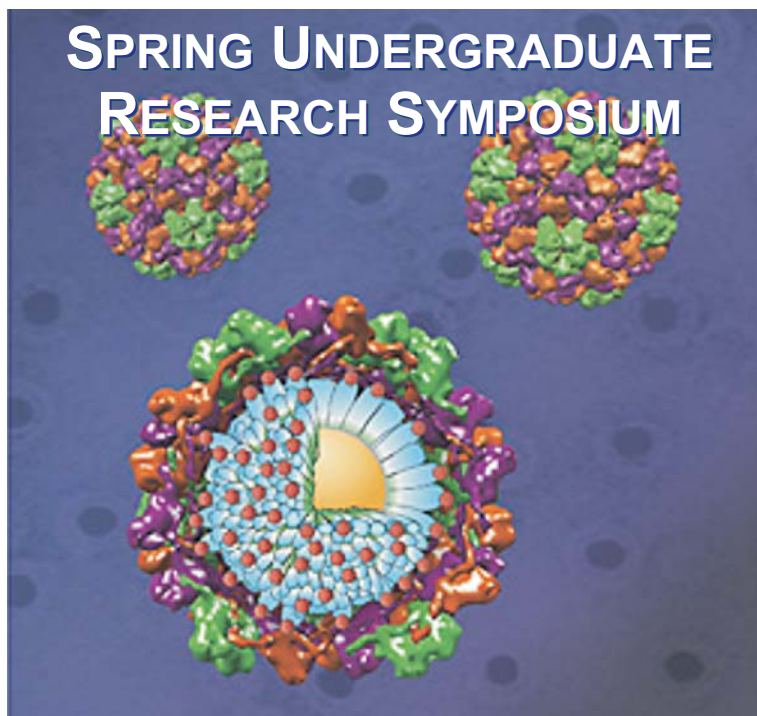


JAMES MADISON UNIVERSITY

DEPARTMENT OF CHEMISTRY

33rd Annual



THURSDAY, APRIL 17, 2008

KEYNOTE ADDRESS: 1:15- 2:15 PM PH/CH 2212

SESSION I: 2:15 - 5:30 PM PH/CH 2212

FRIDAY, APRIL 18, 2008

SESSION II: 1:15 - 5:00 PM HHS 1210

Self-assembled virus-like particle consisting of a bromo mosaic virus protein coat and a functionalized gold nanoparticle core.

Chen et al, *Nano Lett.*, 6 (4), 611-615, 2006

(Copyright ACS Publications)

KEYNOTE ADDRESS:

“Sensors and Sponges: Studies of Ligand Binding and Sponge Secondary Metabolites”



Jonathan D. Dattelbaum, Ph.D. (Class of 1995)
Biochemist and Assistant Professor
University of Richmond
Richmond, VA

ABSTRACT:

The work in my lab covers two diverse topics. The real-time monitoring of glucose concentrations in complex media may have diverse application to bioprocess monitoring and to minimizing health complications caused by diabetes. Site-directed mutagenesis of the *E. coli* glucose/galactose binding protein (GGBP) is used to design and monitor the glucose-dependent spatial realignment of two covalently attached fluorophores. The sensors may be used to measure glucose levels spanning five orders of magnitude (0.04 to 12,000 μM). Importantly, measurements retain signaling abilities even in the presence of physiologically relevant sugar and albumin concentrations. A second, unrelated project examines the relationship between symbiont community structure and secondary metabolite profiles in the common Chesapeake Bay sponge, *Clathria prolifera*. The total carotenoid concentrations are quantified during a 12 month period using both UV/VIS and HPLC methodologies to examine whether natural changes in the symbiont community lead to changes in secondary metabolite profiles. We then cultured pigmented microbes from sponge larvae and investigated the structural and spectroscopic characteristics of specific non-carotenoid secondary metabolites. Our results provide insights into the nature of the sponge-symbiont association under fluctuating environmental conditions. Understanding these relationships has important practical consequences because many compounds produced by sponges have the potential to be beneficial as lead compounds for the pharmaceutical industry.

