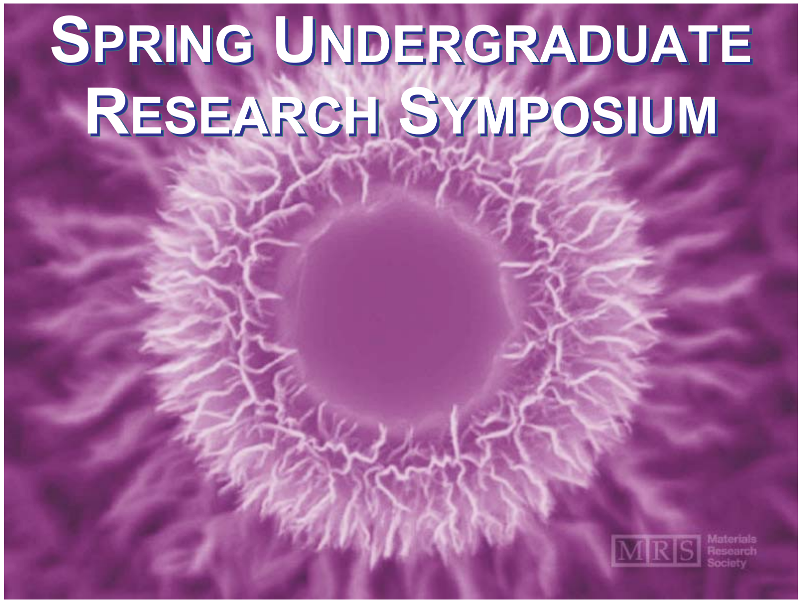
JAMES MADISON UNIVERSITY®

DEPARTMENT OF CHEMISTRY

31st Annual



SPRING UNDERGRADUATE RESEARCH SYMPOSIUM

THURSDAY APRIL 20, 2006

SESSION I: 1:15 - 5:00 PM ISAT 259 (NTELOS ROOM)

FRIDAY APRIL 21, 2006

SESSION II: 1:30 - 3:15 PM PH / CH 2212

KEYNOTE ADDRESS: 3:30 - 4:30 PM ISAT 159

SEM of two-dimensional carbon nanostructures grown on a Ga droplet using microwave enhanced chemical vapor deposition. (13,000 x magnification)

Dr. Yihong Wu
Department of Electrical and Computer Engineering,
National University of Singapore
(2005 Materials Research Society “Science as Art” Award Winner)

STUDENT ABSTRACTS:

Radical Mediated Cyclopropane Fragmentation Approach to Pyrrolidine and Piperidine Synthesis

R. Stephen Andrews and Kevin Minbiole
Department of Chemistry

A method for formation of nitrogen-containing five and six membered heterocycles has been proposed and preliminary research has been conducted. A β-azocyclopropanol substrate has been prepared by a two-step synthesis, and cyclization has been attempted using various oxidants and solvents. The heterocycle has not been synthesized to date, but proof of concept has been accomplished by creating a β-azoethylketone. Prelimiary research on the α-azocyclopropanol substrate has been conducted with the intention of cylcize into the five-membered ring.

Liquid-Phase Characterization of Supported Ruthenium Catalysts

Adam Baird, Katherine Kross and Kathryn Layman
Department of Chemistry

Heterogeneous catalysis at solid-liquid interfaces plays an important role in many industrial applications. For example, silica-supported metal (e.g. Ru) catalysts are used in the oxidization of aqueous organic contaminants, water-gas shift of CO to CO_2, Fisher-Tropsch synthesis of alkanes, and fuel cell applications. Although chemical reactions at the solid-liquid interfaces are important in several catalytic processes, few *in situ* studies have focused on investigating them. Our research efforts focus on using in situ attenuated reflection Fourier transform infrared (ATR-FTIR) spectroscopy to characterize the surface properties of silica-, boehmite-, and NaY zeolite-supported ruthenium (Ru) catalysts in the presence of both gas-phase and liquid-phase water. Specifically, we are studying the adsorption of CO on these catalysts as a function of time, CO concentration, and water concentration. This data will provide information about the nature and concentration of adsorption sites on these catalysts in aqueous environments.

