming H₂O. NH immediately reforms. The reversible potential for reducing O(ads) to OH(ads) is predicted to be -0.60V, well negative of the potential range of interest for oxygen reduction, which means NO and NH will be stable at the potentials of interest. This edge site has an unpaired electron and OOH bonds to a C atom with a strength corresponding to a 0.73V reversible potential. It is concluded that the two-electron reduction product, H₂O₂, can form at a potential close to the 0.695V standard reversible potential. Four-electron reduction requires reducing the H₂O₂ at potentials less than this.

3:50. Redox and Catalytic Behavior of Structurally Different Metalloproteins with Controlled Levels of Water

John J. Moran, Noufissa Zanati, Jeremiah Bolden, Mekki Bayachou, Cleveland State University, Department of Chemistry, 2121 Euclid Ave., Cleveland, Ohio 44115.

Ionic liquid butyl methyl imidazolium tetrafluoroborate is used as a nearly anhydrous medium in which to interrogate proton transfer as a rate determining step in metalloprotein function. We compare the redox characteristics of two distinctly different metalloproteins, nitric oxide synthase and myoglobin, in the near absence of water and/or protons. Protein film voltammetry indicates that key characteristics of electron transfer change not only from aqueous to non-aqueous systems, but that these changes vary from protein to protein. Previous investigation showed that the catalytic reduction of oxygen measured in nearly anhydrous conditions and with carefully controlled additions of water is distinct for each of these two heme proteins. In the current investigation, we show similar trends for the catalytic reduction of nitric oxide and we rationalize the difference in behavior in light of known structural features of the two proteins. Our results highlight the importance of water levels in relation to catalytic efficiency and show that each protein has a different functionality under almost identical low-water conditions. The varying amount of water needed for proper protein function may help us to gain understanding of the role that protons play in biomolecular catalytic processes and how the hydrophilic/hydrophobic nature of the protein's catalytic site and environment regulates its function.

4:10. Development of Analytical Methods to Quantitate the Cannabinoid Receptor Antagonist Surinabant

Melissa A. McCulloch,** Yan Xu, Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115.

Surinabant is a cannabinoid receptor antagonist. Cannabinoids affect neurotransmission via a G-protein coupled CB1 (brain) and CB2 (peripheral tissue) receptors. Several animal studies have shown that surinabant is able to affect biological events including: alcohol and nicotine consumption, the dopamine mediated reward circuitry, as well as, food consumption. To date, surinabant has been investigated in clinical trials for the treatment of obesity and nicotine addiction. At this time there is no analytical method publicly available to study surinabant in biological matrices. In this work liquid chromatography conditions have been optimized for the separation of surinabant and the internal standard. Both UV spectrometry and mass spectrometric conditions have been optimized for the detection of surinabant. This method has been validated using both detection schemes. The method developed can be used in the preclinical and clinical study of surinabant.

4:30. Hemin- and Hemeprotein-catalyzed Electroreduction of Aliphatic Nitro Compounds
Ling Li**, Mekki Bayachou, Department of Chemistry, Cleveland State University, 2399 Euclid Avenue, Cleveland, OH 44115.

Some aliphatic nitro-compounds, such as nitromethane, are recognized as potential carcinogens. They are widely used and it is well established that they are involved in the development of serious health problems upon chronic exposure. Activation of these compounds and generation of reactive metabolites may be a pathway for their potential carcinogenesis. The activation of nitro-compounds is believed to be catalyzed by P450-type xenobiotic metabolizing heme-enzymes through electron transfer. Previous investigations in this laboratory showed that myoglobin immobilized in surfactant thin films on pyrolytic graphite electrode exhibits electrocatalytic activity for the reduction of nitromethane. In this work, we use electrochemical and spectroscopic techniques to characterize, compare, and contrast the catalytic activation of a number of aliphatic compounds, including a series of linear versus branched ones, by hemin and myoglobin in thin films on pyrolytic electrodes. We will highlight the differences in reactivities between bare hemin versus hemin within a protein shell (i.e. a hemeprotein). Hemin- and myoglobin-mediated electrocatalytic activations will also be explored as a function of the size and structure of the nitroalkane substrates as well as other experimental parameters such as pH. Results will be presented and discussed in light of some proposed mechanistic pathways.