STUDENT ABSTRACTS:

Response of Aquatic Chemistry in an Acid Sensitive Trout Stream from Air Pollution Control Measures

Michelle Bender and Daniel M. Downey
Department of Chemistry and Biochemistry, James Madison University

Water Chemistry data for Little Stony Creek (LSC) Northwest Virginia, have been collected since 1989 for long term studies on the effects of acid rain and of limestone (CaCO_3) treatment on streams occupied by native brook trout (*Salvelinus fontinalis*). Limestone is added to the stream once every three years to neutralize acidity. Much of the anthropogenic acidity in LSC originates from regional coal fired power stations in West Virginia such as Mt. Storm power plant, a 1.6 GW station located 180 km northwest of the stream. In 1995, Mt. Storm contributed almost a quarter of WV sulfate emissions, 410,394 tons/year, into the atmosphere. Since 1995, limestone scrubbers installed at Mt. Storm have reduced sulfur dioxide emissions by 97% from about 100,000 to 3,100 tons SO_2 /year. Values for discharge, pH, sulfate concentration, acid neutralizing capacity (ANC) and other parameters for water samples collected monthly from LSC upstream of liming sites have been evaluated to determine whether any changes in water quality have occurred coincident with the implementation of pollution control measures. Data from the National Atmospheric Deposition Program (NADP) air quality monitoring station nearest LSC (Big Meadows, VA) have also been studied. The purpose of this study was to evaluate the data to determine whether limestone mitigation should be continued. LSC sulfate and calcium discharge have decreased while ANC and pH have increased. Although the water quality of LSC has improved, the stream remains sufficiently acidic that liming mitigation must be continued to maintain water quality.

Identification and Correction of Student Misconceptions Through Concept Analysis

Seth Berkeley and Barbara Reisner
Department of Chemistry and Biochemistry, James Madison University

Students often bring prior misconceptions to the chemistry laboratory. These misconceptions are not always resolved because students tend to incorporate new information into their existing, and possibly incorrect, understanding. An experimental section of CHEM 132L employs the MORE (Model, Observe, Reflect, Explain) Thinking Frame to help students resolve their misconceptions. Because the MORE Thinking Frame requires students to directly explain their observations with molecular level models, it provides insights into student beliefs. A conceptions analysis of student coursework was done to uncover conceptions related to spectroscopy. Students described their initial conceptions, then completed two experiments. In the first experiment, students made observations about the relationship between the wavelength of maximum absorbance and the colors that they see. In the second experiment, students used a traditional Beer's law experiment to see how changes in concentration affect transmittance and absorbance. Two coding schemes were developed to identify student conceptions in these labs. Common student conceptions will be presented. By using the coding scheme and performing a conceptions analysis, lab activities can be modified and refined to minimize misconceptions.

The Synthesis of Bicyclo[4.2.0]-7-ene and Other Substituted Cyclobutenes For Reactions with Difluorocarbene

Jennifer Bon and Scott B. Lewis

Department of Chemistry and Biochemistry, James Madison University

This research concerns the synthesis of 3,4-disubstituted cyclobutenes for the purpose of reacting them with two equivalents of difluorocarbene. Bicyclo[4.2.0]-1-octene was synthesized by reacting cyclohexene with trichloroacetyl chloride to form 3,3-dichlorobicyclo[4.2.0]-2-octanone. The dichloro ketone was then reduced using LAH to the corresponding alcohol. The dichloro alcohol was then mesylated using methylsulfonylchloride and subsequently reduced by Na/NH₃(l) at reflux to yield bicyclo[4.2.0]-1-octene. The octene will then be reacted with a source of two equivalents of difluorocarbene and the product characterized. Other cyclobutenes including 1-methyl-2-phenylcyclobutene and 3-hexylcyclobutene have also been prepared by a similar process for reactions with difluorocarbene. The reaction of 3-hexylcyclobutene with a difluorocarbene source produced products whose ¹⁹F NMR spectrum is consistent with difluorobenzene products.

Using Difference Infrared Spectroscopy to Study the Effects of Salt and pH on Nucleotide Binding to Phosphoglycerate Kinase

