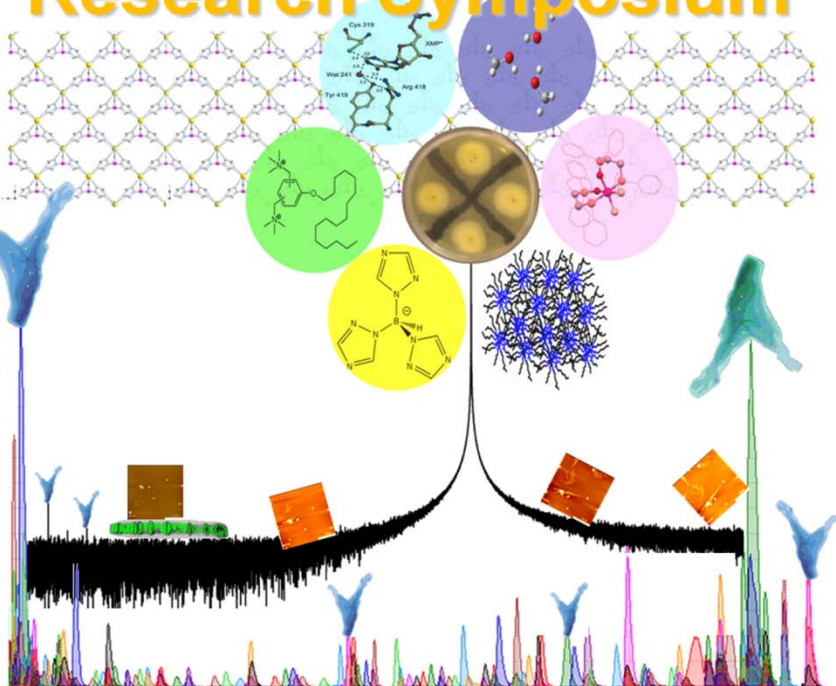


JAMES MADISON UNIVERSITY®

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

Spring Undergraduate Research Symposium

36th Annual



THURSDAY MARCH 24, 2011

ORAL SESSION I: 1:15 – 4:00 PM (ISAT 259)

POSTER SESSION: 4:00 – 5:00 PM (PHYS/CHEM 3348)

FRIDAY MARCH 25, 2011

ORAL SESSION II: 2:15 – 3:30 PM (ISAT 259)

KEYNOTE ADDRESS: 3:45 – 4:45 PM (ISAT 159)

See back cover for image description.

Past Keynote Speakers

Each year we feature a keynote speaker for the Department's annual Spring Undergraduate Research Symposium. We are honored to have had speakers who are alumni of the department and are willing to come back and share with our students their experiences of "life after JMU". We thank each of these speakers and look forward to future alumni participation in the Department of Chemistry Spring Undergraduate Research Symposium.

YEAR	JMU CLASS	SPEAKER	AFFILIATION
2011	1992	Dr. Morgan S. Sibbald	<i>The Sherwin-Williams Company</i>
2010	1988	Dr. Kevin Morris	<i>Carthage College</i>
2009	1988	Dr. Chris E. Holmes	<i>The University of Vermont College of Medicine</i>
2008	1995	Dr. Jonathan Dattlebaum	<i>University of Richmond</i>
2007	1987	Dr. Elizabeth Perry (M.D.)	<i>Signature Healthcare, Inc.</i>
2006	1967	Dr. Carolyn Abitbol (M.D.)	<i>University of Miami (FL) School of Medicine</i>
2005	1975	Dr. Daniel Downey	<i>James Madison University</i>
	1976	Dr. Gary Rice	<i>College of William and Mary</i>
2004	1987	Dr. James (Dusty) Baber	<i>National Institutes of Health</i>
2003	1984	Dr. Fred King	<i>West Virginia University</i>
2002	1977	Dr. Roger Bertholf	<i>University of Florida School of Medicine</i>
2001	1979	Mrs. Kathryn Lam	<i>International Business Machines</i>
1999	1987	Dr. Jose Madalengoitia	<i>University of Vermont</i>
1997	1986	Dr. Fred R. Kinder	<i>Novartis Research Institute</i>
1996	1976	Dr. Terry O. Trask	<i>DuPont Chemicals</i>
1995	1973	Dr. Carl Lentz	<i>Eastman Fine Chemicals</i>
1994	1990	Dr. Michele A. Kelly	<i>University of Maryland Baltimore County</i>
1993	1985	Dr. Cynthia K. Fallon	<i>DuPont Chemicals</i>
1992	1983	Dr. Laurie Locascio	<i>National Institute of Standards and Technology</i>
1991	1983	Dr. Noreen Naiman	<i>North Carolina School of Science and Mathematics</i>
1990	1982	Dr. Matthew T. Stershic	<i>Atomchem North America</i>
1989	1982	Dr. Michael Kinter	<i>Cleveland Clinic Lerner Research Institute</i>
1988	N/A	Dr. Thomas J. Meyer	<i>Los Alamos National Laboratory</i>
1987	1980	Dr. Steven Davis	<i>Naval Research Laboratory</i>
1986	1980	Dr. Steven A. Hackney	<i>Michigan Technological University</i>
1983	1978	Dr. Richard B. Lam	
1982	1975	Dr. Daniel Downey	<i>West Virginia University</i>
1981	1959	Mr. Ronald E. Ney	<i>Environmental Protection Agency</i>
1980	N/A	Dr. Stanley G. Sunderwirth	<i>Metropolitan State College (Denver, CO)</i>
1979	1973	Dr. Carl Lentz	<i>Eastman Fine Chemicals</i>

36th Annual Department of Chemistry and Biochemistry
Spring Undergraduate Research Symposium
Keynote Address

Friday, March 25, 2011 at 3:45pm
ISAT Room 159

**“Not Just a Pretty Face:
Technology Innovations in the
Paints & Coatings Industry”**



Morgan S. Sibbald (JMU Class of 1992), Ph.D.
Program Manager, External Technology & Government Initiatives
The Sherwin-Williams Company
Cleveland, OH

Dr. Sibbald received his B.S. degree in Chemistry in 1992 from James Madison University, having completed undergraduate research under the mentorship of Dr. Benjamin DeGraff. In 1997, he obtained his Ph.D. in Analytical Chemistry from Iowa State University for his dissertation work that focused on the optical properties and electrochemical behavior of surface-modified silver nanoparticles. After graduation, he worked for The Goodyear Tire & Rubber Company, Chemical Division serving in various roles including analytical chemist, synthetic polymer chemist, and product development and applications specialist for latex foam, food grade elastomers, and adhesives. In 2005, Dr. Sibbald joined The Sherwin-Williams Company as a manager of long-term paints and coatings R&D. He is currently an external technology scout responsible for creating technology development partnerships with industry, academic, and government lab resources. He also leads a government contracting program that serves to accelerate development of strategic projects. Dr. Sibbald has a particular interest in “green chemistry” and has been a champion for Sherwin-Williams’ corporate sustainability initiatives. He lives near Akron, Ohio with his wife and two children.

Oral Session I: Thursday March 24th (ISAT 259)

1:15 – 1:30	<u>Patrick J. Wiggins</u> , Kevin P. C. Minbiole, Reid N. Harris	Amphibian Chemical Defense Against the Deadly Fungus <i>Batrachochytrium dendrobatidis</i>
1:30 – 1:45	<u>Jonathan A. Boltersdorf</u> , Paul M. Forester, Barbara A. Reisner	Synthesis and Characterization of Hybrid Frameworks Derived From Poly(triazolyl)borate Ligands
1:45 – 2:00	<u>Lindsay Walton</u> , Donna Amenta, John Gilje, Glenn P.A. Yap	Study of Ruthenium Complexes with Phosphine-Phosphine Oxide Ligands and their Catalytic Behavior
2:00 – 2:15	<u>Jarvis Mitchum</u> , Gina MacDonald	The Effects of Buffers, pH, and Caged-Nucleotides on PGK Activity
2:15 – 2:30	<u>David Warnock</u> , <u>Jon Willcox</u> , Jade Irby, Robert Davis, Samuel John-Rajkumar, Daniel Rabinovich, Kevin Caran, Kevin Minbiole, Kyle Seifert	Synthesis, Colloidal, and Antimicrobial Studies on Bicephalic (Double-headed) Amphiphiles
2:30 – 2:45	<u>Kevin Kindley</u> , Hollee Kitts, Allyson Jones, Katherine Layman	Reactivity of Magnetic Iron Oxide Composites in the Oxidation of p-Cresol and Their Characterization
2:45 – 3:00	----- break -----	
3:00 – 3:15	<u>Courtney Anderson</u> , Daniel K. Havey	Construction of Distributed Feedback Diode Lasers for Applications in High-Resolution Molecular Spectroscopy
3:15 – 3:30	<u>Alan Mo</u> , Victoria L. Brown, Scott A. Paulson, Thomas C. DeVore, Wm. Christopher Hughes, Brian H. Augustine	Improving the Adhesion of Au Thin Films Onto PMMA Substrates Using Organic Solvents
3:30 – 3:45	<u>Amy Clingenpeel</u> , Barbara Reisner, Toni Bost	Progress towards the Synthesis and Analysis of $Li_{1-x}Na_xSr_3RuO_6$ ($0 \leq x \leq 1$)
3:45 – 4:00	----- break -----	