Synthesis and Characterization of Novel Amphiphiphic Macromolecules

Cobbina Benson and Kevin Caran
Department of Chemistry

When amphiphilic molecules are introduced to water or organic solvents, unique colloidal properties are often seen. These properties can then be used in applications such as drug delivery and detergents. Part of the aim of our project is to determine if novel colloidal properties arise from the introduction of catenanes (interlocked macrocycles) to amphiphilic molecules. Our target structures contain a polar head group, the catenane, and a nonpolar tail of various lengths. The catenane portion of the molecule contains a crown ether macrocycle threaded through a tetracationic cyclophane. Our synthesis allows for modification of the catenane (i.e. attachment of alkyl chain) after the catenation step has been performed. This provides us access to a diversity of structures in a single step from a common catenated intermediate. We will present models of proposed aggregation in aqueous and organic media. Dynamic properties of catenanes that may find use in the field of molecular electronics (i.e. rocking, rattling, and rotation) may impart these molecules with unique properties. We also plan to study the effect of colloidal aggregation on these dynamic processes. We are also studying the colloidal properties that result from coordinating bipyridines with cationic macromolecules.

Novel Cyclopropane Mediated Heterocycle Synthesis

Andrew Blanchard and Kevin Minbiole
Department of Chemistry

A cyclopropanol fragmentation approach to the synthesis of oxygen-containing heterocycles has been developed. This strategy condenses cyclopropyl diols with aldehydes to form an acetal, which subsequently reaaranged to furnish keto-oxepane. Efforts to extend this methodology to multiple ring sizes and substitution patterns are presented.

Synthesis and Determination of the Coefficient of Negative Thermal Expansion of $ZrMo_2O_8$

Nicole A. Brehm and Barbara A. Reisner
Department of Chemistry

An exercise for the physical and materials chemistry laboratory that enables students to investigate the temperature effects upon cell constants and phase stability is being developed. The metastable cubic phase of $ZrMo_2O_8$ was synthesized by decomposing $ZrMo_2O_7(OH)_2•2H_2O$. Powder X-ray diffraction was used to identify phases, measure cell constants, and determine the coefficient of thermal expansion. Thermal methods including differential scanning calorimetry and thermogravimetric analysis were used to investigate the decomposition of the starting material and the phase transitions in $ZrMo_2O_8$.

Amphiphilic [2]Catenanes

David Crizer, Coby Benson-Adjei, and Kevin Caran
Department of Chemistry

In the 1960's Wasserman began studies on topologically non-trivial molecules, such as catenanes. Since this point in time, significant interest has been shown towards the synthesis of these unique molecules. We are specifically interested in structures containing two interlocking rings (i.e. [2]catenanes) that bear one or more hydrophobic unites. Our [2]catenanes consist of interlocked crown ethers and cyclophanes where the cyclophanes are modified with a non-polar chain. For this reason, we are synthesizing a number of cyclophane derivatives. After preparing our amphiphillic molecules we will study their colloidal properties utilizing a vast array of colloidal techniques.

Dissociation of DNA-Histone Assemblies Resulting from Protein Side-Chain Functionalization

Christine Colton and Debra Mohler
Department of Chemistry

DNA·histone assemblies can be used to mimic the environment of DNA in a eukaryotic cell allowing for further research in the medicinal chemistry field. Production of methyl radicals in the presence of histone H1·DNA assemblies dissociates the H1·DNA complex, in part due to the conversion of the amines on lysine R groups in H1 into aldehydes, canceling the electrostatic attraction between H1 and DNA. In this experiment, various concentrations of three methyl radical generating organometallic compounds were irradiated for 30 minutes in the presence of the H1·DNA complex to see if dissociation or DNA cleavage would occur. The methyl radical generators used were: $CpW(CO)_3CH_3$, pyridone (N-tert-butoxy-2-pyridone, $C_9H_9NO_2$), and a methyl cobalamin analogue. $CpW(CO)_3CH_3$ generates a metal byproduct as well as the methyl radical, requiring further studies to verify that the methyl radical was causing the dissociation. Pyridone generates both a methyl radical and a tert-butoxy radical depending on concentration; during its reaction with the H1·DNA complex, only DNA cleavage was observed, leading to the conclusion that the reaction was in the concentration range of t-butoxy radical rather than methyl radical. The methyl cobalamin analogue will provide further evidence of whether the methyl radical is the reagent dissociating the H1 from the DNA.