Jamie N. Campbell and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

Phosphoglycerate kinase (PGK) is a single polypeptide (~45kDa) that catalyzes the reversible phospho-transfer reaction between ATP and 3-phosphoglycerate (3PG) to form ADP and 1,3-bis-phosphoglycerate. It has been proposed that phospho-transfer is facilitated by a hinge region in the enzyme that closes when both substrates are bound. Crystal structures and NMR data obtained on the ternary complexes of PGK from different sources have provided evidence from both the open and closed conformations. The conformation and activity of PGK is dependent on salt concentrations, pH and bound substrates. We have performed biochemical studies that have confirmed activation of the phosphate transfer reaction occurs at low salt concentrations and high concentrations of salts inhibit enzyme activity. We have used infrared spectroscopy to investigate how salt and pH influence protein structural changes associated with each of the PGK-substrate conformations. Previous studies in our lab have shown conformational changes due to substrate binding in high salt conditions. Here we present new difference infrared data (PGK-ATP minus PGK and PGK-ADP minus PGK) that were obtained at lower pH (6.5) and at lower salt concentrations. The new data show different vibrational changes and unique differences are associated with nucleotide binding under the lower salt conditions as well as differences due to change in pH. The infrared data indicate unique secondary structures and side chain conformations are associated with each of the PGK-nucleotide complexes.

An Understandable Derivation of the Lorentz Transformation

Whitney Davis and James J. Leary

Department of Chemistry and Biochemistry, James Madison University

In the past chemists have rarely needed to concern themselves with systems in which any particle other than a photon was traveling at a velocity approaching the speed of light. However, as instrumentation becomes more sophisticated and experiments become increasingly more elaborate, it is reasonable to think that at least some chemists will find themselves dealing with things (usually electrons) that are moving "very" fast. In an attempt to open-the-door to some physics that has rarely been encountered by chemists, this presentation will provide a derivation of the equations that are collectively called the Lorentz Transformation. It is these equations that can be used to describe the counter-intuitive properties of space and time that exist when observing things that are moving at a significant fraction of the speed of light.

ATR-FTIR Investigation of P-cresol Oxidation on Alumina-Supported Cobalt Oxide Catalysts

Cynthia Din and Kathryn A. Layman

Department of Chemistry and Biochemistry, James Madison University

p-Hydroxybenzaldehyde (PHBA) is an important intermediate in the synthesis of many pharmaceuticals, perfumes, flavoring agents, and agricultural chemicals. p-Cresol oxidation may reduce the cost, simplify synthesis, and decrease the environmental hazards encountered during the current industrial processes used to synthesize PHBA. Our work explores the oxidation of p-cresol by metal oxides of Cu, Co, Mg, and/or Mn supported on aluminum oxide. These four catalytic metals were chosen for investigation because of their effectiveness in similar reactions. The oxidation of p-cresol was monitored using high performance liquid chromatography (HPLC). Calibration plots were obtained for reactant and products using HPLC in order to better analyze % conversion and % selectivity. Since we plan to use in situ attenuated total reflection Fourier transformation infrared (ATR-FTIR) spectroscopy to monitor p-cresol oxidation on CoAl₂O₄ (30 wt% Co calcined at 900°C), we have also developed IR calibration plots. It was found that % p-cresol conversion and catalytic selectivity to p-hydroxybenzaldehyde depend on the calcination temperature of the supported metal oxide catalyst and the catalyst loading on the Al₂O₃ support. The CoAl₂O₄ (30 wt% Co calcined at 900°C) catalyst has shown to be the most active and selective (95.7% p-cresol conversion and 92.4% selectivity to p-hydroxybenzaldehyde). XRD patterns collected after p-cresol oxidation are similar to those collected prior to reaction, suggesting that CoAl₂O₄ is recyclable and is a potential catalyst for the production of PHBA.

Structural and Thermal Stability of Supramolecular Propargylic Alcohol Organogels

Clayton Dingle and Kevin L. Caran

Department of Chemistry and Biochemistry, James Madison University

Substituted propargylic alcohols have been shown to be a competent class of low molecular weight organogelators (LMOG) in nonpolar n-alkane solvents and silicone oil. The supramolecular structures of the propargylic alcohols are thought to be dictated by π - π stacking of the aryl rings, hydrogen bonding between O-H groups, and weak H-F hydrogen bonding. These interactions allow aggregation preferentially in one direction, forming pseudo infinite channels. Electron microscopy of the xerogels has confirmed the formation of these fibers. The phenyl propargylic alcohol was found to form stable gels in n-alkane solvents with 5-16 carbons in concentrations between 20 and 50 mg/mL. The thermostability of the gels was analyzed using DSC and ball drop tests. Powder XRD was also used to compare the supramolecular aggregation of the gel to the recrystallized solid and the sublimed solid. Different n-alkane solvents (and varying ratios of two) were found to control the transition temperature of the phenyl gel. In general, higher alkanes form gels with higher transition temperatures. For solvent mixtures, a positive linear relationship was found between percentage of the longer n-alkane solvent and the transition temperature.