Biochemistry Session

Host: Dr. Yuh-Cherng Chai

2:30. The Effect of Oxidant and the Non-Oxidant Alteration of Cellular Thiol Concentration on the Formation of Protein Mixed-Disulfides in HEK 293 Cells

Jasen Lee Gilge*, Michael Fisher, Yuh-Cherng Chai Ph.D., Department of Chemistry, John Carroll University

Cells respond to oxidant stress via protein S-glutathionylation, a post-translational modification of protein reactive cysteines forming disulfides with glutathione molecules. In this report, specific S-glutathionylated proteins were demonstrated in human embryonic kidney 293 cells treated with a chemical oxidant, diamide, and a physiological oxidant, hydrogen peroxide. S-glutathionylated proteins were detected by immunoblotting, and glutathione concentrations were determined by high performance liquid chromatography. Furthermore, we show the effect of altering the cellular thiol pool on protein S-glutathionylation by using buthionine sulfoximine, a specific inhibitor of glutathione biosynthesis. Glutathione biosynthesis inhibitors decreased 65% of cellular glutathione while not altering protein S-glutathionylation. Moreover, phenylarsine oxide, which binds to vicinal thiols, was used to determine the possible role of vicinal thiols in the amount of glutathionylation. Our data shows that phenylarsine oxide increased glutathionylation in oxidant-treated cells without decreasing cellular glutathione concentrations. This work was financially supported by a Cottrell College Science Grant from Research Corporation to Y-C C.

2:50. Synthesis and Characterization of Surface Immobilized Liposome

Yong Ma, Hailong Zhang, and Xue-Long Sun, Department of Chemistry, Cleveland State University, Cleveland OH 44115.

Surface-immobilized liposomes are of interest for various potential applications such as localized drug delivery, but their synthesis and characterization are challenging. Conventional liposome immobilization method involves the initial synthesis of the key anchor lipid, followed by formulation of the liposome with all lipid components. In this direct liposome formation method, some of the valuable anchor groups inevitably are facing the enclosed aqueous compartment and thus become unavailable for their intended interaction with their target molecules. Particularly, it is unrealistic if the targeting ligand is only available in minimum amount. Furthermore, lipid-ligand conjugates normally have limited solubility and stability in solvent, or are incompatible with various stages of manufacture. Herein, we report an efficient and chemical selective liposome surface biotinylation through Staudinger ligation and its immobilization onto glass slide *via* specific streptavidin/biotin interaction. The surface-immobilized liposomes are analyzed by AFM and fluorescent imaging techniques by comparing with direct formed biotin-liposome and post grafted biotin-liposome.

3:10. Exploring Staudinger Ligation Method for Chemical Selective Liposome Surface Functionalization

Hailong Zhang**, Yong Ma, and Xue-Long Sun, Department of Chemistry, Cleveland State University, Cleveland OH 44115.

Liposome surface functionalization facilitates enormous potential application of liposomes such as targeted drug and gene delivery. Several chemical modification methods, such as using amide or thiol-maleimide coupling as well as by imine or hydrazone linkage have been developed. However, in many cases there is a lack of specificity resulting in the uncontrolled formation of the number of covalent bonds between liposome and biomolecules of interest. Most recently, copper (I)-catalyzed [3+2] cycloaddition, namely “Click” chemistry has been investigated as it can occur efficiently and selectively between azide and alkyne in aqueous media. However, the key limitation of the Click chemistry is the use of Cu (I) catalyst, which results in residual copper in the liposome and could be a potential concern for liposome application. The Staudinger ligation, in which an azide and triphosphine selectively react to form an amide has been used for chemical selective modification of recombinant protein and cells without physiological harm. Herein, we report an efficient and chemical selective liposome surface functionalization through Staudinger ligation. The effect of reaction conditions on the size and stability of liposome were investigated by dynamic light scattering and the leakage of entrapped 5,6-carboxyfluorescein, respectively. Furthermore, the density and accessibility of grafted lactose residues on the surface of liposome were evaluated.