Poster Session: Thursday March 24th 4:00 – 5:00 pm (Ph/Ch 3348)

<u>Robert Brown</u> , Donna S. Amenta, John W. Gilje, Glenn P.A. Yap	Ruthenium Complexes and their Reactions with the Aminophosphine Ligand 2-(diphenylphosphino) ethylamine
<u>Victoria Brown</u> , Alan K. Mo, Scott A. Paulson, Thomas C. DeVore, Wm. Christopher Hughes, Brian H. Augustine	Spectroscopic Analysis of Poly(methyl methacrylate) Exposed to Various Organic Solvent Pre-Treatments for Enhanced Au Adhesion
<u>Evangelyn Brunson</u> , Jenny Phung, Daniel Rafferty, Bruce E. Wilcox, Christine A. Hughey	Comparison of Sample Preparation Techniques for Isolation of Beer Flavonoids Prior to LC-TOF MS Analysis

<u>Karen Corbett</u> , <u>Tiffanie King</u> , Gina MacDonald	The Effect of Salts on the Structure of the Escherichia coli in DNA Repair Protein, RecA, and on the Bulk Water Structure
<u>Brittany Danzig</u> , Nate Talley, William Cannon, Dr. Gina MacDonald	The Influence of Salts on the Unfolding of RecA-ssDNA Complexes
<u>Robert W. Davis</u> , Kevin P. C. Minbiole	Polycephalic (Multi-headed) Cationic Amphiphiles as Novel Surfactants and Antimicrobial Agents
<u>Branden Deyerle</u> , Yanjie Zhang	Specific Ion Effects on the Phase Behaviors of PEO-PPO-PEO Triblock Copolymers
Melinda Ellis, Anne Battaglia, Daniel M. Downey	Estimation of Nutrient and Sediment Loading in Lake Shenandoah, Rockingham County, Virginia
<u>Seth Ensign</u> , Amanda Hoffman, Puja Mody, Debra L. Mohler	The Synthesis of [(HOOCCH ₂ Ph-Me ₂ diimineO) ₂ BF ₂]CoBr ₂ for Ultrafast Electron Transfer Study
<u>Andrew Evangelista</u> , Michelle Rudman, Lidia Vargas-Claros, Debra L. Mohler	The Synthesis of Tripod Molecules for Ultrafast Photolysis Studies
<u>Justin Hagerman</u> , Yanjie Zhang	Synthesis and Characterization of Amino Acid Surfactants for Biomineralization and Fluorescence Studies
<u>Isaac J. Kimsey</u> , <u>Georgia T. Stoyanov</u> , Kevin P. C. Minbiole	The Construction of Azepines from Cyclopropanol Fragmentation
<u>Sadie Knight</u> , <u>Lindsay R. Walton</u> , Donna S. Amenta, John W. Gilje, Glenn P.A.Yap	Reaction of Ru(NO)Cl ₃ and Ru(NO)Cl ₃ (PPh ₃) ₂ With Ph ₂ P(CH ₂) _n P(O)Ph ₂ (n = 1, 2, or 3)
<u>Alisa Leavesley</u> , Debra L. Mohler	High Yield Synthesis of Labeled Bisphenol-A and its Polycarbonate
<u>Melissa Palmer</u> , Justin Hagerman, Yanjie Zhang	Amino Acid-Amino Acid Interactions at the Air-Water Interface
Daniel Rafferty, Brian Huffman, Evangelyn Brunson, Jenny Phung, Bruce E. Wilcox, Christine A. Hughey	Effect of Protic and Aprotic Solvents on Negative Ion Electrospray Response for a Physicochemically Diverse Group of Acidic Compounds
<u>Casey Rogers</u> , Kevin L. Caran	Demonstrations at JMU
<u>Brandon K. Rugg</u> , Daniel M. Downey	A Survey of Water Chemistry for Forest Service Trout Streams
<u>Jaleal Sanjak</u> , Victoria Mariani	Preparation for a Study of Structural and Conformational Differences Between Extremophilic and 'Normal' 5-Enolpyruvylshikimate-3-Phosphate Synthases
<u>Marco Scaramellino</u> , Victoria Mariani	The Inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS, EC 2.5.1.19) which catalyzes the penultimate step of the shikimate pathway
<u>Justin Sims</u> , Scott Lewis	Synthesis of 1,3-difluorobenzene Compounds

<u>Scott Steehler</u> , Barbara Reisner	Synthesis and Characterization of Na[BH ₂ (im) ₂] and a Nickel Coordination Compound
<u>Kyle Vasquez</u> , Anita J. Vincent-Johnson, W. Christopher Hughes, Brian H. Augustine, Giovanna Scarel	Study of surface energy transitions induced in POSS-MA polymer films by atomic layer deposited oxides
<u>Nathan Williams</u> , Daniel M. Downey	St. Mary's Acid Mitigation Project: Is it time for another dose of medicine?
<u>Megan E. Woods</u> , Thomas C. DeVore	The Thermal Decomposition of 2-Propanol Using a Zinc Sulfide Catalyst

Oral Session II: Friday March 25th (ISAT 259)

2:15 - 2:30	<u>Michael Salim</u> , <u>Ryan Byrne</u> , Michal Sabat, Kevin L. Caran	Dimeric Propargylic Alcohols and Palladium(II)Acetate: A Novel Metallogelator System
2:30 – 2:45	<u>Megan McCoy</u> , Victoria Mariani	Purification and Characterization of Inosine 5'-monophosphate dehydrogenase
2:45 – 3:00	<u>Brooke Stevens</u> , Debra L. Mohler	Synthesis of RNA Analogues
3:00 – 3:15	<u>Everett J. Estes</u> , E.M. Vess, Daniel K. Havey	Cavity Ring-down Measurement of the Temperature Dependence of the Vapor Pressure of H ₂ ¹⁸ O: Analysis and Atmospheric Implications
3:15 – 3:30	<u>Skylar White</u> , Brian Augustine	Real-Time Crystallization Kinetic Analysis of 30 wt. % POSS-MA Thin Films Using Atomic Force Microscopy
3:30 – 3:45	----- break -----	

Keynote Address: Friday March 25th (ISAT 159)

3:45 – 4:45	Dr. Morgan S. Sibbald (JMU Class of 1992)	Not Just a Pretty Face: Technology Innovations in the Paints & Coatings Industry
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Keynote Address

*Friday, March 25, 2011 at 3:45pm
ISAT Room 159*

Not Just a Pretty Face: Technology Innovations in the Paints & Coatings Industry

Dr. Morgan S. Sibbald
The Sherwin-Williams Company

Paints and coatings are generally known for serving two key functions: decoration and protection. We rely on these coatings to add color and character to our homes, to the cars we drive, and to a wide variety of other surfaces in the world around us. These coatings are also serving to protect the surfaces from a variety of environmental hazards, including moisture, UV damage, and biological growth (e.g. mold). What more can coatings do for us? Recent advances in materials and technology integration have enabled a new generation of coatings which are described as functional or “smart” coatings. Functional coatings may clean themselves, may heal themselves from damage, or may pro-actively make our indoor spaces more comfortable or more livable. At the same time, chemists must embrace the principles of ‘green chemistry’ and create more sustainable formulations. This presentation will describe the basic chemistry of paints, recent advances in materials design, and will highlight several examples of functional coatings that are improving the way we live.