Enzymatic Characterization of N-Acylethanolamine-hydrolyzing Acid Amidase

Robert East, Lindsay Pattison, Victoria L. Mariani

Department of Chemistry and Biochemistry, James Madison University

N-acylethanolamine-hydrolyzing acid amidase (NAAA) is acid amidase that catalyzes the hydrolysis of N-palmitoylethanolamine (PEA). PEA is a fatty acid amide which exhibits anti-inflammatory effects. NAAA is predicted to cleave the carbonyl-amide bond in PEA. A current aim is to design an enzymatic assay using reverse phase high performance liquid chromatography (HPLC) to monitor activity of NAAA. A P-AMC substrate, where the ethanolamine side chain of PEA is replaced with a fluorophore, 7-amino-4-methylcoumarin (absorbs 360nm/emits 465nm), will be synthesized. NAAA should cleave the fluorophore from the substrate, yielding palmitic acid and 7-amino-4-methylcoumarin. The products can be quantified with the use of reverse phase HPLC. From the data collected, we can obtain kinetic parameters of NAAA. Site-directed mutagenesis can allow us to further characterize the active site of NAAA and enable us to begin to design reversible competitive inhibitors that can be introduced as a novel class of anti-inflammatory agents.

ICP-MS Surveys of Some Trace Metals of Environmental Interest

Kate Godwin, Daniel M. Downey, James J. Leary

Department of Chemistry and Biochemistry, James Madison University

It is well documented that detrimental changes have occurred in Virginia's water quality. Considerable attention has been directed toward the declining water quality in the Chesapeake Bay, and fish kills in the Shenandoah River were common last year. This work describes a variety of Inductively Coupled Plasma - Mass Spectrometry experiments designed to provide information about a set of elements in water samples from a variety of sources. In three cases it is possible to speculate with considerable confidence about the sources of elements that are never suitable for consumption. Lead was found at elevated levels in water that was distributed via older copper plumbing. Cadmium was found as a companion element in water samples taken from the vicinity of an old zinc mine. Arsenic was found in pond water in an area that was once associated with flocks of free-ranged turkeys.

Formation of Products in the Zn^{2+} / 1,4-Benzenedicarboxylate Systems

Jeremy Harris and Barbara Reisner

Department of Chemistry and Biochemistry, James Madison University

The rational synthesis of inorganic compounds is a significant problem in solid state chemistry. Metal organic frameworks (MOFs) are a class of solid state materials where metal ions are coordinated by multifunctional organic linkers. The mechanism of nucleation and growth of these materials has not been experimentally determined. Through the use of electrospray ionization mass spectrometry (ESI-MS), we are initiating studies to monitor nucleation and crystal growth of MOFs. We are investigating the Zn^{2+} / 1, 4-benzenedicarboxylic acid (H₂BDC) system from which many MOF are known to crystallize. Initial work has focused on two systems: $Zn_3(BDC)_3 \cdot 6CH_3OH$ (MOF-3) and $Zn_4O(BDC)_3 \cdot (DMF)_8(C_6H_5Cl)$ (MOF-5). Synthesis conditions for MOF-5, the best studied material in the Zn^{2+} / BDC system, are being explored to better define synthesis parameter space before ESI-MS studies begin. Preliminary ESI-MS experiments in the synthesis solution for MOF-3 have revealed the presence of an unknown solution species whose identity is concentration dependent.

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

Elizabeth Hochreiter, Gina MacDonald, Jeffrey Molloy

Department of Chemistry and Biochemistry, James Madison University

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 their metabolites in blood. 3,4-dihydroxy phenyl acetic acid (DOPAC), 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 norepinephrine, respectively. Our goal is to find a highly-sensitive, reproducible method for quantitating the concentrations of these compounds in plasma samples. Our initial studies have focused on trying to implement published procedures and use various standards in conjunction with HPLC to determine the best approach for quantitating the neurotransmitters and their metabolites. We have used both coulometric electrochemical detection and fluorescence detection to monitor their concentrations. All of the neurotransmitters and metabolites we wish to study are detectable using electrochemical detection, while only serotonin, dopamine, 5-HIAA and MHPG are detectable using fluorescence detection. Studies on the purification of the neurotransmitters and metabolites from blood have commenced. Purification of the neurotransmitter serotonin, in both platelet rich and platelet free plasma, has been achieved using a previously published blood preparation procedure. The purified 5-HT has been detected using fluorescence detection. The methods for electrochemical and fluorescence detection will eventually be used to simultaneously quantitate the neurotransmitter and metabolite concentrations of plasma samples in our laboratory.