Thermal Decomposition of Alumina Supported Nickel Acetylacetonate

Pamela Dopart and Thomas C. DeVore
Department of Chemistry

The kinetics and thermal decomposition of alumina supported nickel acetylacetonate was studied using evolved gas analysis- Fourier transform infrared spectroscopy (EGA-FTIR) and scanning electron microscopy (SEM). Infrared spectroscopy showed that nickel acetylacetonate decomposes with the loss of 2,4-pentanedione, acetic acid, some carbon dioxide and a significant amount of acetone. The activation energy for the loss of acetone is ~80 kJ/mol. SEM images were done to check for nickel in the decomposition residue.

Accuracy and Precision Considerations in an ICP-MS Trace Analysis Problem in Instrumental Analysis

Ashley M. Lakner, Dana M.Edwards, Daniel M. Downey, and James J. Leary
Department of Chemistry

Students in Instrumental Analysis at JMU routinely analyze commercial (OTC) multivitamin/multimineral supplements for the trace elements chromium, molybdenum, and selenium. All analytical determinations are ultimately performed on an inductively coupled plasma mass spectrometer (ICP-MS). Questions have persisted concerning both the accuracy and the precision with which these experimental determinations can be performed. This work summarizes some of the analytical strategies that have been used to minimize both random and systematic errors associated with this experiment. Estimates of the achievable accuracy have been obtained by repeatedly analyzing solutions of known concentration. Proprietary considerations have made it impossible to know the scatter associated with the formulation and the manufacturing of any component in OTC supplements. However, it is possible to document the random error contributions from other sources (e.g. lab technique, calibration curve, instrument fluctuations); having these values, it becomes possible to estimate the total standard deviation associated with the analytical protocol. When performing replicate determinations on the compositions of an OTC supplement, it is reasonable to assume that any pill-to-pill variation that exceeds the deviations that have been documented must be due to random errors associated with the production process.

Unexpected Hydrolytic DNA Cleavage by $[CpFe(CO)_2]_2$ in the Presence of Trace Amounts of Peroxides

Jessica Glass and Debbie Mohler
Department of Chemistry

Prior work showed that hydrogen peroxide enhanced DNA cleavage by $CpFe(CO)_2Ph$ under ambient light, and a new mechanistic hypothesis involved the production of hydroxyl radical ($^{\cdot}OH$) by $CpFe(CO)_2$ radical. Therefore, study of the reaction of H_2O_2 with $[CpFe(CO)_2]_2$ was undertaken because the photochemistry of this simpler complex had been shown to produce the $CpFe(CO)_2$ radical. Separate trials were run investigating the concentration and time-dependence of DNA cleavage by $[CpFe(CO)_2]_2$, in which the results were analyzed by gel electrophoresis. From these studies, the importance of the concentration of peroxides has been amplified and is being further investigated.

Infrared Studies of Phosphoglycerate Kinase

Amanda Holland and Gina MacDonald
Department of Chemistry

Phosphoglycerate kinase, PGK, is a glycolytic enzyme that catalyzes the reversible phosphoryl transfer reaction between ADP and 1,3-BPG. X-ray crystal structures of PGK isolated from various organisms show both open and closed conformations in the presence of both substrates. The nucleotide-binding induced conformational changes of yeast PGK have been previously studied using difference FT-IR. Difference infrared experiments have been obtained on PGK in D_2O buffer in order to better understand the vibrational changes associated with nucleotide binding. We have now obtained difference spectra of: PGK-ATP-3PG minus PGK-3PG, PGK-ATP minus PGK, PGK-ADP-3PG minus PGK-3PG, and PGK-ADP minus PGK in deuterium oxide. Comparison of these data to those obtained in water has helped in the interpretation of the original data. The D_2O data confirm that unique protein secondary structural changes and side chain conformations are associated with the PGK-ATP-3PG complex.

Synthesis and Characterization of New Lanthanide Sulfonophosphonates

Jaime Mirowsky, and Barbara Reisner
Department of Chemistry

The ligand 2-sulfonoethylsulfonate diethyl ester (SEP) was synthesized and five new lanthanide sulfonophosphonates $Ln(O_3PCH_2CH_2SO_3)\bullet nH_2O$ (Ln = La, Pr, Nd, Gd, Er) were prepared. The larger rare earth metals (La, Pr, Nd, Gd) formed isostructural solids, while the Er phase adopted a different structure; the two phases had different decomposition patterns. Structural models for the $LnSEP\bullet nH_2O$ phases and their thermal analysis will be presented.