STUDENT ABSTRACTS

Construction of Distributed Feedback Diode Lasers for Applications in High-Resolution Molecular Spectroscopy

Courtney Anderson and Daniel K. Havey

Department of Chemistry and Biochemistry, James Madison University

Molecular spectroscopy can have demanding instrumentation requirements. Specifically, high-resolution narrow-linewidth lasers require precision engineering and tend to be prohibitively expensive. One way to circumvent this problem is to construct lasers independently using an array of robust, inexpensive, telecommunications-grade optical components. In this work, we discuss recent efforts to fabricate five distributed feedback (DFB) diode lasers for integration with a custom photoacoustic spectrometer. These lasers were designed to measure gas-phase water, carbon dioxide, and methane. Here, we focus on hardware assembly, laser characterization, and relevant performance metrics.

Synthesis and Characterization of Hybrid Frameworks Derived From Poly(triazolyl)borate Ligands

Jonathan A. Boltersdorf,¹ Paul M. Forester,² and Barbara A. Reisner¹

¹ Department of Chemistry and Biochemistry, James Madison University

² Department of Chemistry, University of Nevada Las Vegas

Porous hybrid inorganic-organic frameworks show promise for storing hydrogen for energy applications by allowing for easy uptake and release of hydrogen. They also are capable of selectively separating carbon dioxide from industrial output wastes. Hybrid frameworks derived from poly(triazolyl)borate ligands and transition metals, alkaline earth, or alkali metals were investigated to produce functional materials for dihydrogen storage and carbon dioxide separation. A new hybrid inorganic-organic framework, Na[HB(trz)₃].DMF (1, trz = triazolate; DMF = dimethylformamide = (CH₃)₂NC(O)H) was synthesized by the recrystallization of Na[HB(trz)₃] from DMF. Compound 1 crystallizes in the noncentrosymmetric Pna2₁ space group with a highly distorted diamond (*dia*) topology. Thermalgravimetric analysis (TGA) and Evolved Gas Analysis –FTIR (EGA-FTIR) measurements indicated that the DMF solvate is lost at 180 °C; the framework decomposes at 300 °C. The ligand and resulting products were analyzed by NMR (Nuclear Magnetic Resonance), IR (Infrared Spectroscopy), and X-ray diffraction, to determine purity and structure. Ongoing work involving solvent removal and gas adsorption related to potential porosity of these materials will be discussed.

Ruthenium Complexes and their Reactions with the Aminophosphine Ligand 2-(diphenylphosphino) ethylamine

Robert J. Brown,¹ Donna S. Amenta,¹ John W. Gilje¹ and Glenn P.A. Yap²

¹ Department of Chemistry and Biochemistry, James Madison University

² Department of Chemistry and Biochemistry, University of Delaware

The aminophosphine ligand Ph₂P(CH₂)₂NH₂ (dppea) was allowed to react with RuCl₂(PPh₃)₃ and RuCl₃(NO). From the first reaction [RuCl(PPh₃)(Ph₂P(CH₂)₂NH₂)₂]⁺Cl⁻ was isolated and characterized by NMR and x-ray diffractions. The ruthenium is octahedrally coordinated with the two Ph₂P(CH₂)₂NH₂ ligands chelating such that the two phosphorus atoms are trans to one another and both cis to the triphenylphosphine. The nitrogen atom of one is trans to a chloride and the other nitrogen atom is trans to triphenylphosphine. This results in all three phosphorus atoms being non equivalent giving rise to an ABX ³¹P NMR spectrum. The product of the reaction of RuCl₃NO and Ph₂P(CH₂)₂NH₂ contains a peak at 1867 cm⁻¹ that indicates the presence of a coordinated NO. This compound is still being characterized.

Spectroscopic Analysis of Poly(methyl methacrylate) Exposed to Various Organic Solvent Pre-Treatments for Enhanced Au Adhesion

Alan K. Mo,¹ Victoria L. Brown,¹ Scott A. Paulson,² Thomas C. DeVore,¹ Wm. Christopher Hughes² and Brian H. Augustine¹

¹ Department of Chemistry and Biochemistry, James Madison University

² Department of Physics and Astronomy, James Madison University

In this study, a variety of organic solvents including chloroform, dichloromethane, chlorobenzene, toluene, hexanes, tetrahydrofuran (THF) and carbon tetrachloride were spun-cast onto samples of poly(methyl methacrylate) (PMMA). Previous work in our group has shown that chlorinated solvents significantly improve the adhesion of vapor deposited Cr/Au thin films onto PMMA substrates. The combination of evolved gas analysis Fourier transform infrared spectroscopy (EGA-FTIR) and thermogravimetric analysis (TGA) were used to characterize and detect bonding between the solvents and PMMA over a week-long study. After seven days, EGA-FTIR spectra confirmed the presence of a C-Cl (774cm^{-1}) band due to chloroform and C-Cl (758cm^{-1}) and C-H (2997cm^{-1}) bands due to dichloromethane. TGA data verified that there was a measurable mass loss of chloroform and dichloromethane after seven days. The model for Cr/Au adhesion will be further discussed.

Comparison of Sample Preparation Techniques for Isolation of Beer Flavonoids Prior to LC-TOF MS Analysis

Evangelyn Brunson, Jenny Phung, Daniel Rafferty, Bruce E. Wilcox and Christine A. Hughey
Department of Chemistry and Biochemistry, James Madison University

The principle objective of this project is to develop a LC/MS method that maximizes the number of flavonoid (antioxidant) compounds identified in beer samples. To date, we have employed several sample preparation schemes and compared the number of compounds detected by an Agilent 6224 time of flight mass spectrometer (TOF-MS). Prior to MS detection, compounds in a Green Flash West Coast I.P.A. were separated with an Agilent Eclipse Plus C18 UHPLC column and ionized by negative electrospray ionization—an ionization technique that selectively ionizes acidic compounds (e.g., phenolics and carboxylic acids). Sample preparation schemes employed prior to LC/MS analysis include de-carbonation and filtration through a $0.5\ \mu\text{m}$ filter followed by: (1) direct LC/MS analysis, (2) lyophilization, reconstitution in 96:3:1 water:methanol:formic acid, and filtration, (3) solid phase extraction (SPE) with a Supelco DPA-6S cartridge (a poly amide resin used for extracting polyphenols) and (4) SPE with a Phenomenex Strata C18-E cartridge. The number of peaks detected from sample prep methods #1 and #2 were 201 ± 3 and 168 ± 53 , respectively. Lyophilization, therefore, is not a viable sample prep technique as large quantities of sample were lost under vacuum. For the DPA-6S SPE experiment, 150 ± 55 and 148 ± 2 peaks were detected in the ethyl acetate eluate and aqueous eluate, respectively. For the C-18-E SPE experiment, 181 ± 26 and 129 ± 1 peaks were detected in the methanol and aqueous eluate, respectively. Future work will include the use of a flavonoid compound database that was developed in-house along with Mass Profiler Pro software to determine if the compounds detected in each sample were the same or different. This will enable us to determine if SPE truly yields more compositional information (e.g., 330-350 compounds) than direct analysis alone (e.g., 200 compounds).

Progress towards the Synthesis and Analysis of $\text{Li}_1-x\text{Na}_x\text{Sr}_3\text{RuO}_6$ ($0 \leq x \leq 1$)

Amy Clingenpeel,¹ Barbara Reisner¹ and Toni Bost²

¹ Department of Chemistry and Biochemistry, James Madison University

² Department of Chemistry, Salem College

The family of compounds $\text{Li}_{1-x}\text{Na}_x\text{Sr}_3\text{RuO}_6$ ($0 \leq x \leq 1$) crystallize as a 1-D metal oxide chain and the properties of these materials depend on the size of the unit cell. Crystals were grown in a silver crucible from $\text{AOH-Sr}(\text{OH})_2$ ($A = \text{LiOH}, \text{KOH}, \text{NaOH}$) at $600\ \text{°C}$ for one week. The crystals were analyzed using Powder X-Ray Diffraction (PXRD) and Atomic Absorption Spectroscopy (AAS) techniques. Powder X-ray diffraction shows a decrease in the cell constants as the amount of Li^+ in the sample increases. AAS is being used as a secondary way to measure Li^+ content. We have been developing an AAS method to analyze the crystals. Results from the analyses of the crystals will be presented.