3:30. Remodeling High Density Lipoprotein by Lecithin Cholesterol Acyltransferase

Rati Lama^{1**}, Zhiping Wu², Xavier Lee², Camelia Baleanu-Gogonea^{1,2}, Stanley L. Hazen^{2,3}

¹Department of Chemistry, Cleveland State University, 2121 Euclid Avenue, Cleveland, OH 44115, ²Department of Cell Biology, Cleveland Clinic, 9500 Euclid Avenue, Cleveland, OH 55195, ³Center for Cardiovascular Diagnostics and Prevention, Cleveland Clinic, 9500 Euclid Avenue, Cleveland, OH 44195.

High-density lipoprotein (HDL), the carrier of “good” cholesterol, participates in reverse cholesterol transport (RCT) by carrying cholesterol from peripheral cells to the liver for excretion. HDL is also known for its anti-oxidant and anti-inflammatory properties. One of the factors that operates in plasma and modifies the shape and lipid composition of HDL is lecithin cholesterol acyltransferase (LCAT), an enzyme that catalyses the esterification of cholesterol to

cholesterol ester, leading to changes in HDL lipid composition and particle size and shape. Our goal is to better understand the catalytic mechanism and structural requirements of LCAT-mediated HDL maturation. To probe the structure of LCAT within the LCAT/nascent HDL complex we will perform small angle neutron scattering (SANS) experiments on the complex of nascent HDL with deuterated LCAT. To resolve the LCAT-HDL complex by SANS we will produce LCAT-HDL complexes with either deuterated LCAT or deuterated apoA1. The use of deuterated LCAT and apoA1 will allow us triangulate the location of each component of the LCAT-HDL complex, and by combining these data with other biophysical techniques (hydrogen-deuterium exchange tandem mass spectrometry, crosslinking, point mutations) we will be able identify specific interactions between LCAT and HDL that are critical for HDL remodeling and maturation.

3:50. Oriented Immobilization of Glyco-Affinity Macroligand and Its Glyco-Capturing Application

Srinivas Chalagalla** and Xue-Long Sun, Department of Chemistry, Cleveland State University, Cleveland, OH 44115.

Functional investigation of biomolecules typically starts by reducing the sample complexity through multidimensional separation methods based on the unique characteristics of the biomolecules followed by identification. We report a chain-end functionalized boronic acid-containing polymer (boropolymer) as oriented multivalent glyco-affinity capture ligands for efficient purification and identification of carbohydrates and carbohydrate-containing proteins. Briefly, a biotin chain-end boropolymer was synthesized *via* a biotin derivatived arylamine initiated cyanoxyl-mediated free-radical polymerization in one-pot fashion. The glyco-capture followed by direct MALDI mass spectrometry identification of the captured carbohydrate was demonstrated by using magnetic bead functionalized with the biotin boropolymer. In addition, oriented and covalent immobilization of an OCN chain-end functionalized boropolymers onto amino functionalized surfaces such as magnetic beads, mica, and glass slide was investigated and confirmed by AFM and fluorescent imaging techniques.

4:10. Induction of metallothionein II to heavy metal ions in *Helianthus annuus*

Chamari Walliwalagedara**¹, Philip Kish¹, Harry van Keulen², Teresa Cutright³, and Robert Wei¹, ¹Dept. of Chemistry, Cleveland State University, Cleveland, OH 44115, ²Dept. of BGES, Cleveland State University, Cleveland, OH 44115; ³Dept. of Civil Engineering, University of Akron, Akron, OH 44325-3905.