The Kinetic Study of the Reaction between 1-Propanol and Copper Aluminum Oxide

Michael E. Peretich and Thomas C. Devore
Department of Chemistry

An example of a heterogeneous catalyst is copper aluminum oxide (Aldrich). The apparent activation energy and order of reaction for the reaction between 1-propanol and copper aluminum oxide were determined at temperatures less than 700 K using flow kinetics. The reaction completely converted 1-propanol to propanal. First-order kinetics determined the apparent activation energy for the production of propanal to be 85 ± 10 kJ mol^{-1}.

Quantitation of Blood Neurotransmitter Metabolites by Means of High Performance Liquid Chromatography (HPLC)

Diego Ramallo, Beth Hochreiter, Gina MacDonald and Jeff Molloy
Department of Chemistry

Neurotransmitters play important and diverse roles in mood and behavior regulation. We are interested in improving methodologies to determine the concentrations of dopamine, serotonin, and norepinephrine metabolites in blood. 3,4-dihydroxy phenyl acetic acid (DOPAC) and 4-hydroxy-3-methoxyphenylacetic acid (HVA), 5-hydroxy-3-indole acetic acid (5-HIAA), and 4-hydroxy-3-methoxyphenylglycol hemipiperazinium salt (MHPG) are found in blood and are metabolites of dopamine, serotonin, and epinephrine, respectively. Our goal is to find a highly-sensitive, reproducible method for quantitating metabolite concentrations in whole blood samples. Our initial studies have focused on trying to implement published procedures and use various metabolite standards in conjunction with HPLC to determine the best approach for quantitating neurotransmitters. We have begun to use HPLC with flourometric and amperometric detection in order to monitor metabolite concentrations. This same method will eventually be used to simultaneously quantitate the metabolite concentrations of blood samples in our laboratory.

Synthetic Progress Towards a New Molecular Scaffold

Ashleigh R. Borges, Karolina Z. Roszak, Christian D. Ziegler, Kevin Caran and Kevin Minbiole

Molecular scaffolds, due to the highly symmetric orientation, can serve as functional points of attachment. The relative positioning of these functional groups can have a profound effect on the aggregation, self-assembly and binding ability of these molecules. The derivatives of these scaffolds bearing small peptides may also be utilized as enzyme mimics where the enforced juxtaposition of the amino acid chain provides a binding pocket that mimics the active site of an enzyme. The variation of the order and identity of the amino acids will allow these molecules to be fine-tuned for various substrates. Furthermore, this molecular scaffold which is based on a perhydrophenale core can be utilized as a rigid core of amphiphilic molecules. Amphiphilic molecules contain polar heads and long, non-polar tails; this covalently bound combination of hydrophilic and hydrophobic groups often contributes to interesting modes of self-assembly into various colloidal aggregates including monolayers, bilayers, and micelles. After the syntheses of our novel amphiphiles have been accomplished, we plan to investigate their usefulness, particularly as drug delivery agents, or as detergents. At the current time, we are in the process of synthesizing two stereoisomeric molecular scaffolds based on a C3-symmetrical, conformationally-fixed trans-trans-trans fused perhydrophenalene system. This scaffold can serve as a unidirectional or discotic core. We have embarked on two synthetic routes. Both take advantage of the highly symmetrical scaffold and the key step is a tandem triple ring closing metathesis. Progress on both routes will be presented.

The Syntheses of Substituted Molybdenum Carbonyl Complexes as Potential Catalysts

Carolyn Segerdell, Taryn Cummens, Donna Amenta and John Gilje
Department of Chemistry

We are interested in molybdenum complexes that may be used as catalysts in epoxidation reactions. In this study we have sought to prepare complexes with the general form CpMo(CO)$_3$(CH$_2$)$_n$—R, where n ranges from 4-6 and where R is the tosyl group (OTs) or CpMo(CO)$_3$. The anion CpMo(CO)$_3$- was allowed to react in a 2:1 ratio with TsO(CH$_2$)nOTs, n = 4-6. The ditosylates as well as the molybdenum complexes resulting from these reactions were characterized using ^{1}H and ^{13}C NMR spectroscopy as well as infrared spectroscopy.

Cyclopropane Fragmentation Strategies for the Assembly of Nitrogenous Heterocycles

Erik M. Stang and Kevin P.C. Minbiole
Department of Chemistry

A novel method of preparing nitrogenous heterocycles has been attempted for the synthesis of natural products. This method first attempts to condense a β-amino alcohol with an aldehyde producing an aminal. Under Lewis acid promotion, the aminal is expected to rearrange to a keto-azepine. The reaction has been attempted utilizing various Lewis acid promoters and nitrogen protecting groups.