The Effect of Salts on the Structure of the Escherichia coli in DNA Repair Protein, RecA, and on the Bulk Water Structure

Karen Corbett, Tiffanie King and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

RecA is a DNA repair protein from Escherichia coli. High concentrations of a salt have been shown to induce changes in RecA structure. Attenuated total reflectance infrared (ATR-IR) spectroscopy was utilized to study how RecA structures are altered in the presence of a variety of salts. Infrared absorbance spectra of RecA were obtained in the presence of 1M concentrations of chloride and sulfate salts that have been previously shown to alter the aggregation state of RecA. These new experiments compliment previous work and show salt-induced changes in RecA structure and aggregation. In order to determine if the salts influence bulk water structure that may influence protein structure we obtained infrared spectra on water with the same salts used for the RecA studies. These studies show that the addition of some salts alters the OH vibrations and may influence water structure.

The Influence of Salts on the Unfolding of RecA-ssDNA Complexes

Brittany Danzig, Nate Talley, William Cannon and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

The Escherichia coli RecA protein is a multifunctional enzyme that is involved in homologous recombination, DNA repair, and initiating the SOS response. RecA is typically a DNA-dependent ATPase. However, high salt concentrations are known to activate RecA mediated ATP hydrolysis in the absence of DNA. Previous experiments in our lab followed the thermally induced unfolding of RecA in various salt solutions and found that RecA stability is dependent on the concentration and nature of the salt ions present in solution. In order to better understand the nature of the salt ion-RecA interactions this study continues to monitor RecA unfolding in a broader range of salt concentrations and in the presence of single stranded DNA. Circular Dichroism (CD) was used to follow RecA unfolding in various solution conditions. The current studies show that the presence of single stranded DNA does not significantly influence the melting temperature of RecA at high salt concentrations as compared to RecA in the absence of DNA. However, RecA-ssDNA complexes in low concentrations of salts show different unfolding transitions that are more similar to RecA-ssDNA complexes in the absence of salt. The present studies help explain the concentration dependent nature of ion-RecA interactions that alter structure, aggregation and protein stability.

Polycephalic (Multi-headed) Cationic Amphiphiles as Novel Surfactants and Antimicrobial Agents

Robert W. Davis and Kevin P. C. Minbiole

Department of Chemistry and Biochemistry, James Madison University

Antibiotic resistance in bacteria has become an increasing problem worldwide, leading to the need for fast development of new antibiotics. MRSA infections have become more prevalent and more deadly due to highly resistant "super-bugs." A novel set of cationic amphiphiles were developed by Dr. Kevin Caran that show antimicrobial activity comparable to known antibiotics. The positively charged head groups interact with the slightly negative cell surface, allowing the hydrophobic carbon tail to disrupt the cell membrane. Using these structures and analyzing biological data, a new series of cationic amphiphiles were proposed and synthesized, hoping to increase effectiveness of these compounds.

Specific Ion Effects on the Phase Behaviors of PEO-PPO-PEO Triblock Copolymers

Branden Deyerle and Yanjie Zhang

Department of Chemistry and Biochemistry, James Madison University

The Hofmeister series, first noted in 1888, ranks the relative influence of ions to affect the physical behavior of a wide variety of aqueous processes ranging from colloidal assembly to protein folding. In this presentation, the effects of sodium salts with 10 anions on the phase behaviors of a poly-(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer were investigated by using an automated melting point system. It was found that the ability of anions to change the phase transition temperatures followed the Hofmeister series. Kosmotropic and chaotropic anions modulated the phase transition temperature of the polymer through separate mechanisms. Namely, kosmotropic anions salted the polymer out by changing the hydration water around the polymer, while chaotropic anions worked through binding to the hydrophobic moieties and changing the interfacial tension at the polymer/aqueous interface. Ongoing research is being conducted to investigate the effects of amino acids on the phase transition temperature of the polymer.

Estimation of Nutrient and Sediment Loading in Lake Shenandoah, Rockingham County, Virginia

Melinda Ellis, Anne Battaglia and Dr. Daniel M. Downey
Department of Chemistry and Biochemistry, James Madison University

Lake Shenandoah, located in Rockingham County, Virginia and owned by the Virginia Department of Game and Inland Fisheries, is a recreational reservoir that supports a sport fishery for warm water fish species. The lake experiences chronic fishery and aesthetic management problems due to macrophyte growth, sedimentation, and eutrophication. A study done in 1996-97 showed there was a problem with nutrient and sediment loading due to past agricultural practices and land development in the watershed. The purpose of this study was to assess the sediment and nutrient loading and to determine if it has significantly changed in the past fourteen years since the land use has changed from primarily agricultural uses to suburban development. Water quality parameters including pH, ANC, Ca²⁺, Mg²⁺, Na⁺, Cl⁻, NO₃⁻, SO₄²⁻, ammonia (NH₃/NH₄), turbidity, conductivity, and total phosphorus were measured for both feeder streams entering the lake. Results from both the lake and stream water, and sediment chemistry showed that there are excess nutrients and considerable sediment buildup in the prongs of the lake. Results have shown that Congers Creek is the greatest contributor to the eutrophication of Lake Shenandoah as it delivered 48.6% of the total phosphorus, 77.1% of the nitrate-nitrogen, 66.4% of the ammonia-nitrogen, and 48.3% of the total transported solids. Although the development has leveled off in the watershed, sediment and nutrients will continue to be delivered to the lake via the feeder streams. Data collected for this study will provide information useful for management directives for mitigation and restoration of Lake Shenandoah.

The Synthesis of [(HOOCCH₂Ph-Me₂diimineO)₂BF₂]CoBr₂ for Ultrafast Electron Transfer Study

Seth Ensign, Amanda Hoffman, Puja Mody and Debra L. Mohler
Department of Chemistry and Biochemistry, James Madison University

To better understand interfacial electron transfer behavior, [(HOOCCH₂Ph-Me₂diimineO)₂BF₂]CoBr₂ was synthesized in a multistage process. Previous work indicates that this complex can reduce the overpotential necessary in hydrogen evolution from the electrolysis of water in model hydrogen generating systems. Transient absorption femtosecond IR spectroscopy (TAFT-IR) will be used to characterize the rate of electron transfer in cobalt ligands anchored to colloidal cadmium selenium quantum dots at regular picosecond intervals. Absorption changes at wavenumbers representing the ligands to the metal complex are of particular interest due to the necessity to understand activity in this complex.

Cavity Ring-down Measurement of the Temperature Dependence of the Vapor Pressure of H₂¹⁸O: Analysis and Atmospheric Implications

Everett J. Estes, E.M. Vess and Daniel K. Havey
Department of Chemistry and Biochemistry, James Madison University

The vapor pressure of H₂¹⁸O is an important parameter in atmospheric science. Specifically, it has relevance in analysis of ice core data which helps scientists to learn about the composition of the atmosphere as a function of time. In this study, optical measurements of the vapor pressure of H₂¹⁸O were made using a cavity ring-down spectrometer interfaced with a national primary humidity standard. H₂¹⁸O line shapes were analyzed using an array of theoretical line profiles in order to extract ew(T), the temperature-dependent vapor pressure. Line shape effects were investigated in detail. A bias in the extracted vapor pressure was identified if the common Voigt profile was used for data analysis. A more comprehensive Galatry profile was required to eliminate this bias.

The Synthesis of Tripod Molecules for Ultrafast Photolysis Studies

Andrew Evangelista, Michelle Rudman, Lidia Vargas-Claros and Debra L. Mohler
Department of Chemistry and Biochemistry, James Madison University

To better understand the influence of anchoring groups on the rate of interfacial electron transfer, adamantane tripod derivatives with carboxyl methyl anchoring groups were synthesized and bonded to the perylene compound. The specific goal of this work is to create an anchoring complex for later study by femtosecond IR spectroscopy.

