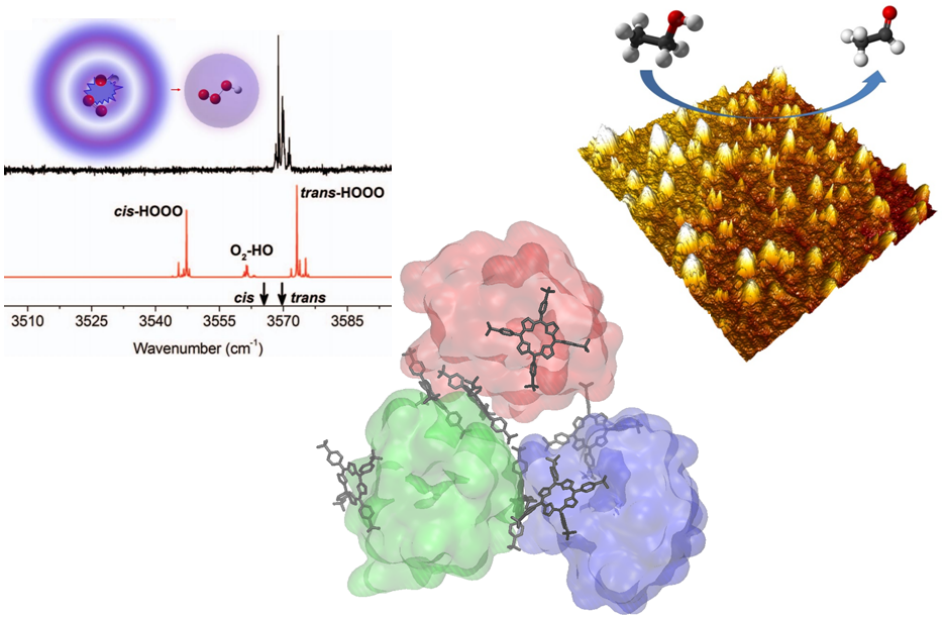
JAMES MADISON UNIVERSITY®

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY



41ST ANNUAL SPRING UNDERGRADUATE RESEARCH SYMPOSIUM

THURSDAY APRIL 14, 2016

ORAL SESSION I: 2:00 – 4:00 PM (HHS 2210)

POSTER SESSION: 4:30 – 5:30 PM (PHYS/CHEM LOBBY)

FRIDAY APRIL 15, 2016

ORAL SESSION II: 1:15 – 3:15 PM (PHYS/CHEM 2212)

KEYNOTE ADDRESS: 3:30 – 4:30 PM (ISAT 159)

See back cover for image description.

The 41st Annual Department of Chemistry and Biochemistry Spring Undergraduate Research Symposium is dedicated to the memory of our dear friend and colleague

Dr. Benjamin A. DeGraff, Jr.

December 23, 1938 - December 18, 2015

It is not an exaggeration to suggest that Professor Emeritus Benjamin A. DeGraff, who died in December, was largely responsible for making the chemistry department what it is today. As department head from 1972 to 1978, he recruited new faculty to teach and to do research in all the major areas of chemistry, led the process that resulted in certification by the ACS, and was the first faculty member who provided stipends to students for summer research. Perhaps most significantly, he accomplished all this while leading departmental efforts to maintain collegiality, an exemplary balance between teaching and research, and a dedication to undergraduate education.

Ben also distinguished himself at the university level. Under his leadership, the department established the university's first educational leave program, and in 1977 he was the first JMU faculty member to be awarded a Fulbright scholarship.

After stepping down as head, Ben continued a vigorous research program, often with student collaborators, that yielded more than 120 publications. He developed the department's laser course and, for ten years, received NSF funding to bring 130 college faculty members from 40 states to JMU to learn how to introduce the new technology on their campuses. In 2002, some of those faculty members recognized Ben's efforts in a symposium at the annual national meeting of the ACS.

Ben was truly a gentleman and a scholar. He always led by example and generously shared the credit for many of his accomplishments with his colleagues. Those of us who were privileged to know him and to work with him will always miss him, but we know that his influence will live on for as long as chemistry is done at JMU.

41st Annual Department of Chemistry and Biochemistry
Spring Undergraduate Research Symposium

Keynote Speaker

Dr. Reid Gadziala, Pharm.D., BCNP, MBA

(JMU Class of 2007)

Cleveland Clinic
Cleveland, OH

Dr. Gadziala graduated from the JMU Department of Chemistry in 2007 and immediately proceeded to receive both his Doctorate of Pharmacy and MBA in 2011 at the Medical College of Virginia and School of Business at Virginia Commonwealth University. Upon completion, further specialization was obtained as an authorized user of nuclear isotopes through the University of New Mexico. The first three years of employment were spent developing drugs utilizing low-energy radioisotopes with Radiology Services of Northern Virginia, and assisting in opening the newest lab for Triad Isotopes in Richmond, VA. In 2015, Dr. Gadziala was recruited by PETNET Solutions to direct the high-energy nuclear lab at the Cleveland Clinic. Additionally in 2015, Dr. Gadziala completed his board certification in nuclear pharmacy through the Board of Pharmaceutical Specialties. His passions include teaching/mentoring students and traveling every chance he gets. Through all his schooling and professional development, he attributes his success to the preparation obtained at James Madison, and gets back here as often as possible to check in on his Alma Mater!

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 Spring Symposium.

Year	JMU Class	Speaker	Affiliation
2016	2007	**Dr. Reid Gadziala**	*Cleveland Clinic*
2015	1994	**Dr. Michael Leopold**	*University of Richmond*
2014	1996	**Dr. Dana McGraw Dattelbaum**	*Los Alamos National Laboratory*
2013	1999	**Dr. Christy Vestal Martin**	*Vorbeck Materials*
2012	1994 N/A	**Dr. Melissa C. Rhoten** **Dr. Orde Q. Monro**	*Longwood University* *University of KwaZulu-Natal*
2011	1992	**Dr. Morgan S. Sibbald**	*The Sherwin-Williams Company*
2010	1988	**Dr. Kevin Morris**	*Carthage College*
2009	1988	**Dr. Chris E. Holmes**	*The University of Vermont College of Medicine*
2008	1995	**Dr. Jonathan Dattlebaum**	*University of Richmond*
2007	1987	**Dr. Elizabeth Perry (M.D.)**	*Signature Healthcare, Inc.*
2006	1967	**Dr. Carolyn Abitbol (M.D.)**	*University of Miami (FL) School of Medicine*
2005	1975 1976	**Dr. Daniel Downey** **Dr. Gary Rice**	*James Madison University* *College of William and Mary*
2004	1987	**Dr. James (Dusty) Baber**	*National Institutes of Health*
2003	1984	**Dr. Fred King**	*West Virginia University*
2002	1977	**Dr. Roger Bertholf**	*University of Florida School of Medicine*
2001	1979	**Mrs. Katheryn Lam**	*International Business Machines*
1999	1987	**Dr. Jose Madalengoitia**	*University of Vermont*
1997	1986	**Dr. Fred R. Kinder**	*Novartis Research Institute*
1996	1976	**Dr. Terry O. Trask**	*DuPont Chemicals*
1995	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*
1994	1990	**Dr. Michele A. Kelly**	*University of Maryland Baltimore County*
1993	1985	**Dr. Cynthia K. Fallon**	*DuPont Chemicals*
1992	1983	**Dr. Laurie Locascio**	*National Institute of Standards and Technology*
1991	1983	**Dr. Noreen Naiman**	*North Carolina School of Science and Mathematics*
1990	1982	**Dr. Matthew T. Stershic**	*Atomchem North Amercia*
1989	1982	**Dr. Michael Kinter**	*Cleveland Clinic Lerner Research Institure*
1988	N/A	**Dr. Thomas J. Meyer**	*Los Alamos National Laboratory*
1987	1980	**Dr. Steven Davis**	*Naval Research Laboratory*
1986	1980	**Dr. Steven A. Hackney**	*Michigan Technological University*
1983	1978	**Dr. Richard B. Lam**	
1982	1975	**Dr. Daniel Downey**	*West Virginia University*
1981	1959	**Mr. Ronald E. Ney**	*Environmental Protection Agency*
1980	N/A	**Dr. Stanley G. Sunderwirth**	*Metropolitan State College (Denver, CO)*
1979	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*