Metallothionein gene (MT) was induced in *Helianthus annuus* (Dwarf Sunflower) when exposed to nickel (Ni) or cadmium (Cd). Expression of the gene translation products however could not be easily seen as a phenotype, although the expression of MT genes was detected primarily through the examination of elevated levels of MT RNA. Difficulty of detection of MTs could be because the MTs in plants consist of high number of cysteine molecules and low aromatic amino acids. Metallothioneins are small molecular weight proteins with high number of cysteine molecules, therefore their primary role is believed to play an important role in metal homeostasis and give tolerance to, or detoxifies toxic metals (e.g., Cd, Hg, Cr, and Pb). The exact function of MTs in plants however is still unclear. In order to better understand the role of MTs in plants, we investigated the metal binding properties MT II with respect to its affinity, capacity, and selectivity. Sufficient quantities of MT were obtained by cloning the *mt* gene in fusion with the glutathione-S-transferase (GST) gene of the expression vector pGEX-4T-1. The

fusion protein was then overexpressed in *Escherichia coli* and purified on a glutathione-agarose column. The purified apoMT was examined for its binding behavior toward a number of toxic metals including Ni, Cu, Cd, Zn and Pb.

4:30. Synthesis and Separation of Methyl-Substituted Cucurbiturils

Ben Baldwin*, Neil Cole-Filipiak, and Michael Nee, Department of Chemistry and Biochemistry, Oberlin College, Oberlin OH 44074.

Partially methyl-substituted cucurbituril ranging in size from CB[5] to CB[7] were synthesized from glycoluril and 3a-monomethyl and 3a,6a-dimethyl tetracyclic glycoluril, using 1-aminiumadamantane as a guest template to encourage larger homologue formation. This remarkably simple synthesis has been held back by the difficulty in separating the various sizes, as well as the varying extents of methylation. Efforts at separation and characterization of products have included attempts with column chromatography and affinity chromatography. In order to isolate the larger CB[7] homologues, Merrifield resin was functionalized with guest-template molecules known to selectively bind CB[7]. Initial efforts involved direct addition of 1-aminoadamantane to Merrifield resin, but modest binding of CB[7] was attributed to steric hindrance of the aromatic groups on the resin. In an attempt to lengthen the distance between the adamantyl group and the resin different spacer groups are being attached to the 1-aminoadamantane.

4:50. Designing perhydrolases for removal of lignin from lignocellulosic biomass

Romas J. Kazlauskas, Biochemistry, Molecular Biology, and Biophysics Department, University of Minnesota, Gortner Lab of Biochemistry, 1479 Gortner Ave, St. Paul, MN 55108.

Replacing the current biofuels feedstock - corn - with lignocellulosic biomass such as wood, switchgrass or agricultural wastes is a key current goal of bioenergy research. Recalcitrance - inefficient release of sugars from lignocellulosic biomass - is the key problem that must be solved to make this replacement. Our proposed solution is an unnatural enzyme-catalyzed reaction to make a strong oxidant - peracetic acid. Using a combination of amino acid sequence comparison, site-directed mutagenesis, and x-ray crystallography, we have identified two different molecular mechanisms that enzymes use to favor perhydrolysis over hydrolysis. Enzyme-generated peracetic acid can remove lignin from aspen wood and subsequent saccharification can release > 90% of the available sugars in contrast to only 22% with peracetic acid pretreatment. Current challenges are to increase the amount of peracetic acid generated.

5:10. Teaching enzymes to catalyze new reactions

Romas J. Kazlauskas, Biochemistry, Molecular Biology, and Biophysics Department, University of Minnesota, Gortner Lab of Biochemistry, 1479 Gortner Ave, St. Paul, MN 55108.