Synthesis and Characterization of Amino Acid Surfactants for Biomineralization and Fluorescence Studies

Justin Hagerman and Yanjie Zhang

Department of Chemistry and Biochemistry, James Madison University

Chirality is one of the most distinctive signatures of nature. Ever since Louis Pasteur discovered the existence of two non-superimposable forms of tartrate crystals, the phenomenon of chirality has inspired scientists from various fields. In this research, a series of amino acid surfactants with varying hydrocarbon chain lengths were synthesized by reacting amino acids with acyl chlorides. The amino acids studied were alanine, aspartic acid, glutamic acid, histidine, phenylalanine, tryptophan, valine, and glycine (achiral). The hydrocarbon chain lengths were six, twelve, and eighteen. Once synthesized, the amino acid acted as a hydrophilic headgroup and the long, nonpolar chain acted as a hydrophobic tail. A strong focus of the experiment was improving the percent yield by altering conditions such as concentration, pH, temperature, time, and solvent composition used for synthesis. Purified products were characterized using FT-IR and NMR spectroscopy to ensure the integrity of the synthesized material. These amino acid surfactants were employed as model systems to investigate the interactions between chiral molecules at the air-water interface and in aqueous solutions. It was found that two chiral surfactants interact differently when racemic mixture and enantiomerically pure samples presented in solutions, determined by the fluorescence of C12-L-tryptophan. These amino acid surfactants will also serve as model templates for biomineralization to understand how biomineral growth is mediated by proteins in natural systems.

The Construction of Azepines from Cyclopropanol Fragmentation

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Our group has extended a cyclopropanol fragmentation strategy previously described for the preparation of oxygenated ring systems to nitrogenous systems. The construction of azeepines (7-membered nitrogen-containing rings) has been previously developed, albeit in low and inconsistent yields at first. Our approach begins with N,N-dibenzyl-protected amino acid ethyl esters which were transformed to cyclopropanols via the Kulinkovich reaction and mono-deprotected. Resulting benzylamino cyclopropanols were then reacted with various aldehydes to form amins. Subsequently, various Lewis acids were used to promote the rearrangement of the amination into the azeepine. A variety of solvents, substituents, temperatures, Lewis acids, and purification strategies are being examined to increase the yield and reliability of azeepine formation.

Reactivity of Magnetic Iron Oxide Composites in the Oxidation of p-Cresol and Their Characterization

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In order to remove metal cations from contaminated ground water, magnetic iron oxide composites are being investigated. These composites can be supported on various ratios of NaY zeolites, aluminum oxide, and silica. A previously published procedure to synthesize these composites was varied in order to create a more effective and practical adsorbent. The composites were then characterized using IR spectroscopy, the magnetic susceptibility, and the x-ray power diffraction (XRD). In order to determine the amount of Cu^{2+} uptake by the composite, atomic absorption (AA) was used. The optimal temperature for the synthesis of these composites is 25°C. Magnetic susceptibility and Cu^{2+} uptake and the were influenced by six factors: 1) support; 2) support to iron oxide mass ratio; 3) time of iron oxide particle formation; 4) iron source; 5) stirring time; and 6) NaOH addition time. Interestingly, the support influences the degree of correlation between Cu^{2+} uptake and magnetic susceptibility. XRD data indicates that structure of NaY zeolite (SiO_2 : Al_2O_3 mole ratio = 4.9) was the least corroded during composite synthesis. These metal composites have also shown unselective reactivity in the oxidation of p-cresol to p-hydroxy benzaldehyde also known as PHBA.

Reaction of Ru(NO)Cl₃ and Ru(NO)Cl₃(PPh₃)₂ With Ph₂P(CH₂)_nP(O)Ph₂ (n = 1, 2, or 3) Sadie E. Knight,¹ Lindsay R. Walton,¹ Donna S. Amenta,¹ John W. Gilje¹ and Glenn P.A. Yap²

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Ru(NO)Cl₃(PPh₃)₂ reacts with Ph₂PCH₂P(O)Ph₂ (dppmO) or Ph₂P(CH₂)₂P(O)Ph₂ (dppeO) to form RuCl₃NO[Ph₂PCH₂P(O)Ph₂]₂ or RuCl₃NO[Ph₂P(CH₂)₂P(O)Ph₂]₂, respectively. Alternatively, RuCl₃NO[Ph₂P(CH₂)₂P(O)Ph₂]₂ forms from the reaction of Ru(NO)Cl₃·H₂O and Ph₂P(CH₂)₂P(O)Ph₂ and we have tentative evidence that RuCl₃NO[Ph₂P(CH₂)₃P(O)Ph₂]₂ forms from an analogous reaction with Ph₂P(CH₂)₃P(O)Ph₂. Depending on conditions either a mixture of RuCl₃NO[Ph₂PCH₂P(O)Ph₂]₂ and RuCl₃NO[Ph₂PCH₂P(O)Ph₂] or {RuCl₂NO[Ph₂PCH₂P(O)Ph₂]₂}⁺Cl⁻ can be isolated from the reaction between Ru(NO)Cl₃ and Ph₂PCH₂P(O)Ph₂. The cation, {RuCl₂NO[Ph₂PCH₂P(O)Ph₂]₂}⁺ is also observed when RuCl₃NO[Ph₂PCH₂P(O)Ph₂]₂ is allowed to react with AgBF₄. The AgBF₄ reaction with RuCl₃NO[Ph₂P(CH₂)₂P(O)Ph₂]₂ is more complex. Preliminary NMR results indicate that several products result. Among these is one in which NO is lost and the ruthenium is oxidized to Ru(III): {RuCl₂[Ph₂P(CH₂)₂P(O)Ph₂]₂}⁺BF₄⁻. This is the first example in which a Ph₂P(CH₂)₂P(O)Ph₂ ligand chelates a ruthenium.

All complexes have been characterized by IR, NMR, and, in several cases, by x-ray crystallography.

High Yield Synthesis of Labeled Bisphenol-A and its Polycarbonate

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Bisphenol A and polycarbonate were synthesized using a variety of methods in order to optimize the synthesis of each compound. The overall goal of this work is to synthesize labeled polycarbonate to analyze the structure of blended tri-p-tolylamine and polycarbonate using solid state NMR.

Purification and Characterization of Inosine 5'-monophosphate dehydrogenase

Megan McCoy and Victoria Marian

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Inosine 5'-monophosphate dehydrogenase (IMPDH) catalyzes the rate-limiting step in the biosynthetic pathway for guanine ribonucleotide production. IMPDH is found in almost all living organisms corresponding with guanine nucleotides being essential for cellular proliferation. If a way to inhibit IMPDH can be found then cellular proliferation, in theory, could be stopped in tumors leading IMPDH inhibitors to be possible anticancer and antiviral drugs. Mesophilic (growth between 15 and 40°C), thermophilic (growth between 60 and 80°C), and psychrophilic (growth below 15°C) IMPDH will be cloned and then tested for both activity through assays and structural stability in variable environments through circular dichroism (CD). Information collected can be used to design inhibitors to disrupt IMPDH structure.

The Effects of Buffers, pH, and Caged-Nucleotides on PGK Activity

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3-Phosphoglycerate Kinase (PGK) is a potential drug target for combating protozoan parasites that cause diseases such as sleeping sickness and leishmaniasis (Blattner, J. et. al. (1995) *PNAS*, 11596-11600). PGK is the first ATP- producing enzyme in glycolysis. PGK is a two-domain "hinge-bending" enzyme, that catalyzes the reversible phospho-transfer between 1,3-bisphosphoglycerate (1,3-bPG) and ADP to form ATP and 3-Phosphoglycerated (3-PG). We determined rates for the reaction converting ATP and 3-PG to 1,3-bPG and ADP using an enzyme-coupled assay. Different Buffers (Hepes and MES) and different pH levels (7.5, 6.5, and 5.5) were studied to determine if PGK activity is directly influenced by solution conditions. PGK activity was studied to determine if the nucleotides competed for active sites. Activity assays were performed in the presence of the caged nucleotides (caged-ADP and caged-ATP) to determine if they inhibit substrate binding. The activity assays suggest that the caged-ADP competed with the PGK substrate binding sites to inhibit phospho-transfer while the caged-ATP inhibition was dependent on solution at all pH. The activity

assays confirm that PGK activity increases from pH 5.5 to 7.5 and is increased in Hepes as compared to MES Buffer.