Oral Session I: Thursday April 14th (HHS 2210)		
2:00 pm	Kathleen T. Krist, Harry Hu, Brian H. Augustine, Wm and Dr. Christopher Hughes	Utilizing Chloroform Post-Treatment to Improve the Adhesion of Au Thin Films onto PMMA
2:15 pm	Daniel Marzolf, Aidan M. McKenzie, C. Alexander Hudson and Dr. Oleksandr Kokhan	Multimerization of Solution State Proteins by Water Soluble Porphyrins
2:30 pm	Rachel A. Policke, Dr. Chris E. Berndsen, and Dr. Nathan T. Wright	Re-examination of the Structure and Elasticity of the Titin Ig65-70 Segment and Its Comparison to Obscurin Ig58-59
2:45 pm	Alexandra M. Moore, Jessica L. Shott and Dr. Brycelyn M. Boardman	Polymerization and Characterization of Functionalized Palladium Complexes with Benzothiadiazole Co-monomers
3:00 pm	Hunter Wilson and Dr. Isaiah Sumner	Investigating the Hydrogen Bonding Environment of Gcn5 utilizing Molecular Dynamics Simulations
3:15 pm	Kirstie Thompson, Elizabeth A. Rogers, Dr. Kyle Seifert and Dr. Kevin Caran	The Effect of Hofmeister Series Counterions on the Colloidal and Antimicrobial Properties of Triple-Headed Cationic Amphiphiles
3:30 pm	Emily A. Todd, Dr. Reuven Wiener, and Dr. Christopher E. Berndsen	Structural and computational study of Ufm1
3:45 pm	Tye S. Thompson, W. Tyler Price, Anthony P. Allsbrook and Dr. Yanjie Zhang	Cation Effects on Caffeine Partitioning Thermodynamics

(Student presenters underlined)

(See next page for Thursday poster presentations.)

Poster Session: Thursday April 14th 4:30 – 5:30 pm *(Phys/Chem lobby)*	
Kevin Pyszka and Dr. Daniel M. Downey	Stream Acid Mitigation Plan for Two Jefferson National Forest Streams
Robert J. Sherman, Dr.John Gilje, Dr. Donna Amenta, Cristian Hrib and Frank Edelmann	Preparation of Ruthenium Complexes of N-Triazolylpropanamide Derivatives
Julia E. Beiro, Robert J. Sherman, Dr. Donna Amenta and Dr.John Gilje	Preparation and characterization of metal/ligand complexes using substituted N-triazolylpropanamide ligands
Ruth F. Menger and Dr. Scott B. Lewis	The synthesis of 1,3-difluoro-2-methyl-4-phenylbenzene from a one-pot reaction of difluorocarbene and 1-phenyl-2-methylcyclobutene
Dalton R. Gibbs and Dr.Chris E. Berndsen	Investigation of the affinity of putative protozoan UBA5 UFM1 binding domains to human UFM1
Vivian H. Lam, David T. Boyle, Wil J. Andahazy, Nicholas L. Tosti, Jeremy A. Wilke, Cameron Z. Stopak, Daniel A. Schlosser and Dr. Ashleigh E. Baber	Nanoscale Investigation of a TiO_2/Au(111) Surface Using Atomic Force Microscopy and X-ray Photoelectron Spectroscopy
Matthew Davisson, Matthew Bowen, Ashley L Creighton, Madelaine W Fritsche, Austin Kilgore and Dr. Debbie Mohler	Synthesis of Antisense Nucleic Acid Monomers
Daniel A. Corbin, Devon M. Shircliff, Brian J. Reeves and Dr. Brycelyn M. Boardman	Metallopolymers from Direct Polymerization of Functionalized Cobalt Chalcogenide Clusters and Thiophene Comonomers
Kenna L. Salvatore and Barbara A. Reisner	Coordination Compounds Derived from the 3,5-dimethyl-1,2,4-triazolate anion (dmtrz)
Kearney M. Foss, Karen Fortmann and Dr. Christine A. Hughey	LC/MS Metabolic Profiling of an Amber Ale Fermented with Four Different Yeast Strains
Wil J. Andahazy, David T. Boyle, Cameron Z. Stopak, Vivien H. Lam, Daniel A. Schlosser, Dylan M. Boeckmann, and Dr. Ashleigh E. Baber	Using Inverse Model Catalysts to Investigate CO_2 Chemistry
Cassidy E. Jackson and Dr. Chris E. Berndsen	Fluorescent Assay of Ubiquitin Conjugation
Melanie Odenkirk, Dr. Chrisi Hughey and Dr. Stephen Lucas	The Effects of Mobile Phase Modifiers on the Negative Ion Electrospray Ionization of Indoles and Phenols
Elijah T. Roberts and Dr. Barbara A. Reisner	Synthesis of alkali metal hydrotris(3,5-dimethyl-1,2,4-triazolyl)borates
Kortnie E. Holton and Dr. Linette Watkins	Identification of Novel Folate Metabolizing Enzymes
Alanna Hutchinson-Lundy, Austin Crithary, Jonathan Schmitz and Dr. Linette Watkins	Comparison of Stability and Kinetic Properties of DszB from N. asteroides A3H1 and R. erythropolis IGTS8
Walker Jones, Aaron Davis, Serban Zamfir, and Dr. Isaiah Sumner	Computational Analysis of the Mechanism of the Ubiquitin Conjugating Enzyme UBC 13
Christian Cabino and Dr. Daniel Downey	Why is the Stream Drying Up? A Spreadsheet to Calculate Lake Evaporation and Tailwater Discharge

(Student presenters underlined)

Oral Session II: Friday April 15th (Phys/Chem 2212)		
1:15 pm	Matthew Bowen, Matt Davisson and Dr. Deborah Mohler	Synthesis of Antisense Nucleic Acid Monomers
1:30 pm	Allyn Letourneau and Dr. Nathan T. Wright	High Resolution Structure of Titin Zlg10
1:45 pm	David T. Boyle, Wil J. Andahazy, Vivien H. Lam, Daniel A. Schlosser, Cameron Z. Stopak and Dr. Ashleigh E. Baber	Reactivity of Ethanol on TiO_2 Nanoparticles Supported on an Au(111) Surface
2:00 pm	Taylor Light and Dr.Gina MacDonald	Cation-Specific Influences on the Solvation and Solvent Accessibility of Alanine-Rich Peptides
2:15 pm	Nicholas D. Cooper and Dr. Thomas C. DeVore	Thermal Dehydration of the Tutton Salt $K_2Cu(SO_4)_2$-6 H_2O
2:30 pm	Kristin R. McKenna, John Marafino, Brenna Walsh, Kirstie Thompson, Louis Damiano, Brenden Wimbish, Gabriel Fitzgerald, Jhosdyn Barragan and Dr. Kevin Caran	The Synthesis and Characterization of Several Triscationic Amphiphilic Antibacterial Agents
2:45 pm	William T. Price and Dr. Barbara A. Reisner	Mechanisms and Kinetics of Solvent Loss in $Na[BH(C_2H_2N_3)_3]$
3:00 pm	Byron H. Young and Dr. Chris E. Berndsen	Investigating the GCN5 Histone Acetyltransferase Chemical Mechanism