Changing the catalytic activity of enzymes provides insight into how nature evolves new enzymes and also creates unnatural catalysts to solve synthetic problems. We have explored three ways to change the catalytic activity of enzymes: replace the active site metal, replace amino acids residue to enhance an existing minor catalytic activity, or replace amino acids residue to create a completely new catalytic activity. An example of metal replacement is replacing the active site zinc in carbonic anhydrase with manganese to create a stereoselective oxidation catalyst. An example of mutagenesis to enhance catalytic activity is a Leu29Pro mutation in *Pseudomonas* esterase to enhance perhydrolysis over hydrolysis. The resulting

variant is an efficient catalyst for synthesis of peracetic acid. Examples of a completely new catalytic activity are multiple mutations in an esterase to create an oxynitrilase.

INORGANIC/ORGANIC CHEMISTRY SESSION

Host: Dr. Al Hepp

2:30. Synthesis and Structures of M(ethylenediamine)₃[MoS₄] (M = Mn, Co, Ni)

Hadley A. Iliff,* Hengfeng Tian, and Catherine M. Oertel, Department of Chemistry and Biochemistry, Oberlin College, 119 Woodland St., Oberlin, OH 44074.

Tetrathiomolybdate anions, MoS₄²⁻, are precursors to hydrodesulfurization catalysts and can also be viewed as building blocks for hybrid inorganic-organic materials. Compared with the large number of network compounds based on molybdenum oxides, very few hybrid compounds have been prepared with tetrathiomolybdate as a structural component, due partly to the challenges of crystallizing sulfide-based networks. Solvothermal reactions between ammonium tetrathiomolybdate and transition metal salts have been carried out in ethylenediamine, which acts as both the solvent and a ligand. Using this method, a new polymorph of Ni(C₂N₂H₈)₃[MoS₄] was synthesized, exhibiting a different packing of complex cations and anions than in the structure previously reported by Bensch and coworkers.¹ Two new compounds, Co(C₂N₂H₈)₃[MoS₄] and Mn(C₂N₂H₈)₃[MoS₄], have been prepared and found through single-crystal X-ray diffraction to be isostructural to the new Ni(C₂N₂H₈)₃[MoS₄] polymorph. Structural comparisons between the polymorphs of Ni(C₂N₂H₈)₃[MoS₄] and with the Mn and Co analogues will be discussed.

1. Ellermeier, J.; Näther, C.; Bensch, W. "Tris(ethylenediamine-N,N')nickel(II) tetrathiomolybdate," *Acta. Cryst.* **1999**, C55, 501-503.

2:50. E-Z Photoisomerization of Diphosphenes: The Involvement of a Dark Phantom State

John L. Payton^{1,*} and M. Cather Simpson^{1,2} 1. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7708. 2. Departments of Chemistry and Physics, The University of Auckland, Building 301 Level 5, 23 Symonds Street, Auckland, NZ 1142

Over the past few decades there has been a heightened interest in molecular devices such as molecular switches, organic light emitting diodes (OLEDs), molecular wires, and numerous other molecularly engineered devices. These devices are generally organic based materials that tend to exploit E-Z isomerization of carbon-carbon, nitrogen-nitrogen, and/or carbon-nitrogen double bonds. As robust and intriguing as current literature is on these compounds, many have neglected the possibility of substituting heavier main group elements, such as phosphorus, into these systems. The newer heavier atom based systems may introduce new and exciting properties that are not available to their lighter atom based cousins. Here we have studied the E-Z isomerization of aryl-diphosphenes (*i.e.*, Ar-P=P-Ar) exploring both the thermal and excited states during the three proposed pathways. Those pathways are rotation about the central phosphorus-phosphorus double bond (*i.e.*, C-P=P-C), an in-the-plane inversion about the P=P-C bond angle, and dissociation of the phosphorus-phosphorus double bond. CASPT2 calculations will be presented on the three proposed pathways showing that conical intersections play a key role in photoisomerization of diphosphenes.

3:10. Synthesis of Larger Cucurbiturils through the “Template” Method

Craig Packard*, Edward Huang, and Michael Nee, Department of Chemistry and Biochemistry, Oberlin College, Oberlin OH 44074.