A Cyclopropane Fragmentation Approach to the Synthesis of Azepines and Oxepanes

Kevin Jellerson, Alison Whitehurst, Kevin P. C. Minbiole

Department of Chemistry and Biochemistry, James Madison University

Cyclopropanol fragmentation is a promising approach to the synthesis of oxepanes and azepines, oxygen and nitrogen-containing 7-membered rings, respectively. In the azepine synthetic route, α -amino cyclopropanol is first condensed with an aldehyde or acetal to form an aminal. Mercury (II) chloride can then be used to break the strained cyclopropane forming an iminium intermediate which can then form an azepine. In practice, an aminal was formed using paraformaldehyde and formic acid. After exposure to $HgCl_2$ in ether or acetone, NMR data suggests the azepine was in fact formed. On the other hand, the synthesis of cis and trans oxepanes has already been developed, but has only been demonstrated with racemic products. To open the door to optically active oxepanes, cyclocondensation chemistry developed by Nelson has been explored to synthesize homo-chiral β -lactones. This strategy also allows for greater functionalization of resultant heterocycles. The synthesis of β -lactones was achieved by utilizing a trimethylsilane-quinidine (TMSQ) complex to catalyze the cyclocondensation of a substituted aldehyde with an acid chloride. Kulinkovich reactions were then performed on the subsequent lactones to afford homo-chiral α -hydroxy cyclopropanols, which could in turn be used in the oxepane synthesis developed by the Minbiole group.

Characterization of Hydrated Ru/Al₂O₃

Thomas Kenderdine, Diana Gottschalk, Kathryn A. Layman
Department of Chemistry and Biochemistry, James Madison University

Aqueous-phase carbohydrate reformation (ACR) is being investigated as a methodology to improve current H₂ fuel cell technologies since ACR has the potential to increase safety and improved H₂ storage density. The development of CO tolerant catalysts is necessary before the use of indirect reformation fuel cells become feasible because CO, a byproduct of ACR, deteriorates the performance of fuel cells. Ru facilitates CO oxidation since it is effective at capturing OH or H₂O, the usual oxygen source for CO oxidation. Therefore, the investigation of Ru in varying amounts of water is extremely important for the development of effective heterogeneous catalysts for fuel cells and these industrial processes. Our research uses in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, thermogravimetric analysis (TGA), and evolved gas analysis (EGA) to investigate the adsorption and reactivity of CO on hydrated Ru/Al₂O₃. The physicochemical properties of these materials have been determined via X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and BET methodologies. We will present ATR-FTIR data of CO adsorption on Ru/Al₂O₃ deposited on ZnSe and Ge internal reflection elements (IRE), and the adsorption of ¹²C and ¹³C isotopic mixtures on Ru/Al₂O₃. Transmission FTIR spectra collected during an EGA study of hydrated Ru/Al₂O₃ exposed to CO indicate that CO migrates from linearly-bonded sites to a bridge-bonded site when the sample is heated above 150°C. EGA and TGA studies suggest that CO is oxidized to CO₂ at elevated temperatures.

Cyclopropane Fragmentation Approaches to the Synthesis of Piperidines

Marita C. Lawler and Kevin P. C. Minbiole
Department of Chemistry and Biochemistry, James Madison University

The ring expansion of hydroxycyclopropanes can be exploited for the stereocontrolled formation of oxygenated heterocycles such as oxepanes. Progress has been made toward the synthesis of nitrogenous heterocycles, particularly piperidines, via analogous fragmentation / recondensation strategies. This method condenses a carbamate-substituted cyclopropyl alcohol with an aldehyde or acetal, producing an aminal. Under Lewis acid promotion, the aminal is expected to rearrange to form a piperidine. This rearrangement is still under investigation.