(Student presenters underlined)

Special Announcements (ISAT 159)	
3:30pm	Announcement of Chemistry and Biochemistry Student Award Winners

Keynote Address: Friday April 15th (ISAT 159)		
3:35 - 4:35 pm	Dr. Reid Gadziala JMU Class of 2007	Linear accelerators hope to bring nuclear independence to the U.S. in coming years

Keynote Address

Friday, April 15, 2016 at 3:35pm
ISAT Room 159

Linear accelerators hope to bring nuclear independence to the U.S. in coming years

Dr. Reid Gadziala, Pharm.D., BCNP, MBA
(JMU Class of 2007)
Cleveland Clinic
Cleveland, OH

Widespread use of radioisotopes for diagnostic imaging is still in its infancy. The Molybdenum 99/Technetium 99 Generator was not created until 1958, with mass production of the generator unavailable until 1967.

Though the first commercial Mo99/Tc99 generator was made available through U.S.-based companies, those companies still-- to this day-- rely on reactor-produced Mo99 from outside the United States. This deficiency reached the forefront of medical discussion on May 14th, 2009, when the world's largest reactor, the Canadian National Research Universal reactor, suffered a sudden power outage, and was deemed unusable until early 2010. With 40 percent of the worldwide supply of Mo99 unexpectedly being removed from the market, the planet's remaining seven reactors could not keep up with the global demand. This was particularly true in the United States. The nuclear industry had to rapidly adapt to the change, diagnosing patients with less effective, but non-reactor based radioisotopes.

Though the Canadian NRU reactor is back online and worldwide supply of Mo99 has stabilized, a large push has been initiated to reduce our reliance on reactor produced Mo99 using highly enriched uranium. A race has begun to establish a domestic, reliable supply of Mo99 using linear particle accelerators. Not only will this reduce dependence on highly enriched uranium as a parent isotope, but it will ensure local oversight of one of the most the most important tools modern medicine has conceived.

STUDENT ABSTRACTS

(Student presenters underlined)

Using Inverse Model Catalysts to Investigate CO_2 Chemistry

Wil J. Andahazy, David T. Boyle, Cameron Z. Stopak, Vivien H. Lam, Daniel A. Schlosser, Dylan M. Boeckmann, and Dr. Ashleigh E. Baber
Department of Chemistry and Biochemistry, James Madison University

The demand for energy is at an all-time high and rapidly increasing, due to the exponential growth in the global population. A major consequence of the combustion of fossil fuels is the release of CO_2, a greenhouse gas, which also contributes to ocean acidification. Materials are being developed that catalytically convert CO_2 into usable liquid fuels, which is the first step in creating a carbon neutral cycle. The use of inverse model catalysts (oxide particles supported on metals) helps to elucidate important reaction mechanisms and the catalytically active site for CO_2 hydrogenation reactions such as the reverse water gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) or the formation of hydrocarbons. Here, using TiO_2 nanoparticles supported on Au(111) we investigate the oxide/metal interface for activity related to CO_2 chemistry. Atomic force microscopy (AFM) and temperature programmed desorption (TPD) experiments are conducted on clean Au(111), TiO_x/Au(111) ($x<2$), and TiO_2/Au(111) in order to characterize how CO_2 interacts with these surfaces. CO_2 adsorption is enhanced due to the presence of TiO_2 nanoparticles compared to Au(111). The stabilization of CO_2 indicates its promise for possible low temperature catalysis which will be investigated in future studies.

Preparation and Characterization of Metal/Ligand Complexes Using Substituted N-Trizaolylpropanamide Ligands

Julia E. Beiro, Robert J. Sherman, Dr. Donna Amenta and Dr. John Gilje
Department of Chemistry and Biochemistry, James Madison University

The synthesis and characterization of previously unreported substituted N-triazolylpropanamide ligands N,N-dimethyl-(N-benzotriazole)-propanamide, 1, 3-(N-(5-methylbenzotriazole))-propanamide, 2, and 2-methyl-(N-(1,2,4-triazole))-propanamide, 3, have been accomplished. Each synthesis produced multiple isomers in varying amounts. Isomers of 1 were synthesized from the reaction of benzotriazole and N,N-dimethylacrylamide in the presence of triton B. The reaction of ruthenium(II)chloridetristriphenylphosphine with isomeric mixtures of 1 resulted in predominately one isomer. We propose that the predominate isomer contains a chelating ligand. Isomeric mixtures of 1 were also allowed to react with ruthenium(II)chloridetristriphenylphosphine in a 2 to 1, metal to ligand, molar ratio resulting in a bridged diruthenium complex. The reaction of isomeric mixtures of 1 with manganese(II)chloridetetrahydrate is currently under investigation. Isomers of 2 were synthesized from the reaction of 5-methylbenzotriazole and N,N-dimethylacrylamide in the presence of triton B. The reaction of ruthenium(II)chloridetristriphenylphosphine with isomeric mixtures of 2 resulted in three new ruthenium complexes. Isomers of 3 were synthesized from the reaction of 1,2,4-triazole and methacrylamide in the presence of triton B. The reaction of ruthenium(II) chloridetristriphenylphosphine with isomeric mixtures of 3 resulted in two new ruthenium complexes.

Synthesis of Antisense Nucleic Acid Monomers

Matt Bowen, Matt Davisson and Dr. Deborah Mohler
Department of Chemistry and Biochemistry, James Madison University

Due to RNA's ability to be used as a natural therapeutic for its gene silencing capabilities, antisense oligonucleotides have been studied for their wide variety of uses as therapeutic drugs or for use as a tool for studying gene function. However, to avoid problems with degradation of the sugar-phosphate backbone, synthetic oligonucleotide analogs that lack traditional ribose-phosphate backbone are being developed and will be studied for their ability to bind DNA and to silence gene expression.

Reactivity of Ethanol on TiO_2 Nanoparticles Supported on an Au (111) Surface

David T. Boyle, Wil J. Andahazy, Vivien H. Lam, Daniel A. Schlosser, Cameron Z. Stopak and Dr. Ashleigh E. Baber

A fundamental understanding of ethanol and the mechanism by which this important alcohol reacts at interfaces is of significant importance for the petroleum industry, as ethanol is used as an everyday fuel and additive in automobile gasoline. Other simple alcohols (methanol and propanol) have shown reactivity on TiO_2/Au(111) inverse model catalysts, but the role of the oxide/metal interface has not yet been investigated. In order to fully understand TiO_2/Au(111) interfacial sites, which are hypothesized to be the active site of the catalyst, a systematic study of ethanol reactivity on the surface was carried out. The reactivity of ethanol with nanoparticle TiO_2 —a reversibly reducible material utilized for the storage of chemically reactive oxygen—supported on Au(111) was studied using ultrahigh vacuum temperature programmed desorption (TPD) and atomic force microscopy (AFM). The TiO_2 nanoparticle reactivity differed from bulk TiO_2(110) and resulted in the conversion of ethanol to acetaldehyde, which desorbed from the surface over a range of 400 K to 550 K. A coverage dependent study of TiO_2 supported on Au(111) was performed to investigate the role of TiO_2/Au(111) interfacial sites on the oxidation of ethanol to acetaldehyde.