Improving the Adhesion of Au Thin Films Onto PMMA Substrates Using Organic Solvents

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One of the recent trends in microfabrication technologies is to produce devices such as flat panel displays, sensors, photovoltaic and lab-on-a-chip devices on polymeric substrates. The deposition of metal thin films is a critical component in the processing of these devices. In particular, vapor deposited Au thin films are widely used in many of these technologies. The properties that make gold useful are its corrosion resistance, high infrared reflectivity, and outstanding electrical and thermal conductivity (~11% and ~34% better than Al, respectively). Unfortunately, gold is a relatively inert metal that has notoriously poor adhesion to polymers. The techniques to improve Au thin film adhesion (e.g. chemical etching, corona discharge, plasma treatment, and irradiation) have resulted in limited success. In this study, there was a 72% improvement in Au thin film adhesion when poly(methyl methacrylate) (PMMA) was spun-cast with chloroform prior to metal deposition. Physical adhesion was measured through scotch-tape tests and corresponding image analysis. The altered PMMA surfaces was characterized through, atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), evolved gas analysis FTIR (EGA-FTIR), thermal gravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS). Experiments with solvents spun-cast onto PMMA suggest that a positive correlation exists between solvent polarity and percent gold adhesion. After samples were put into an ultra-high vacuum chamber, a positive correlation was noted between the solvent's acidic nature and percent gold adhesion. Recently, we've found that exposing PMMA to saturated chloroform gaseous environment has a similar effect as spin-casting solvents onto PMMA.

Amino Acid-Amino Acid Interactions at the Air-Water Interface

Lelissa Palmer, Justin Hagerman and Yanjie Zhang

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Amino acid surfactants were employed as a model system to understand amino acid-amino acid interactions at the air-water interface. Specifically, N-stearoyl-glutamic acids with different chiralities (L-, D-, and DL-) were spread at the air-water interface on subphases containing varying concentrations of arginine at pH 5. The change in mean molecular area of N-stearoyl-glutamic acid at certain surface pressures as a function of arginine concentration is used to quantify the interaction between glutamic acid and arginine. It was found that N-stearoyl-glutamic acids with different chirality displayed varied affinity to arginine.

Effect of Protic and Aprotic Solvents on Negative Ion Electrospray Response for a Physicochemically Diverse Group of Acidic Compounds

Daniel Rafferty, Brian Huffman, Evangelyn Brunson, Jenny Phung, Bruce E. Wilcox, Christine A. Hughey; Department of Chemistry and Biochemistry, James Madison University

Negative ion electrospray (ESI) is widely used to ionize acidic compounds for MS detection, yet the mechanisms of ionization are not well understood due to the many variables that affect ionization. Here we present results from the first phase of a multi-phase study that aims to gain a better understanding of how solution conditions affect negative ion ESI response for a group of 30 physicochemically diverse compounds and, thereby, gain a better understanding of the mechanisms of ionization. Specifically, we compare the response of acidic analytes in protic (water, methanol) and aprotic (acetonitrile, acetone) solvents through flow injection experiments conducted on an Agilent 6460 triple quadrupole mass spectrometer with a jet stream ESI source. Previous work by others suggested that nonpolar character ($\log P$) of a molecule is a better predictor of negative ion response than acidity, as nonpolar compounds favor the surface of the ESI droplet where they are more efficiently converted to gas phase ions. Our data support these results as carboxylic acids exhibited a lower response than less acidic compounds such as phenolics. However, our data set, which is more comprehensive than what has been used in other ESI studies, demonstrates that $\log P$ alone does not predict negative ion response. Stearic acid, a straight chain n-carboxylic acid with a pKa of 4.78 and significant nonpolar character ($\log P = 7.83$), exhibited a lower ESI response than phenolic compounds with lower $\log P$ values. In addition, our preliminary data demonstrates the important role of solvent. The response of acids was greatly improved with methanol compared to acetonitrile. Stearic acid exhibited a ~200X improvement! However, little gain was observed for the phenolics that already produced a high response. The enhanced acid

responses in methanol (a protic solvent) are likely due to its ability to solvate and stabilize negative ions.

Demonstrations at JMU

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All novel and established chemistry demonstrations within the department were organized into handouts, which give instructions on how to do each demonstration. Lesson plans and problem sets were also developed for selected demonstrations to increase the appeal of doing demonstrations in the classroom. The handouts, lesson plans, problem sets, and an appendix were compiled into a handbook. The handbook was formatted into a demonstration website for ease of access in the department as well as externally. Internally, "Demo Kits" were assembled to provide instructors with the ability to easily perform a demonstration in class without the hassle of preparing and gathering the materials. A demonstration workshop was held for 12 high school teachers as a way to positively impact communities beyond JMU. Current endeavors include further developing our online resources to include information about Virginia Standards of Learning (SOL) coverage for each demonstration.

A Survey of Water Chemistry for Forest Service Trout Streams

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Ninety-one streams in the George Washington and Jefferson National Forests were sampled during the late winter and early spring of 2010 for water chemistry assessment. Streams were selected and samples collected by personnel from the various US Forest service districts. All the streams were located in the valley and ridge geophysical province of Virginia and ranged from the West Virginia border area in northwestern Virginia to near the Tennessee border in southwestern Virginia. All streams were perennial, but varied in size from small spring creeks to third order. Water chemistry parameters included pH, acid neutralization capacity (ANC), conductivity, and sodium, potassium, magnesium, calcium, chloride, sulfate, nitrate and aluminum concentrations. Range values for these parameters were: pH 4.52 to 8.28; ANC -27.7 to 2729 $\mu\text{eq/L}$; conductivity 12.6 to 293. $\mu\text{S/cm}$; Na^+ 12.5 to 169. $\mu\text{eq/L}$; K^+ 6.4 to 28.2 $\mu\text{eq/L}$; Mg^{2+} 18.1 to 304. $\mu\text{eq/L}$; Ca^{2+} 26.1 to 3703. $\mu\text{eq/L}$; Cl^- 10.8 to 289. $\mu\text{eq/L}$; SO_4^{2-} 12.4 to 393. $\mu\text{eq/L}$; NO_3^- 0.2 to 33.7 $\mu\text{eq/L}$; Al^+ ND to 533 $\mu\text{g/L}$. The water chemistry for each stream was evaluated based on the type of bed rock geology and land use in the stream's watershed. These data will be used for future Forest Service projects including acid precipitation mitigation, timber cutting, controlled burns and other activities.

Dimeric Propargylic Alcohols and Palladium(II)Acetate: A Novel Metallogelator System

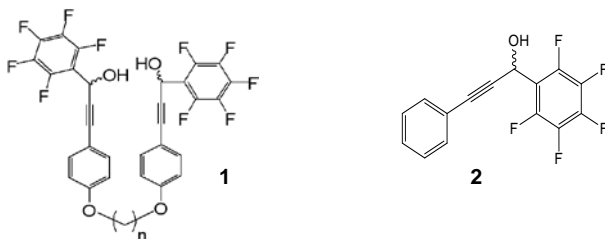
Michael A. Salim,¹ Ryan M. Byrne,¹ Michal Sabat² and Kevin L. Caran¹

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We report the synthesis and preliminary study of dimeric propargylic alcohols (**1**) that interact with palladium (II) acetate to gel organic liquids. Four derivatives, varying in linking chain length ($n = 6, 8, 10, 12$), were synthesized and initially tested for gelation capacity without the inclusion of metals. The compounds failed to gel organic liquids and inhibited gelation of the monomeric derivative (an otherwise efficient gelator) in quantities as low as 0.4% by mass. When mixed with two molar equivalents of $\text{Pd}(\text{OAc})_2$, the 6 and 10 carbon linking-chain alcohols formed robust gels in dichloromethane. Structural studies with scanning electron microscopy (SEM) and small angle x-ray scattering (SAXS) suggested the formation of lamellar aggregates with a regular 14 Å spacing. Metallogelation studies of the dimeric propargylic alcohols with different metals, solvents, and linking chain structures will be presented.

In order to study this novel metallogelator system, the more fundamental metal-monomer interaction has been explored. Preliminary ^1H and ^{13}C NMR experiments suggest Pd^{2+} coordination by the propargylic alcohol (**2**) and partial oxidative cleavage of the sp-sp^3 carbon bond. A gradual darkening of the $\text{Pd}(\text{OAc})_2$ – alcohol solutions was observed, and its quantification by UV-VIS spectroscopy will be discussed.