Ruthenium Complexes of Bis(diphenylphosphino)ethane Monoxide

Morgan Moyer and John W. Gilje
Department of Chemistry and Biochemistry, James Madison University

Ruthenium complexes with phosphine ligands are of catalytic interest. The Ph₂P(CH₂)(CH₂)P(O)Ph₂ ligand is relatively unstudied, but is interesting because it potentially can coordinate through both phosphine and phosphoryl moieties. With Ru(II) the interactions of O=PR₃ are generally weaker and more labile than those between Ru(II) and PR₃. Thus Ph₂P(CH₂)(CH₂)P(O)Ph₂ potentially is a hemilabile ligand which can coordinate strongly to Ru(II) through phosphine and more weakly through oxygen. The reaction of Ph₂P(CH₂)(CH₂)P(O)Ph₂ with RuCl₃•3H₂O followed by the addition of CH₂O in 2-ethoxyethanol produces RuHCl(CO)(Ph₂P(CH₂)(CH₂)P(O)Ph₂)₃. Similar reactions produce RuH₂(CO)(Ph₂P(CH₂)(CH₂)P(O)Ph₂)₃ when a small amount of KOH is added. This reaction also appears to produce Ru(CO)₃(Ph₂P(CH₂)(CH₂)P(O)Ph₂)₂ if hot KOH is used. RuHCl(CO)(Ph₂P(CH₂)(CH₂)P(O)Ph₂)₃ can be converted to RuH₂(CO)(Ph₂P(CH₂)(CH₂)P(O)Ph₂)₃ by reaction with KOH in several solvents. The non-first order ³¹P spectra have been analyzed and combined with the ¹H spectra indicate the above formulations. The stereochemistry about the ruthenium appears to be octahedral, with meridional coordination of the ligands. The CO is cis to the ligands. In the monohydride, chlorine is cis to all ligands and the hydride is trans to one and cis to the other two. The stereochemistry of the dihydride is that of the monohydride with hydride replacing chloride. In these complexes only the phosphine moiety appears to bind to the metal.

Dissociation of DNA-Histone Assemblies Caused by the Radical-Mediated Modification of Lysine Side Chains

Matt (BC) Patterson and Debra L. Mohler
Department of Chemistry and Biochemistry, James Madison University

The treatment of plasmid DNA/histone H1 assemblies with methyl radical produced by the photolysis of CpW(CO)₃CH₃ causes dissociation of the protein from the DNA. Progress towards determining the mechanism of this process will be described.

Cloning and Expression of a Novel Enzyme, N-Acylethanolamine Hydrolyzing Acid Amidase

Lindsey Pattison, Robert E. East, Victoria L. Mariani
Department of Chemistry and Biochemistry, James Madison University

N-Palmitoylethanolamine (PEA) is a saturated NAE which exhibits immunosuppressive, anti-nociceptive, antioxidant and also neuroprotective effects. In addition, PEA also exhibits anti-inflammatory effects in a wide range of mammalian tissues. PEA is expressed locally in infected areas; however, it is rapidly hydrolyzed to palmitic acid and ethanolamine by N-acylethanolamine hydrolyzing acid amidase (NAAA). In addition NAAA has some self processing activity. Characterization of the structure and function of NAAA is of interest as the enzyme poses future applications as an inhibitory-drug target for inflammation. In order to identify potential inhibitors and drug targets, the gene encoding NAAA was isolated from rat lung tissue and cloned into a bacterial plasmid. The recombinant NAAA will be expressed from E. coli and purified. The kinetic parameters of NAAA will be analyzed using reversed phase HPLC. These data will give us a comprehensive analysis of the substrates preferred by NAAA to lead us to the design of a novel class of potential inhibitors.

Desorption of Nitric Acid From Boehmite and Gibbsite

Matthew Ross and Thomas C. DeVore
Department of Chemistry and Biochemistry, James Madison University

Solid state Fourier transform infrared spectroscopy (FTIR), evolved gas analysis-FTIR (EGA-FTIR), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been used to investigate the desorption of nitric acid from boehmite and from gibbsite. Samples containing between 3% and 36% adsorbed nitric acid by mass were prepared by placing the mineral in 70% nitric acid solution or by the adsorption of nitric acid vapors in humid air. FTIR established that water solvated nitrate was the main species adsorbed on the surface of either mineral under these conditions. The water solvated nitrate vaporized as nitric acid at ~ 400 K with an enthalpy of desorption of ~ 50 kJ/ mol for both surfaces. A second nitric acid desorption occurred at ~ 450K and had an enthalpy of desorption of 85 kJ/ mol (95 kJ/ mol) for boehmite (gibbsite). This was assigned as desorption of partially solvated aluminum hydroxylated nitrate. Monodentate and bridging nitrate were also observed on the boehmite. These species desorbed at ~ 725 K as NO₂ and O₂ with an enthalpy of reaction of ~ 55 kJ/ mole NO₂ desorbed.