Why is the Stream Drying Up? A Spreadsheet to Calculate Lake Evaporation and Tailwater Discharge

Christian Cabino and Dr. Daniel Downey
Department of Chemistry and Biochemistry, James Madison University

Water enters lakes and reservoirs through influent streams, direct rainfall and springs and exits by discharge, evaporation and absorption into the underlying geology. Loss of water by evaporation has the potential to substantially reduce downstream discharge. In this presentation we describe a model published by Fennessy and Vogel (1996) that quantifies the amount of water loss due to evaporation from a lake/reservoir system for the eastern United States. We have created an excel spreadsheet program for use by lake and fisheries managers based on this paper. The calculated evaporation rate is based upon readily available data including lake elevation, longitude, average monthly temperature, and average daily temperature without the need for onsite data collection associated with other models. We have tailored this program to fit most manmade water bodies in Virginia and neighboring states. Climate data were obtained from the National Ocean and Atmospheric Administration (NOAA) First Order weather observatories online. The spreadsheet also calculates reduction in downstream discharge from watershed size, yield, and average annual rainfall in conjunction with the evaporation rate. Elevation, longitude, watershed size, lake surface area, and other information were available from the National Inventory of Dams Online. Any given Water Year data may be obtained from the US Geological Survey website. This spreadsheet can be used to demonstrate the effect of impoundments on historically free flowing streams as a contributor to downstream dewatering that is particularly acute during periods of high temperatures and low rainfall.

Thermal Dehydration of the Tutton Salt $K_2Cu(SO_4)_2$-6 H_2O

Nicholas D. Cooper and Dr. Thomas C. DeVore
Department of Chemistry and Biochemistry, James Madison University

Tutton salts, a series of monoclinic crystals having a general formula of $M_2^{I}M^{II}(SO_4)_2*6H_2O$, where M^{I} is a monovalent cation and M^{II} is a divalent cation, have garnered attention recently as possible energy storage media for use in solar cells. These salts tend to have a reversible dehydration step and a high enthalpy of fusion lending themselves towards good materials for solar energy conversion. This investigation focused on the dehydration of the Tutton salt $K_2Cu(SO_4)_2$-6 H_2O in order to establish the enthalpy change and the decomposition mechanism as this compound dehydrates using TGA, DTA, and DSC. PXRD was used to provide crystallographic and structural information. Isoconversional methods and model fitting approaches were used in order to test the kinetics of the dehydration phase and validate enthalpic data from DSC measurements. The dehydration appears to occur in two separate steps with four waters of hydration leaving in the first step and the final two leaving slightly afterwards. Phase changes in the lattice of the salt were found to be dependent upon the sample mass used heating rate showing that the dehydration step occurs by a multi-step mechanism.

Metallopolymers from Direct Polymerization of Functionalized Cobalt Chalcogenide Clusters and Thiophene Comonomers

Daniel A. Corbin[1], Devon M. Shircliff[1], Brian J. Reeves[2], Dr. Brycelyn M. Boardman[1]
[1]Department of Chemistry and Biochemistry, James Madison University
[2]Department of Chemistry, Colorado State University

Hybrid organic-inorganic bulk heterojunction (BHJ) photovoltaic devices have recently gained interest within the scientific community for their potential to offer higher efficiency solar cells at a lower cost than those in the current market; however, the orthogonal properties of organic and inorganic materials cause the two to interact poorly within the devices. Since the BHJ architecture relies on good interaction between the donor (organic) and acceptor (inorganic) materials, this has proven to be a large obstacle to developing a more ideal hybrid solar cell. To overcome this issue, a series of metallopolymers were synthesized. A modified Stille coupling with $(Me_3Sn)_2(C_4H_2S)$ and varying ratios of $Co_6Se_8(Br(C_4H_2S)P(Ph)_2)$ (1) to $Br_2(C_4HS)(CH_2)_5CH_3$ were used to isolate poly(cluster-co-thiophene-co-hexylthiophene)$_{a\text{-}d}$ ($PCLTHT_{a\text{-}d}$). All of the polymers were characterized using UV-Visible, Nuclear Magnetic Resonance, and Fluorescence Spectroscopy, as well as Atomic Force Microscopy, Pyrolysis, and Mass Spectrometry. Not only do $PCLTHT_{a\text{-}d}$ exhibit a wide range of solubility, a problem that has long plagued inorganic photovoltaics, but they also show increased charge transfer efficiency compared to representative simple mixtures of 1 and poly(thiophene-co-hexylthiophene).

Synthesis of Antisense Nucleic Acid Monomers

Matthew Davisson, Matthew Bowen, Ashley L Creighton, Madelaine W Fritsche, Austin Kilgore and Dr. Debbie Mohler
Department of Chemistry and Biochemistry, James Madison University

Due to RNA's ability to be used as a natural therapeutic for its gene silencing capabilities, antisense oligonucleotides have been studied for their wide variety of uses as therapeutic drugs or for use as a tool for studying gene function. However, to avoid problems with degradation of the sugar-phosphate backbone, synthetic oligonucleotide analogs that lack traditional ribose-phosphate backbone are being developed and will be studied for their ability to bind DNA and to silence gene expression.

LC/MS Metabolic Profiling of an Amber Ale Fermented with Four Different Yeast Strains

Kearney M. Foss, Karen Fortmann and Dr. Christine A. Hughey
Department of Chemistry and Biochemistry, James Madison University

Brewer's yeast is known to contribute over 500 flavor-active compounds to beer. Here we profiled a 20-barrel batch of amber ale that was equally divided and fermented by White Labs with Bedford British ale yeast, Dusseldorf alt yeast, Tennessee whiskey yeast and Abbey ale yeast. Untargeted metabolomic profiling was conducted by positive and negative ion ESI LC q-TOF MS. Mass Profiler Professional was used to align and filter molecular features (MFs, unique mass and retention time) found in all replicate samples ($p \leq 0.05$). Retained MFs were searched against a KEGG-curated metabolite database for *Saccharomyces cerevisiae* with an allowed mass error of ≤15 ppm. Database hits were used in a multi-omics experiment to simultaneously match assignments in the positive and negative ion data to metabolites in known yeast pathways. Pathways related to carbohydrate and amino acid metabolism, which contribute to flavor and aroma in beer, were of primary interest. A sensory panel determined that the yeasts imparted distinctly different flavor profiles (fruity to spicy) to the beers. These differences are likely reflected in their different MS-profiles. Principle component analysis revealed that Tennessee whiskey yeast differs significantly from the other yeasts. This is likely the result of its isolation in a distilling setting vs. a brewing setting. Tentatively identified metabolites matched to 41 pathways; initial efforts have focused on five pathways in which 25-40% of the metabolites have been matched to the KEGG-curated library and 12-18% have been RT-matched to standards. Polyamine synthesis and the methionine salvage pathway are of particular interest since they involve the metabolite 5-methylthioadenosine (5-MTA), which has been proposed as a marker for beer oxidation during storage (Food Chem. 135, 2012, 1284-1289). However, both pathways do not differentiate the yeast strains, as the concentration of target metabolites varies little across strains. As we work to increase the number of confirmed metabolite identifications, we hope to better understand how of these and other metabolites vary as a function of yeast strain and, ultimately, contribute to beer flavor.