Cucurbiturils are polycyclic molecules composed of glycoluril subunits bridged by methylene groups, which can act as hosts for a wide range of cationic or uncharged guests. Recent research has shown that cucurbiturils come in a variety of sizes, ranging from 5-10 subunits. However, specificity in the synthesis process is limited, and skewed towards the formation of smaller cucurbiturils, especially the 6-subunit form (cucurbit[6]uril or CB[6]). Current work suggests that the formation of larger cucurbiturils might be encouraged via the seeding of CB-forming reactions with guest molecules that bind strongly to larger CBs, such as substituted aminiumadamantanes. Additionally, this method could be used to synthesize milligram quantities of CB[9], a species which has been detected, but not isolated.

3:30. From Bench Top to Market: Growth of Multi-Walled Carbon Nanotubes by Injection CVD Using Fe Org

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Preferential oriented multiwalled carbon nanotubes were prepared by the injection chemical vapor deposition (CVD) method using either cyclopentadienyliron dicarbonyl dimer or cyclooctatetraene iron tricarbonyl as the iron catalyst source. The catalyst precursors were dissolved in toluene as the carrier solvent for the injections. The concentration of the catalyst was found to influence both the growth (i.e., MWNT orientation) of the nanotubes, as well as the amount of iron in the deposited material. As deposited, the multiwalled carbon nanotubes contained as little as 2.8% iron by weight. The material was deposited onto tantalum foil and fused silica substrates. The nanotubes were characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and thermogravimetric analysis. This synthetic route provides a simple and scalable method to deposit MWNTs with a low defect density, low metal content and a preferred orientation. Subsequently, a small start-up was founded to commercialize the deposition equipment. The contrast between the research and entrepreneurial environments will be discussed.

3:50. Chemical Processing of Non-Crop Plants for Jet Fuel Blends Production

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The use of biofuels has been gaining in popularity over the past few years due to their ability to reduce the dependence on fossil fuels. Biofuels as a renewable energy source can be a viable option for sustaining long-term energy needs if they are managed efficiently. We describe our initial efforts to exploit algae, halophytes and other non-crop plants to produce synthetics for fuel blends that can potentially be used as fuels for aviation and non-aerospace applications. Our efforts have been dedicated to crafting efficient extraction and refining processes in order to extract constituents from the plant materials with the ultimate goal of determining the feasibility of producing biomass-based jet fuel from the refined extract. Two extraction methods have been developed based on communitation processes, and liquid-solid extraction techniques. Refining

procedures such as chlorophyll removal and transesterification of triglycerides have been performed. Gas chromatography in tandem with mass spectroscopy is currently being utilized in order to qualitatively determine the individual components of the refined extract. We also briefly discuss and compare alternative methods to extract fuel-blending agents from alternative biofuel sources.

4:10. Synthesis, decomposition and characterization of Fe and Ni Sulfides and Fe and Co Nanoparticles for Aerospace Applications

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We describe several related studies where simple iron, nickel, and cobalt complexes were prepared, decomposed, and characterized for aeronautics (Fischer-Tropsch catalysts) and space (high-fidelity lunar regolith simulant additives) applications. We describe the synthesis and decomposition of several new nickel dithiocarbamate complexes. Decomposition resulted in a somewhat complicated product mix with NiS predominating. The thermogravimetric analysis of fifteen tris(diorganodithiocarbamato)iron(III) has been investigated. Each undergoes substantial mass loss upon pyrolysis in a nitrogen atmosphere between 195° and 370°C, with major mass losses occurring between 279° and 324°C. Steric repulsion between organic substituents generally decreased the decomposition temperature. The product of the pyrolysis was not well defined, but usually consistent with being either FeS or Fe₂S₃ or a combination of these. Iron nanoparticles were grown in a silica matrix with a long-term goal of introducing native iron into a commercial lunar dust simulant in order to more closely simulate actual lunar regolith. This was also one goal of the iron and nickel sulfide studies. Finally, cobalt nanoparticle synthesis is being studied in order to develop alternatives to crude processing of cobalt salts with ceramic supports for Fischer-Tropsch synthesis.