Investigation of Antifungal Compounds Found in Bacteria Isolated from the Four-Toed Salamander, *Hemidactylium scutatum* and the Redback Salamander, *Plethodon cinereus*
Christian Scwantes¹, Robert M. Brucker², Kevin P. C. Minbiole¹, Reid N. Harris²

¹Department of Chemistry and Biochemistry, James Madison University

²Department of Biology, James Madison University

Populations of frogs and other amphibians are decreasing worldwide, due in large part to chytridiomycosis, a fungal infection. *Batrachochytrium dendrobatidis*, the cause of chytridiomycosis in amphibians, can be fought by certain antifungal compounds. The secondary metabolite 2,4-diacetylphloroglucinol (2,4-DAPG) has previously been found to be produced by the bacterial isolate *Lysobacter gummosus*, which was isolated from a Redback salamander, *Plethodon cinereus*, caught in the JMU Arboretum. We have investigated known compounds pyrrolnitrin, pyoluteorin, and 2,4-DAPG that may be found on amphibian skin. Preliminary results from a total of eleven bacterial isolates indicated pyrrolnitrin was present on six isolates and pyoluteorin on two isolates. More recent results have not completely supported these findings. We have identified two unknown compounds from the bacterial isolate *Janthinobacter lividum*, as indole-3-carboxaldehyde and violacein. Additionally, we have found that these compounds exist on amphibian skin at a concentration high enough to inhibit the fungal pathogen. This is the first time either of these compounds has been identified on a vertebrate.

pH Dependence of the Formal Hydrolysis of DNA Phosphodiester by [CpFe(CO)₂]² and Hydrogen Peroxide

Danni Simpson and Debra L. Mohler

Department of Chemistry and Biochemistry, James Madison University

Cleaving DNA in a hydrolytic manner with synthetic agents is becoming very important in molecular biology, either models for restriction enzymes or for targeting specific DNA sequences to block gene expression. The organometallic compound [CpFe(CO)₂]² in the presence of peroxide performs the formal hydrolysis (or cleaving) of plasmid DNA. To determine its actual mechanism of cleavage, various aspects of this system are being examined including its kinetics, temperature dependence, and pH dependence. Here, the pH dependence of this process is described.

Analysis of Fish Otoliths and Tissue for Trace Elements From the Shenandoah River System Using ICS-MS

Wesley Storm and Daniel Downey

Department of Chemistry and Biochemistry, James Madison University

Trace elements and other pollutants introduced by human activity in the Shenandoah River watershed may be contributing to stress and fish mortality. To assess the extent of biological contamination, archived otoliths (ear bones) of 336 smallmouth bass (*Micropterus dolomieu*) and redbreast sunfish (*Lepomis auritus*) collected from multiple locations in the Shenandoah River and its tributaries in 2004-2006 were analyzed. Following cleaning to remove biological fluids and tissue, the otoliths were dissolved in nitric acid solution with heat and ultrasonication and analyzed for eighteen trace elements by inductively coupled plasma mass spectrometry (ICP-MS). As only the archived otoliths were available, twenty-five additional smallmouth bass were collected at a single location in the South Fork Shenandoah River near Front Royal, Va. and livers, tissue, and otoliths removed from these fish from for analysis and comparison. Tissue and liver samples were analyzed by ICP-MS after microwave assisted digestion using nitric acid / hydrogen peroxide mixture. To date, fourteen trace elements have been found in varying amounts including aluminum, antimony, arsenic, cadmium, cobalt, copper, chromium, lead, manganese, molybdenum, nickel, selenium, vanadium and zinc. In some cases the elements are found only in the tissue and livers, while other elements have been found in the otoliths and not in the tissue. This presentation will discuss the concentrations found for the trace elements and possible significance in contributing to stress in the Shenandoah River fish kills.