Preparation for a Study of Structural and Conformational Differences Between Extremophilic and 'Normal' 5-Enolpyruvylshikimate-3-Phosphate Synthases

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The shikimate pathway, which links the metabolism of carbohydrates to aromatic amino acid biosynthesis, is only found in plants, fungi, and bacteria. Because of this aforementioned exclusivity, EPSP synthase is a promising target for antibiotic, antiparasitic, and herbicide development. Through structural characterization of thermophilic, mesophilic, and psychrophilic EPSP synthases, we hope to elucidate which particular moieties outside of the active site are pivotal to function. The *aroA* gene encodes for the expression of 5-Enolpyruvylshikimate-3-phosphate (EPSP) synthase which catalyzes the reversible reaction forming EPSP from shikimate-3-phosphate (S3P) and phosphoenolpyruvate (PEP) in the sixth step of the shikimate pathway. S3P is synthesized via Shikimate Kinase, the product of the *aroK* gene, which catalyzes the reversible reaction for making S3P from shikimic acid and ATP in the fifth step of the shikimate pathway. Shikimic acid can be purchased for ~\$83/g while S3P can be purchased for ~\$194/mg. Here we report successful cloning of the *aroA* gene from cDNA libraries of *Thermus thermophilus*, *Colwellia psycherythaea* as well as the cloning of both the *aroA* and *aroK* genes from *Escherichia coli* into pET SUMO Vector with His-tag. The enzymes are purified via DEAE anion exchange and Nickel(II) affinity chromatography. All actions proceed towards the ultimate goal of performing structural and kinetic analysis on the various EPSP synthases.

The Inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS, EC 2.5.1.19) which catalyzes the penultimate step of the shikimate pathway

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The herbicide Round Up™ inhibits the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS, EC 2.5.1.19) which catalyzes the penultimate step of the shikimate pathway which is used in plants and bacteria to help create the aromatic amino acids: phenylalanine, tyrosine, and tryptophan. In addition, to herbicides, EPSPS is considered a prospective target for the development of novel antibiotics. *Escherichia coli* cells containing a plasmid with DNA that encodes for EPSPS were grown and induced with IPTG (Isopropyl β-D-1-thiogalactopyranoside) to express protein. The protein was collected and loaded on a nickel affinity column. A dialysis was run in an effort to exchange the buffer solution of the protein, and this pure sample was tested for activity and loaded on SDS-PAGE.

Synthesis of 1,3-difluorobenzene Compounds

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The synthesis 1,3-difluoro-2-isopropylbenzene and 1-isopropyl-2,4-fluorobenzene were undertaken through a one pot synthesis with isopropylcyclobutene and a phenyl trifluoromethyl mercury carbene reagent. Purification and characterization are currently underway through column chromatography and GCMS, ¹H NMR, ¹³C NMR, and ¹⁹F NMR.

Synthesis and Characterization of Na[BH₂(im)₂] and a Nickel Coordination Compound

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In an attempt to produce hybrid inorganic-organic frameworks derived from poly(imidazolyl)borate ligands, sodium dihydrobis(imidazolyl)borate, Na[H₂B(im)₂], was synthesized by reacting NaBH₄ in an imidazole flux under N₂. A nickel coordination compound of unknown composition was synthesized through a solvothermal reaction between Na[BH₂(im)₂] and nickel(II) acetylacetonate yielding yellow octahedral crystals. The techniques of NMR, FT-IR, single crystal X-ray diffraction, powder X-ray diffraction, thermogravimetric analysis, evolved gas analysis-IR, and elemental analysis have been used to help identify the identity of the nickel coordination compound.

Characterization of $\text{Na}[\text{BH}_2(\text{im})_2]$ with these methods, and our current structural model for the nickel coordination compound will be presented.

Synthesis of RNA Analogues

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The synthesis of stable RNA analogues that can bind via Watson-Crick base pairing is a goal of therapeutic siRNA treatments. One method of synthesis of the RNA analogues is using a single step polymerization. Advances in the synthetic approaches using ring opening metathesis on synthetic monomers will be discussed in this paper.

Study of surface energy transitions induced in POSS-MA polymer films by atomic layer deposited oxides

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The surface properties of polymers such as polyhedral oligomeric silsesquioxane methacrylate [POSS-MA] can be altered to tailor surface wetting, biofouling and electroosmotic flow characteristics for use in microfluidic devices through atomic layer deposition (ALD). ALD is a chemical means to deposit thin films on substrates ranging from metals to polymers. The use of low temperature ALD allows for the coating of polymers such as POSS-MA without degradation. By varying the growth temperature and number of ALD cycles a broad variety of growth conditions can be exploited. POSS-MA coated silicon samples were used to grow amorphous Al_2O_3 of 5, 20, 40 and 60 cycles at reaction temperatures of 40, 60 and 90 °C. Contact angle measurements confirmed that the transition from hydrophobic to hydrophilic lies between 20 and 40 cycles for all the temperatures tested and the hydrophilicity was observed to be higher for the samples that were coated at higher temperatures. Fourier transform infrared (FTIR) spectroscopy measurements have shown that the characteristic peaks of POSS-MA at $1050\text{-}1218\text{cm}^{-1}$ (Si-O-Si), $1700\text{-}1760\text{cm}^{-1}$ (C=C) and $2800\text{-}3040\text{cm}^{-1}$ (CH_2 , CH_3) remain unchanged after the deposition process proving that the ALD process does not change the intermolecular bonds between the polymer. A broad -OH peak and the peaks associated with Al_2O_3 were observed on the a- Al_2O_3 coated polymer films. It is believed that these new peaks contribute to the increased hydrophilicity.

Study of Ruthenium Complexes with Phosphine-Phosphine Oxide Ligands and their Catalytic Behavior

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$\text{RuCl}_3\text{NO}(\text{PPh}_3)_2$ reacts with two equivalents of $\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2$ (dppmO) or $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ (dppeO). In these reactions both triphenylphosphines are replaced with ligand. $\text{RuCl}_3\text{NO}[\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2]_2$ and $\text{RuCl}_3\text{NO}[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2]_2$ were characterized with IR and NMR spectroscopy, as well as x-ray crystallography. The complexes are octahedral with the two coordinated ligands trans to one another, displaying AA'XX' spin systems. Coupling constants and chemical shifts were determined by simulations using Spinworks. Both complexes can also be synthesized by heating two equivalents of ligand with one equivalent of $\text{RuCl}_3\text{NO}\cdot\text{H}_2\text{O}$. A chloride can be abstracted from $\text{RuCl}_3\text{NO}[\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2]_2$ when reacted with AgBF_4 . NMR spectra indicate that the removal of a chloride allows the phosphoryl oxygen of the ligand to coordinate to the open site. A complex containing the same cation can be synthesized by reaction of a 2:1 molar ratio of dppmO to $\text{RuCl}_3\text{NO}\cdot\text{H}_2\text{O}$ at room temperature. Both products have been characterized using IR and NMR spectroscopy, and x-ray crystallography in the case of the $\text{RuCl}_3\text{NO}\cdot\text{H}_2\text{O}$ reaction. Crystals of $\text{RuCl}_2[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2]_2^+\text{BF}_4^-$ were obtained from the reaction of $\text{RuCl}_3\text{NO}[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2]_2$ and excess AgBF_4 . In this reaction NO is abstracted and Ru(II) is oxidized to Ru(III). Preliminary ^{31}P data indicates that there are other products in this reaction. The differences in catalytic abilities of these complexes have yet to be determined.

Synthesis, Colloidal, and Antimicrobial Studies on Bicephalic (Double-headed) Amphiphiles

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³ Department of Chemistry, The University of North Carolina at Charlotte at Charlotte

A series of bicephalic (double-headed) biscationic amphiphiles with two cationic heads, an aromatic spacer, and a single hydrophobic tail were synthesized. The orientation of the hydrocarbon tail relative to the normal of the aggregate interface was altered by changing the location of the head groups on the aromatic ring. The head groups were located in the 2,3-, 2,4-, 2,6-, and 3,5- positions. The critical micelle concentration (CMC) was determined using conductivity and proton nuclear magnetic resonance spectroscopy (¹H NMR). Minimal inhibitory concentration (MIC) and minimal bactericidal concentration (MBC) of the derivatives was determined. The effect of cationic architecture on colloidal and antimicrobial properties was investigated by synthesizing 2,3- and 3,5- derivatives with pyridinium and imidazolium head groups. NMR experiments show slow, moderate, and fast exchange kinetics relative to the NMR timescale.