4:30. Synthesis, characterization, and processing of copper, indium, and gallium dithiocarbamates for energy conversion applications

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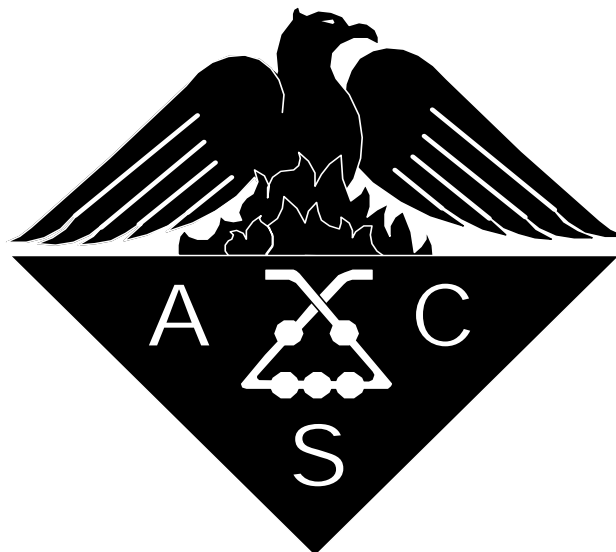
Ten dithiocarbamate complexes of indium(III) and gallium(III) have been prepared and characterized by elemental analysis, infrared spectra and melting point. Each complex was decomposed thermally and its decomposition products separated and identified with the combination of gas chromatography/mass spectrometry. Their potential utility as photovoltaic materials precursors was assessed. Bis(dibenzylidithiocarbamato)- and bis(diethylidithiocarbamato)copper(II), Cu(S₂CN(CH₂C₆H₅)₂)₂ and Cu(S₂CN(C₂H₅)₂)₂ respectively, have also been examined for their suitability as precursors for copper sulfides for

the fabrication of photovoltaic materials. Each complex was decomposed thermally and the products analyzed by GC/MS, TGA and FTIR. The dibenzyl derivative complex decomposed at a lower temperature (225-320°C) to yield CuS as the product. The diethyl derivative complex decomposed at a higher temperature (260-325°C) to yield Cu₂S. No Cu containing fragments were noted in the mass spectra. Unusual recombination fragments were observed in the mass spectra of the diethyl derivative. Tris(bis(phenylmethyl)carbamodithioato-*S,S'*), commonly referred to as tris(*N,N*-dibenzylthiocarbamate)indium(III), In(S₂CNBz₂)₃, was synthesized and characterized by single crystal X-ray crystallography. The compound crystallizes in the triclinic space group *P*1(*bar*) with two molecules per unit cell. The material was further characterized using a novel analytical system employing the combined powers of thermogravimetric analysis, gas chromatography/mass spectrometry, and Fourier transform infrared (FT-IR) spectroscopy to investigate its potential use as a precursor for the chemical vapor deposition (CVD) of thin film materials for photovoltaic applications. Upon heating, the material thermally decomposes to release CS₂ and benzyl moieties into the gas phase, resulting in bulk In₂S₃. Preliminary spray CVD experiments indicate that In(S₂CNBz₂)₃ decomposed on a Cu substrate reacts to produce stoichiometric CuInS₂ films.

4:50. Intramolecular Photocyclization of Acyclic Tethered bis-Enones

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Photocyclization reactions are a synthetically useful method for the formation of ring structures. Recent research on the mechanism of closure of a tethered bis-ester system found that photocyclization follows the [2+2] “Rule of Fives” for ring formation. Investigations of the analogous bis-enone system have shown similar products, but with less efficiency and with a greater amount of side products. Current work on photocyclization of the bis-enone system tethered to a cyclohexane ring suggests an entirely different mechanism of cyclization when single bond rotation is eliminated. The system has been found to follow the rule of fives, and it proceeds much faster than the photocycloaddition of the unhindered bis-enone system. Evidence suggests the predominance of hydrogen abstraction in the formation of products.



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