Investigation of the affinity of putative protozoan UBA5 UFM1 binding domains to human UFM1

Dalton R. Gibbs and Dr. Christopher E. Berndsen
Department of Chemistry and Biochemistry, James Madison University

Post translation modification of proteins is a method of biological signaling wherein a protein tag is added to an existing enzyme to flag it for some purpose. Ufmylation is one such post translation modification pathway known to be up regulated in metastatic cancers and metamorphosis in some protozoans. In Ufmylation, UFM1 is added various targets via an activation cascade similar to that of ubiquitin, in which UFM1 is activated by an E1, transferred to an E2 which works in conjunction with an E3 to transfer UFm1 to its target substrate. The E1 in the Ufmylation pathway, Ubiquitin Activating Enzyme 5 is the subject of our study. The binding affinity of the UFM1 binding domain of human UBA5 to human UFM1 was determined by florescence polarization binding assay. The data for the human peptide and Ufm1 were compared with the binding affinity of the putative UBA5 binding domain from the human parasite T. brucei to human UFM1. Molecular modeling was used to further examine the possible molecular level interactions causing the shift in affinity from one species to another. These results suggest a specificity mechanism for Ufm1 activation, which may lead to improved targeting of the Ufm1 pathway in parasites for the treatment of human disease.

Identification of Novel Folate Metabolizing Enzymes

Kortnie E. Holton and Dr. Linette Watkins
Department of Chemistry and Biochemistry, James Madison University

Vitamin B9, also known as folic acid, is a critical nutrient that serves as a cofactor in many metabolic pathways. Currently, there are only assays to detect one form of folic acid in food products. In an effort to identify enzymes that could be used in assays to detect multiple forms, soil bacteria was grown using folic acid as a single carbon source. A gram-negative bacterium capable of growing on folic acid was grown up in single-carbon source media with folate as the sole carbon source. Cells were harvested, lysed, and the cell lysate was run through a folate affinity column. Protein eluted off the column was quantified using a BCA assay, concentrated, and run on a SDS-PAGE gel. The resulting bands were excised and digested with trypsin in preparation for LC mass spectrometry. Chromosomal DNA was isolated from "popcorned" cells using a Qiagen Miniprep Kit. PCR was performed on the isolated DNA before ribosomal 16s sequencing.

Comparison of Stability and Kinetic Properties of DszB from N. asteroides A3H1 and R. erythropolis IGTS8

Alanna Hutchinson-Lundy, Austin Crithary, Jonathan Schmitz and Dr. Linette Watkins
Department of Chemistry and Biochemistry, James Madison University

Dibenzothiopehene (DBT) and its derivatives comprise up to 60% of the organosulfur contamination of crude oil. The enzyme 2-(2'-hydroxyphenyl) benzenesulfinate desulfinase (DszB) catalyzes the carbon-sulfur bond cleavage in the final, and rate-limiting step in the biodesulfurization of DBT. The DszB enzyme from Nocardia asteroides A3H1 and Rhodococcus erythropolis IGTS8 was overexpressed in E. coli, purified and characterized kinetically. Kinetic assays revealed a sigmoidal response when the velocity was plotted against [S], calling into question the monomeric structure of the enzyme. Size exclusion chromatography and formaldehyde cross-linking was conducted to further investigate the oligomerization of HPBS desulfinase. The stability of the enzyme was measured under various storage conditions and increased stability was observed upon immobilization of the enzyme to CNBr-activated Sepharose beads. These studies aid in the understanding of the factors that control the rate and stability of the desulfinase enzyme to learn how to make it more economically feasible.

Fluorescent Assay of Ubiquitin Conjugation

Cassidy E. Jackson and Dr. Chris E. Berndsen
Department of Chemistry and Biochemistry, James Madison University

Ubiquitination of proteins is a post translational protein modification linked to protein degradation, cell cycle regulation, and DNA damage repair. Many of the functions of ubiquitin and ubiquitin like proteins are still unknown and the catalytic mechanisms of the conjugating enzymes are partially known. The assays of ubiquitin/ubiquitin-like protein conjugating include observing changes in migration on gel electrophoresis or radioactive tags which are expensive and require special handling. We are optimizing a fluorescence based assay that quantifies the cleavage of ATP to AMP by the E1 ubiquitin/ubiquitin-like protein activating enzyme. This assay permits study of the kinetics of ubiquitin conjugation in a discontinuous manner and is highly sensitive. We are optimizing the conditions for monitoring E2 dependent ubiquitin chain formation in order to determine the mechanism of E1 and E2 enzymes. This assay will help in the understanding of the mechanism of ubiquitin and ubiquitin like protein conjugation.

Computational Analysis of the Mechanism of the Ubiquitin Conjugating Enzyme UBC13

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Ubc13 is an E2 enzyme that catalyzes a post translational modification of proteins called lysine ubiquitination, i.e. the addition of ubiquitin to the lysine of a target protein via a thioester aminolysis reaction. Lysine ubiquitination is important because, one of its functions is to signal for the degradation of damaged proteins, and defects in ubc13 are linked to different disorders. The accepted mechanism for Ubc13-catalyzed ubiquitination is a stepwise mechanism that creates an oxyanion intermediate. This intermediate is hypothesized to be stabilized by a nearby asparagine residue, which is known as the “oxyanion hole.” However, the validity of the accepted mechanism has come into question because, there has never been a comprehensive study of the ubiquitination mechanism, the accepted mechanism was inferred from the reverse reaction, and recent studies suggest a different role for the oxyanion hole. In our study, we use molecular dynamics to examine the hydrogen bond environment of the active site in two structures of Ubc13 and determine the likelihood for the formation of the oxyanion hole. Furthermore, we present initial data wherein we calculate the energies of the different possible steps of the reaction coordinate with the ONIOM quantum mechanics/molecular mechanics (QM/MM) extrapolation procedure.

Utilizing Chloroform Post-Treatment to Improve the Adhesion of Au Thin Films onto PMMA

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The metallization of Au onto plastics is an important processing step in applications such as the aerospace and automotive industries, the field of microelectronics, and the fabrication of microfluidic devices. While its corrosion resistance and excellent electrical and thermal conductivity make Au a useful choice, its inertness results in poor adhesion to polymer surfaces. Previous studies have indicated that exposing commercially available poly(methyl methacrylate) (PMMA) sheets to chloroform vapor following Au deposition significantly improves adhesion. In this study, we utilized magnetron sputtering to deposit Au thin films onto 1.50 mm thick PMMA and exposed the samples to vapor released from chloroform heated on a hot plate set at 70°C. The force required to remove the Au thin films was determined by placing samples on a polisher spinning at 150 rpm and utilizing UV-VIS spectroscopy to measure the transmittance of 700 nm light through the films to quantify their removal as a function of applied polishing force. The Au thin films were also characterized using atomic force microscopy (AFM). AFM images demonstrated a progressive roughening of the surface corresponding to an increase in applied force. Additionally, these images support a model in which the chloroform treatment softens the PMMA surface, producing a softened layer that the polisher removes simultaneously with the Au thin film. Following the attainment of quantitative data demonstrating the effectiveness of chloroform post-treatment, the vapor exposure procedure was applied to selectively pattern a series of PMMA samples.