Real-Time Crystallization Kinetic Analysis of 30 wt. % POSS-MA Thin Films Using Atomic Force Microscopy

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Poly(propylmethacrylisobutyl POSS co-methylmethacrylate) (POSS-MA) is a co-polymer that contains polyhedral oligomeric silsesquioxane (POSS) cages co-polymerized to a poly(methyl methacrylate) (PMMA) backbone. 2 mg/mL of 30 wt.% POSS-MA is dissolved in chloroform and deposited onto samples of oxidized Si wafers using spin casting. Immediately after spin casting, these samples are analyzed using atomic force microscopy (AFM) over the course of approximately 8-10 hours while being heated in a range of 25-45° C. After approximately 2 hours, a typical sample exhibits the first sign of dendritic crystallization growth. Once this crystallization is complete, the pixel areas of the dendritic structures are measured using the AFM software on the complete time-series of AFM scans. These varying area determinations are normalized and then fit to the Avrami plot by graphing $\ln(-\ln(1-f))$ vs. $\ln(\text{time})$ with "f" being the normalized area and the time being the time after deposition. From this graph, the resulting slope is the dimensionality of growth constant and the y-intercept is the natural logarithm of the diffusion constant. Data shows the dimensionality of growth constant to vary from 1.72 to 2.15 and the natural logarithm of the diffusion constant to vary from -9.02 to -14.14 when the scan is conducted at 35° C. This data is consistent with the literature values of two dimension crystallization kinetics in polymer thin films.

Amphibian Chemical Defense Against the Deadly Fungus *Batrachochytrium dendrobatidis*

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Decades of global climate change, pollution, and deforestation have led to worldwide amphibian decline. However, an additional factor identified in 1998, known as the deadly fungal pathogen *Batrachochytrium dendrobatidis*, continues to plague lake and mountainside habitats of frogs and salamanders. In remote populations of amphibians that do survive, cutaneous bacteria defend amphibians by inhibiting the chytrid fungus. Of the flora present on the amphibian skin, *Pedobacter cryoconitis*, *Chryseobacterium* spp., *Pseudomonas fluorescens*, *Lysobacter gummosus*, and *Janthinobacterium lividum* show anti-fungal properties through anti-microbial metabolites. Previous research has shown that *Janthinobacterium lividum* produces indole-3-carboxaldehyde (MIC=68.9 μM) and violacein (MIC=1.82 μM) while *Lysobacter gummosus* produces 2,4-diacetylphloroglucinol (IC50=7.54 μM). Using similar models to isolate and identify these anti-fungal metabolites, research is underway to determine the anti-chytrid metabolites of *Pedobacter cryoconitis* and *Chryseobacter* spp. In order to successfully identify anti-microbial metabolites from cutaneous bacteria, tests utilizing a 96 well-plate were run to isolate different anti-chytrid metabolites produced by *Pedobacter cryoconitis* and *Chryseobacterium* spp. Metabolites from these two bacteria were separated into fractions through High Performance Liquid Chromatography as a preliminary step. B.d. zoospores were harvested in 1% tryptone broth in a 96 well-plate. Next the metabolite fractions, dissolved in DMSO and sterile deionized water, were added. Resulting differences in absorbance, indicative of anti-chytrid activity, distinguishes metabolite efficacy. ¹H-NMR, ¹³C-NMR, UV-Vis analysis, and mass

spectroscopy are next used for chemical structure identification. When identified and isolated, these anti-fungal metabolites will serve as a basis for further bioaugmentation of amphibian species in hopes of finding a cure against the deadly B.d. pathogen.

St. Mary's Acid Mitigation Project: Is it time for another dose of medicine?

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This presentation will address the longevity of limestone applications in the St. Mary's Wilderness, Augusta County, Virginia and the process of data collection and interpretation used to predict the need for retreatment. Water samples were collected at various time intervals from 1999-2010 and analyzed for pH, acid neutralizing capacity (ANC), base metal cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), major acid anions (Cl^- , SO_4^{2-} , NO_3^-) and aluminum (Al) concentrations. The resultant chemical data supplemented biological data for fish, amphibians and aquatic insects. On March 20, 1999 and November 4, 2005 the St. Mary's River and six of its tributaries were treated with 140 and 230 tons of limestone, respectively, (>99% CaCO_3) delivered by helicopter. Intensive water chemistry monitoring was conducted for the initial (1999) liming project, but due to budget limitations, limited water chemistry data were collected subsequent of the second (2005) liming. For the initial liming project, twenty-two samples were taken on a quarterly basis at locations in the watershed both upstream and downstream of the liming sites from January 1999 until April 2005. In addition, three sample locations (one at St. Mary's and two at control streams) were monitored weekly. For the six year period following the first liming (1999-2005) key water chemistry parameters for St. Mary's River increased with pre-liming averages to post-liming averages as follows: pH 5.36 ± 0.22 to 6.05 ± 0.51 ; ANC -9.1 ± 7.9 to 23.8 ± 29.3 $\mu\text{eq/L}$; calcium/hydronium ratios 5.1 ± 2.9 to 83.5 ± 101 ; calcium/magnesium ratios 0.7 ± 0.03 to 1.6 ± 0.6 . As a result of the increased pH, aluminum concentrations decreased from 78 ± 32 to 52 ± 40 ppb during this period. Other strong acid anions and base metal cations did not significantly change. The pH, ANC, calcium/hydronium ratios and calcium/magnesium ratios increased as a result of the limestone treatment. These data were used to develop the second liming project and to produce a predictive model for limestone treatment applications. In 2010, data were collected to provide an estimate on how soon re-liming will be necessary. From these data and the model for limestone consumption a third limestone treatment has been recommended to be implemented by 2012.

The Thermal Decomposition of 2-Propanol Using a Zinc Sulfide Catalyst

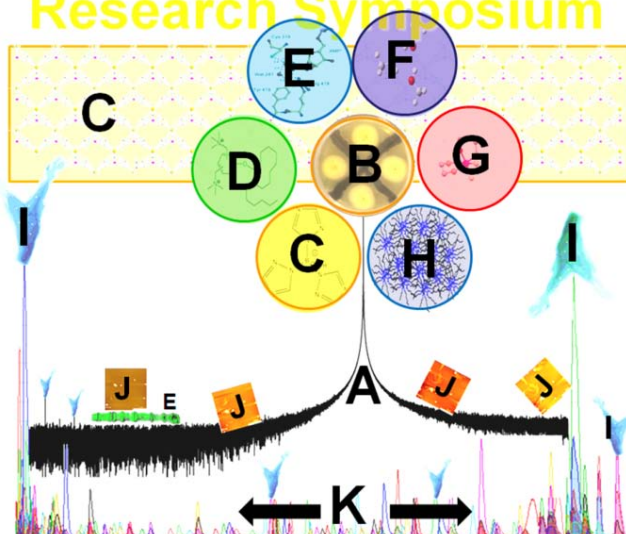
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In an effort to create a hydrogen source, the thermal decomposition of 2-propanol over a zinc sulfide catalyst was investigated. The reaction produced hydrogen gas and acetone at temperatures between 500K and 600K with masses of zinc sulfide catalyst between 0.2932 g and 0.7097 g. The activation energy and A factor found were found to be 66 kJ/mol and approximately 1.3×10^5 $\text{mmol}^{-2} \text{s}^{-1}$ for a conversion factor of 0.2 respectively. The data was fit using the mechanism reported by Rioux *et al* [1]. The activation energy for the reaction step is 84 ± 5 kJ/mol and ΔH_{ads} and ΔS_{ads} for the adsorption of isopropanol on ZnS were found to be 20 ± 5 kJ/mol and $-35 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. While mass of the catalyst did not affect the activation energy, it lowered the temperature needed to completely convert the 2-propanol to acetone.

1. Rioux, R. M.; Vannice, M. A. Hydrogenation/dehydrogenation reactions: Isopropanol dehydrogenation over copper catalysts *Journal of Catalysis* **2003**, *216*, 362-376.

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