Synthesis and Colloidal Study of Cationic Gemini Surfactants: A Series of Experiments to Introduce Nanoscience Into Introductory, Organic, Physical and Upper-Level Chemistry Laboratories

Stephanie Torcivia and Kevin L. Caran

Department of Chemistry and Biochemistry, James Madison University

In an effort to integrate nanoscience concepts throughout the chemistry curriculum at James Madison University (JMU), several new experiments have been designed and implemented in our undergraduate laboratories. The synthesis of a gemini amphiphile, ethanediyl- α,ω -bis(dodecyldimethylammonium) dibromide, referred to as "12-2-12", was optimized and a critical micelle concentration (CMC) study was completed. Formation of micelles in water was studied using several indirect techniques: surface tension, conductivity, and diffusion rate (DOSY). In addition, fluorescent techniques were used to study the colloidal properties of aqueous samples of 12-2-12 using the fluorescent probes pyrene and 4-(Dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran). Various aspects of the synthesis and colloidal analysis of 12-2-12 have been implemented in several labs at JMU including the organic chemistry, physical chemistry, and a new upper-division nanoscience course, Science of the Small. Also, students from a local high school participated in a modified version of this colloidal study. The experiments were successfully performed by students in laboratory courses during the 2006-2007 academic year. Subsequently, conditions for parallel synthesis in a large microwave were optimized to be used in a future iteration of the organic teaching laboratory. The dibromide form of 16-2-16 was converted to the dihydroxide (via ion exchange), which was then mixed with an equimolar amount of D- (or L-) tartaric acid yielding 16-2-16 with a chiral tartrate counterion. Aggregates of this compound were characterized by NMR and SEM. This ion exchange will be implemented in the Science of the Small course during the Spring 2009 semester. In addition, CMC and Krafft temperature studies for several novel biscationic single chained amphiphiles were completed.

The Synthesis of Chlororheniumtricarbonyl Complexes of Substituted and Unsubstituted 2,2'-Bipyridine Ligands

Dien Tu and Debra L. Mohler

Department of Chemistry and Biochemistry, James Madison University

Determining the nature of the contact between surfaces and molecular adsorbates is crucial to improving applications involving such systems. To probe the effects of the anchoring groups in adsorbates on interfacial electron transfer, we are investigating the synthesis and properties of chlororheniumtricarbonyl complexes of 2,2'-Bipyridine-4,4'-bis(phosphonic acid), 4,4'-dimethyl-2,2'-bipyridine, and 2,2'-bipyridine. Progress towards the preparation of these compounds will be discussed

***In-Situ* Photopolymerized Micromolding as a Technique for the Fabrication of Poly(Methyl Methacrylate) Microfluidic Devices**

Patrick L. Turner¹, Wm. Christopher Hughes², Brian H. Augustine¹

¹Department of Chemistry and Biochemistry, James Madison University

²Department of Physics and Astronomy, James Madison University

Microfluidic devices have generated great interest as a method for small-scale chemical and biological applications, termed micro-total analysis systems (μ -TAS). In devices where UV detection methods are used, the most common fabrication material used to date is silica based glass, but because of long processing times and the necessity to use harsh chemicals, other viable materials, such as polymers, are being explored. We have developed a reproducible, rapid room-temperature technique using poly(methyl methacrylate) (PMMA) for the fabrication of microfluidic devices. This technique involves the injection of a photosensitive solution of PMMA between a flat PMMA substrate and a crystallographically etched silicon master. Upon UV illumination the solution photopolymerizes to yield the channel structure without altering the original surface chemistry. We have expanded on this technique by embedding gold reflective layers within the channel structure as well as fabricating devices with co-polymer blends. PMMA microfluidic devices for IR mediated PCR were successfully fabricated and characterized by scanning electron microscopy, atomic force microscopy and profilometry. Devices were also tested for use with extrinsic Fabry-Perot interferometry.

Characterizing the Desorption of (2,4) Pentanedione on Boehmite

Curtis White and Thomas C. DeVore

Department of Chemistry and Biochemistry, James Madison University

Solid state FT-IR, evolved gas analysis (EGA FT-IR) and proton NMR were used to investigate the absorption of (2,4) pentane dione on boehmite. FT-IR spectra taken of the (2,4) pentane dione, boehmite, and (2,4) pentane dione on boehmite indicated a chemical reaction occurred. An EGA of the compound revealed that acetone was released as it was heated to 400°C. An IR of the residue indicated that acetate had formed. These results were similar to those of basic Al acetate heated to 400°C and could, with further research, lead to a better characterization of this intermediate.