Nanoscale Investigation of a TiO_2/Au(111) Surface Using Atomic Force Microscopy and X-ray Photoelectron Spectroscopy

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Inverse model catalysts (oxide nanoparticles supported on metal substrates) have shown high reactivity for industrial catalytic reactions. In particular, TiO_2 nanoparticles supported on Au(111) have shown promise for alcohol (methanol and propanol) decomposition, water gas shift, and hydrogen dissociation reactions. The growth and reactivity of TiO_2/Au(111) inverse model catalysts were fully characterized in an effort to elucidate the relationship between the surface morphology and its reactivity. The successful deposition of TiO_2 on Au(111) was confirmed by X-ray photoelectron spectroscopy. Optical and atomic force microscopy (AFM) images of Au(111), roughened Au(111), and TiO_2/Au(111) were obtained. In the presence of 10% surface coverage of TiO_2, nanoparticles ~30 nm in diameter were well dispersed across the entire surface as observed via AFM. This coverage of TiO_2 showed reactivity towards ethanol and enhanced interaction with carbon dioxide compared to clean Au(111).

High Resolution Structure of Titin ZIg10

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Titin domains ZIg9/10 bind to obscurin domains Ig58/59 during myofibrillogenisis. Mutations in this region lead to hypertrophic cardiomyopathy (HCM) in humans. While the cellular consequences of this interaction are well characterized, the molecular determinants governing this structure are unknown. Previous work from our lab has solved the high-resolution structure of the obscurin domains of the complex. Here, we describe the solution structure of titin domain ZIg10. This region folds as a typical Ig-like domain and will be used as a building block to solve the titin/obscurin binding complex. (Supported by Jeffress Memorial Fund, Research Corporation Cottrell College Grant, NSF-REU (CHE-1461175)).

Cation-Specific Influences on the Solvation and Solvent Accessibility of Alanine-Rich Peptides

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Studies in our lab correlated salt-induced changes in protein solvation to changes in water structure, protein aggregation and thermal stability. In order to better isolate and identify how salts influence protein structure and solvation, we extended our studies to include small peptides. Previous studies with alanine-rich peptides have correlated co-solvent-induced changes in solvation with stability. We utilized Attenuated Total Reflectance infrared spectroscopy (ATR-FTIR) and circular dichroism (CD) to study salt-induced changes in these peptides in ^1H_2O and ^2H_2O. Our data suggests ion-specific changes that reflect differences in peptide structure and/or solvation. CD spectra show significant secondary structure changes, particularly of the uncapped peptide, in the presence of some salts. These structural changes correlate with infrared experiments performed on partially dehydrated peptide thin films that show differences in the structure and $^1H/^2H$ exchange of the peptides. The $^1H/^2H$ exchange experiments show some salts alter peptide solvation and suggest changes in the solvent accessibility of the peptide. Peptide infrared data also show specific cation interactions to the peptide backbone. Furthermore, our data suggest cations preferentially influence solvation in an order consistent with the Hofmeister series, with Ca^{2+} and Mg^{2+} showing the most significant changes in peptide solvation.

Multimerization of Solution State Proteins by Water Soluble Porphyrins

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Interactions between charged porphyrins and complimentary or similarly charged proteins provide important model systems for studies of electron transfer processes, artificial photosynthesis, and control of protein-protein interactions. Typically, the experimental results are analyzed and discussed assuming that the proteins exist in a monodisperse state. Here, we explored interaction of four solution-state proteins (horse heart cytochrome c, hen egg-white lysozyme, 3-heme c-type cytochrome PpcA from Geobacter sulfurreducens, 2-heme cyt c4 from Pseudomonas stutzeri) with several cationic and anionic water-soluble derivatives of tetraphenylporphyrin. Combined small- and wide-angle X-ray scattering experiments revealed quick formation of multimers with a wide range of complex sizes. Thermodynamic interaction parameters and complex binding stoichiometries were established with isothermal calorimetry. The obtained results demonstrate that multimerization of solution-state proteins by large water-soluble ligands appears to be a wide-spread phenomenon controlled by a delicate interplay of electrostatic and hydrophobic forces. Molecular level mapping of the binding sites allows us to build a theory explaining the size of the formed complexes and provides opportunities for targeted design and assembly of multi-subunit protein complexes.

The Synthesis and Characterization of Several Triscationic Amphiphilic Antibacterial Agents

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M-P,12,12, a triscationic amphiphile, was characterized for its antibacterial and colloidal properties as well as its ability to associate with sodium dodecyl sulfate (SDS). This amphiphile has a mesitylene core, one pyridinium headgroup, and two dimethyldodecylammonium tails. The critical aggregation concentration (CAC) for M-P,12,12 was determined by three different methods. According to isothermal titration calorimetry (ITC), the CAC is 2.54 mM, conductivity studies determined the CAC to be 2.07 and the alpha value to be 0.188, and nuclear magnetic resonance (NMR) spectroscopy yielded a CAC value of 1.74 mM. In addition to this study, several reactions were undertaken to install either a caffeine or acridine head group onto the mesitylene core or to add both one trimethylammonium and one pyridinium head group each to the core. Other reactions involved the synthesis and incorporation of long-chain (20-22 carbon) amines into the amphiphiles.

The synthesis of 1,3-difluoro-2-methyl-4-phenylbenzene from a one-pot reaction of difluorocarbene and 1-phenyl-2-methylcyclobutene

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Previous studies show that 1,2-disubstituted cyclobutenes can be used in reaction with difluorocarbene to produce 1,3-difluorobenzenes. A pathway to the synthesis of these types of compounds is of interest due to their presence in fluoroquinolone antibacterials, resins, and insecticides. The synthesis is unique because the fluorine atoms from the difluorocarbene are not adjacent to each other when the ring expands to a benzene ring. This study focuses on the reaction of difluorocarbene with 1-phenyl-2-methylcyclobutene, which was synthesized in one-pot in 4 steps starting from 1-phenyl-1-propyne and zirconocene dichloride.

Polymerization and Characterization of Functionalized Palladium Complexes with Benzothiadiazole Co-monomers

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The synthesis of functionalized phosphine ligands was performed to isolate palladium complexes capable of polymerization. The ligands were prepared via lithium halogen exchange with n-butyllithium followed by the addition of chlorodiphenylphosphine. The reactions of 2,5-dibromothiophene and 4,7-dibromobenzo[c]-1,2,5-thiadiazole under these conditions produced 2-bromo-5-diphenylphosphinothiophene (**1**) and 4-bromobenzo-7-diphenylphosphino-1,2,5-thiadiazole (**2**) respectively. Compounds **1** and **2** were purified via column chromatography and then allowed to react with dichloro(1,5-cyclooctadiene)palladium(II). The polymerizable metal complex bis(2-bromo-5-diphenylphosphinothienyl)dichloropalladium(II) (**3**) results from **1** while no palladium complex was isolated from the reaction with **2**. Compound **3** was then allowed to react with 2,5-bis(trimethylstannyl)thiophene, 2,5-dibromo-3-hexylthiophene, and 4,7-dibromobenzo[c]-1,2,5-thiadiazole in various ratios to produce three sets of co-polymers. Characterization of the co-polymers using ^{1}H and ^{31}P NMR, UV-Visible spectroscopy, and fluorescence spectroscopy indicates covalent attachment of **3** into the polymer backbone. Scanning electron microscopy was used to distinguish the difference between metal- and polymer-containing domains, and cyclic voltammetry was used to calculate electronic levels. Manipulation of the co-monomer ratios also results in the ability to fine tune the optical properties of the co-polymers and potentially extend the lifetime of the exciton diffusion step in the charge generation process.