Kinetics Measurements Using NMR

Adam Taylor and Thomas DeVore
Department of Chemistry

Spin-rotation constants for methanol and ethanol in the liquid phase and relaxation times of methanol in both the liquid and gas phases were measured with 1H NMR. Spin-rotation constants were measured using spectra from 273K to 293K. The spin-rotation constant for methanol was 10 kHz, and the spin-rotation constant for ethanol was 30 kHz. Relaxation times were recorded for liquid-phase at 296K and for gas-phase at 320K. For the liquid-phase, the relaxation of the equivalent hydrogen on the methyl group (4.08 ppm) was 384.2 ms, and the relaxation of the hydrogen on the alcohol (5.69 ppm) was 3.91s on the 300 MHz NMR. For the gas-phase, the relaxation of the equivalent hydrogen on the methyl group (6.19 ppm) was 96.43 ms, and the relaxation of the hydrogen on the alcohol (2.781) was 6.41 ms on this instrument. Also, data gathered from the 400 MHz and 600 MHz instruments indicated a relationship between the field strength and the relaxation times.

In-Situ Monitoring of Polymer Biodegradation Using Atomic Force Microscopy

Patrick L. Turner and Brian H. Augustine
Department of Chemistry

Atomic force microscopy (AFM) was used to monitor the enzymatic degradation of patterned samples of polyhydroxyalkanoate (PHA) thin films deposited onto gold substrates. Poly-3-hydroxybutyrate-co-poly-3-hydroxyvalerate [P(3HB-3HV)] thin films were prepared by the selective dewetting of soft lithographically patterned gold substrates with feature sizes down to 10 μm. The samples were subjected to an enzyme solution containing 20 μL of Tris-Cl buffer solution and 20 μL harvested enzyme solution produced from *Streptomyces sp.* bacterium. The liquid cell capability of the AFM allowed for the taking of in-situ and real-time measurements throughout the biodegradation process. The collected data was then externally analyzed by comparing changes in surface area with time to measure the degradation rate. Future progress concerns a study of changes in biodegradation kinetics as a result of applied nanonewton forces to PHA surfaces. Advancements in soft lithography are also an area of future interest.

Monitoring Substrate Binding of Yeast Phosphoglycerate Kinase

Ellen M. White and Gina M. MacDonald
Department of Chemistry

Phosphoglycerate kinase (PGK) catalyzes the reversible reaction in which a phosphate is transferred from ATP to 3-phosphoglycerate (3-PG) to form ADP and 1,3-bisphosphoglycerate (1,3-bPG). It has been proposed that the binding of two substrates initiates a hinge-bending motion that brings two domains closer together to facilitate the phosphate transfer reaction. Crystal structures to date have not shown both the open and closed conformation of PGK in the same species. (Kovari, Z.; Vas M. Proteins. 2004, 55, 198-209.) To better understand the conformational changes associated with substrate binding to yeast PGK we obtained numerous difference infrared spectra. PGK-ATP minus PGK, PGK-3PG-ATP minus PGK-3PG, PGK-3PG-ADP minus PGK-3PG and PGK-ADP minus PGK difference spectra were compared to identify unique vibrations associated with each PGK form. Difference infrared spectra obtained of PGK in the presence of two substrates show distinct vibrations that may result from amino acid and structural changes in the hinge region and/or increased interactions between the two domains.

Synthesis and Characterization of Polymer Brushes

Kathryn Zimmermann, Brian Augustine, and Chris Hughes[+]
Department of Chemistry, [+]Department of Physics

Polymer brushes refer to a layer of polymer that is joined at one end to another surface. In this project the polymer brush is bound to a silicon dioxide surface that has been modified with a thin monolayer of poly glycidyl methacrylate. The purpose of this project is to demonstrate a method in which polymer brush can be bound to a surface and then characterized using contact angles, atomic force microscopy, and spectroscopic ellipsometry. We followed the literature procedure of Izanov and co-workers in which we produced oxidized silicon wafers with surfaces bound to a monolayer of poly glycidyl methacrylate and then annealed to a polymer brush layer of carboxy terminated polystyrene. Characterization of the thickness and roughness of each layer was then performed using the V-Vase Spectroscopic Ellipsometer and the Digital Instruments Dimension 3100 AFM. The characterization of the polymer brushes has potential application to the surface chemistry of microfluidic devices, which continues to be of great interest in the biomedical community.