The Effects of Mobile Phase Modifiers on the Negative Ion Electrospray Ionization of Indoles and Phenols

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Negative electrospray ionization (ESI) generates deprotonated ions, $[M-H]^-$, for mass spectrometric detection. The efficiency of molecule-to-ion conversion is dependent on the physiochemical properties of the analytes and the solvent composition. Here we investigated both. The negative ion ESI response of systematically substituted weakly acidic indoles and phenols with a pK_a range from 4.44 to 18.23 was measured in 80:20 methanol:water (the control) and methanol:water with 1 mM of different mobile phase modifiers. Modifiers used were weak acids (formic and acetic acid), neutral salts (ammonium acetate, ammonium formate and ammonium fluoride) and a weak base (ammonium hydroxide). Generally, compounds with moderate or strong electron withdrawing groups (CN, CF_3 and NO_2) exhibited higher ionization efficiencies compared to compounds with electron donating groups (NH_2, OCH_3). The ranking of low to high responders was generally consistent across all solvent systems. Not surprisingly, the compound classes responded differently to the modifiers. The response of indoles exhibited a higher response in NH_4F (~5X) and NH_4OH (~2X) and a lower response in the other modifiers compared to the control. In addition, the lowest responding compounds exhibited the greatest increase in response upon addition of the fluoride ion. However, these gains were not observed with phenols. In fact, most phenols, especially the high responders, generally decreased upon addition of the modifier. Future work will measure ionization of these compounds at different modifier concentrations. As we amass data, the relationships between solution pH, analyte pK_a and ionization efficiency will be explored in hopes of elucidating the ionization mechanisms involved in negative ion ESI for different compound classes.

Re-examination of the Structure and Elasticity of the Titin Ig65-70 Segment and Its Comparison to Obscurin Ig58-59

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Previously published crystal structure data of Ig65-70 (six tandem domains of titin, also known as I6) suggests that this region has a rigid structure with discrete hinge points and follows a carpenter's ruler model. However, the carpenter's ruler model does not agree with a more recent in silico work, which suggests that all tandem Ig domains are bendable. In order to reconcile the differences between these two models, we re-analyzed the titin I6 crystal structure data. We chose to prioritize B-factors over R-factors to compensate for potential crystal packing interactions. We found that the apparent rigid regions of I6 can also be seen as flexible, depending on the method used to solve the crystal structure. We then compared the new data with our previous structural and elasticity findings of an unrelated tandem Ig region, obscurin Ig58-59, and found that these domains are also more flexible than the experimentally derived models would suggest.

Mechanisms and Kinetics of Solvent Loss in $Na[BH(C_2H_2N_3)_3]$

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The hydrotris(1,2,4-triazolyl)borate ligand was used to assemble frameworks to see the structural effects and kinetics of solvent loss in the framework. Three frameworks, $Na[BH(C_2H_2N_3)_3]\cdot$solvent (solvent = water, dimethylformamide, isopropanol), were synthesized under solvothermal conditions. Powder X-ray diffraction (PXRD) indicates that the three solvates have different structures. The solvent of crystallization can be removed upon heating; isothermal thermalgravimetric analysis (TGA) shows solvent loss by a 3-D diffusion mechanism. Variable temperature PXRD shows a slight loss of crystallinity upon desolvation, indicating some framework decomposition. Upon solvent loss, the structures of the desolvated materials are identical. These activated frameworks adsorb water from the atmosphere. Details of the structural properties, thermal behavior, and kinetics of solvent loss of $Na[BH(C_2H_3N_3)_3]\cdot$solvent are reported.

Stream Acid Mitigation Plan for Two Jefferson National Forest Streams

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North Fork Potts Creek and North Fork Stony Creek are two Appalachian Mountain streams in the Jefferson National Forest of West Virginia and Virginia. Both streams flow from the same mountain on opposite sides of the ridge. Both have acceptable cold water and thermal habitat for brook trout (*Salvelinus fontinalis)* but originate within watershed geology of little natural carbonate bearing minerals. The combination of the near absence of natural buffer and acid precipitation have created conditions of relatively low pH (pH < 5) and other water quality values which result in poor trout biomass and recruitment. In the present study water chemistry has been evaluated for the purpose of designing a mitigation strategy by the single point, single application method of introducing base material ("liming") near the headwaters. Physical size, watershed geology and discharge values have been evaluated for the two streams. Water samples have been collected and analyzed for pH, acid neutralizing capacity (ANC), base cations (Ca^{+2}, Mg^{+2}, K^+, and Na^+), strong acid anions (Cl^-, SO_4^{-2}, and NO_3^-), and aluminum. These physical and chemical parameters have been used along with results of previous liming studies to propose a single point, single application of 50 and 100 tonnes, respectively, for a 4 to 5 year treatment. Research done with help by the NSF-REU Grant CHE-1461175, United States Forest Service- George Washington and Jefferson National Forests Dawn Kirk, USFS fisheries biologist.

Synthesis of alkali metal hydrotris(3,5-dimethyl-1,2,4-triazolyl)borates

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Alkali metal hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate, $A[BH(dmtrz)_3]$ (A = Na, K), have been synthesized to explore the coordination chemistry of the ligand and to fabricate metal-organic frameworks. The compounds were synthesized from a flux of the ligand at 240 °C. The compounds were characterized by FT-IR and ^1H NMR. The compounds exhibit the characteristic IR B-H stretch at ~2500 cm^{-1} and NMR data are consistent with the methyl protons on the ligand. Work towards refining the synthesis will be presented.

Coordination Compounds Derived from the 3,5-dimethyl-1,2,4-triazolate anion (dmtrz)

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In an effort to explore the coordination chemistry of the 3,5-dimethyl-1,2,4-triazolate anion, its reaction chemistry was explored with metal ions including Mg^{2+}, Sr^{2+}, Ba^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, La^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3+}, and Er^{3+}. Evaporation, solvothermal synthesis, and diffusion were used in an effort to crystallize these materials. Powder X-ray diffraction (PXRD) data indicate that three novel coordination compounds were synthesized by evaporation from ethanol. The reaction between $Co(NO_3)_2\cdot6H_2O$ or $Ni(NO_3)_2\cdot6H_2O$ and Hdmtrz produced orange and blue octahedral crystals, respectively. Colorless rod-shaped crystals were produced in the reaction between $GdCl_3\cdot6H_2O$ and Hdmtrz. Samples were analyzed with PXRD and FT-IR and have been sent out for single crystal X-ray analysis. The synthesis and characterization of these compounds will be discussed.

Preparation of Ruthenium Complexes of N-Triazolylpropanamide Derivatives

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2-Methyl-3-[N-benzotriazole]-propanamide was successfully synthesized from the reaction of 1,2,3-benzotriazole and methacrylamide in the presence of Triton B. Two isomers formed, 2-methyl-3-[1N-benzotriazole]-propanamide (1) and 2-methyl-3-[2N-benzotriazole]-propanamide (2), and were separated by fractional recrystallization. Isomer 1 has been characterized by NMR and IR spectroscopy and x-ray crystallography. Isomer 2 has been characterized by NMR and IR spectroscopy. Single crystals of 2 have been obtained and are awaiting x-ray analysis. Separate reactions of both 1 and 2 with excess tris(triphenylphosphine) ruthenium(II) chloride (4) appear to yield mainly bridged diruthenium complexes, which are being characterized.

The Effect of Hofmeister Series Counterions on the Colloidal and Antimicrobial Properties of Triple-Headed Cationic Amphiphiles

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Antibacterial resistance is becoming increasingly prominent causing a great need for novel antibacterial products. Several series of novel amphiphilic molecules have been synthesized with promising antibacterial results. In an amphiphile series with three hydrophilic heads and one hydrophobic tail, a linear hydrocarbon chain with 18 carbons is more antibacterial than those with longer or shorter tails. Previously, this compound has been synthesized with three bromide counterions. In this work, a group of compounds with varying anionic Hofmeister series counterions have been prepared via ion exchange. Each new amphiphile in this series has three quaternary ammonium headgroups and an 18-carbon hydrophobic tail. The effects of varying the anionic counterions on antibacterial and colloidal properties will be reported. It was predicted that the presence of more chaotropic counterions within the series would lower the critical aggregation concentration (CAC) and increase the antimicrobial potency of the compound tested, and that more kosmotropic counterions would cause the opposite effect. A general trend of increasing critical aggregation concentration (CAC) with increasing kosmotropic nature of counterions has been observed. At this point no obvious trend between the Hofmeister series and the antibacterial potency have been observed, although significant changes in potency have been seen with varying ions. Counterion exchanges were also completed on an amphiphile with three quaternary ammonium headgroups and two 12-carbon hydrophobic tails, the most potent of the corresponding series, to determine whether specific counterion effects on antibacterial potency are applicable to other amphiphile series.

Cation Effects on Caffeine Partitioning Thermodynamics

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This work reports results from Hofmeister cation effects on caffeine partitioning between an aqueous and organic cyclohexane phase. The standard Gibbs free energy for caffeine partitioning is measured in the presence of a series of twelve chloride salts in the aqueous phase at varied salt concentrations and temperatures. Cations seem to have less effect overall than the anions studied previously. For monovalent Na^+, K^+, Rb^+, and Cs^+, the Gibbs free energy associated with caffeine partitioning changes linearly with increasing salt concentration. While in the presence of Li^+, NH_4^+, and all the divalent cations studied herein the Gibbs free energy for caffeine partitioning shows a non-linear dependence on salt concentration. The temperature dependence of the Gibbs free energy for caffeine partitioning with the ion series is also investigated to determine the enthalpy and entropy for caffeine partitioning. The entropy and enthalpy associated with the transfer in the presence of all salts are positive, which means caffeine transfer from aqueous to organic phase is entropically driven.

Structural and computational study of Ufm1

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Ufm-ylation is the process by which the ubiquitin-fold modifier, Ufm1, is transferred to a substrate lysine. This pathway is crucial for morphology changes in some parasites and is linked to regulation of ER stress and breast cancer. The ubiquitin activating enzyme, Uba5, is necessary in the process of Ufm1 conjugation; however the chemistry that this enzyme employs is unknown. A 2Å crystal structure of Ufm1 in the P1 space group was solved through molecular replacement and largely matches the published NMR structure. Alignment of several Ufm1 structures showed perturbations in a few regions including a loop known to interact with the activating protein Uba5. Molecular dynamics simulations were performed to determine if interaction of Ufm1 led to structural changes in this loop suggesting an allosteric binding mechanism.

Investigating the Hydrogen Bonding Environment of Gcn5 utilizing Molecular Dynamics Simulations

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Post-translational modifications (PTMs) can have a profound effect on protein structure and function. One such PTM involves the acetylation of free lysine residues. An essential acetylation reaction involves the transfer of the acetyl group from acetyl CoA to a histone (a protein involved in DNA binding). This transfer neutralizes of the positively charged lysine, which allows for the DNA to be exposed for transcription. An enzyme that catalyzes this reaction is Gcn5. Details regarding the reaction mechanism still remain obscured. Current mechanistic hypotheses suggest that the reaction occurs through a tetrahedral oxyanion intermediate, which is stabilized by a hydrogen bond to an oxyanion hole. We use molecular dynamics (MD) simulations to probe the interactions between the histone residue and Gcn5, including the putative oxyanion hole. Furthermore, we examine the change in enzymatic interactions as we change the protonation state of the lysine and the length of the interacting histone.

Investigating the GCN5 Histone Acetyltransferase Chemical Mechanism

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Enzyme catalyzed protein acetylation involves the transfer of an acetyl group to a lysine side chain within the substrate. This process serves many vital cellular purposes including the regulation of gene expression and controlling of the circadian rhythm. Defects in enzymatic acetylation have been linked to many common diseases such as cancer, insomnia, and anemia. Despite decades of research into the biological function of protein acetylation, the enzymatic mechanism of acetyl transfer is unknown. We have worked to characterize the mechanism of acetyl-transfer utilized by the yeast protein acetyltransferase General Control Nonderepressible 5 (GCN5) using deuterium solvent isotope effects. These analyses have allowed us to characterize the occurrence of proton transfer during catalysis as well as gain a general knowledge of the transition state structure. These results will be coupled with QM/MM computational modeling of the GCN5 acetyl-transfer reaction in order to gain an explicit understanding of the mechanism of catalysis. The collection of these results set the groundwork for further investigation into the catalysis mechanisms of other acetyltransferases and may aid in development of treatment for acetyl-transfer associated illness.

2016 Department of Chemistry and Biochemistry Student Award Winners

Amenta Award	Kirstie Thompson
R.D. Cool Award	Daniel Corbin
J.W. Chappell Scholarship	Aidan Wiley
Palocsay Award in Undergraduate Research	David Boyle
Service Award	Renna Nouwairi
J. W. Chappell Award	Tony Allsbrook
American Institute of Chemists	Ruth Menger
Degesch America Award	Aidan McKenzie
ACS-Award	Kathleen Krist
Hypercube Scholar	Hamilton Young
Casali Scholarship	Tony Allsbrook
Outstanding Student Researcher Award	*to be announced*

American Chemical Society Divisonal Awards

ACS Analytical	Tony Allsbrook
ACS Inorganic	Tyler Price
ACS Organic	Kristin McKenna

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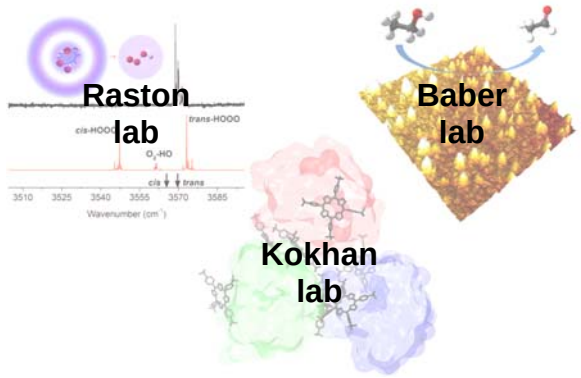

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