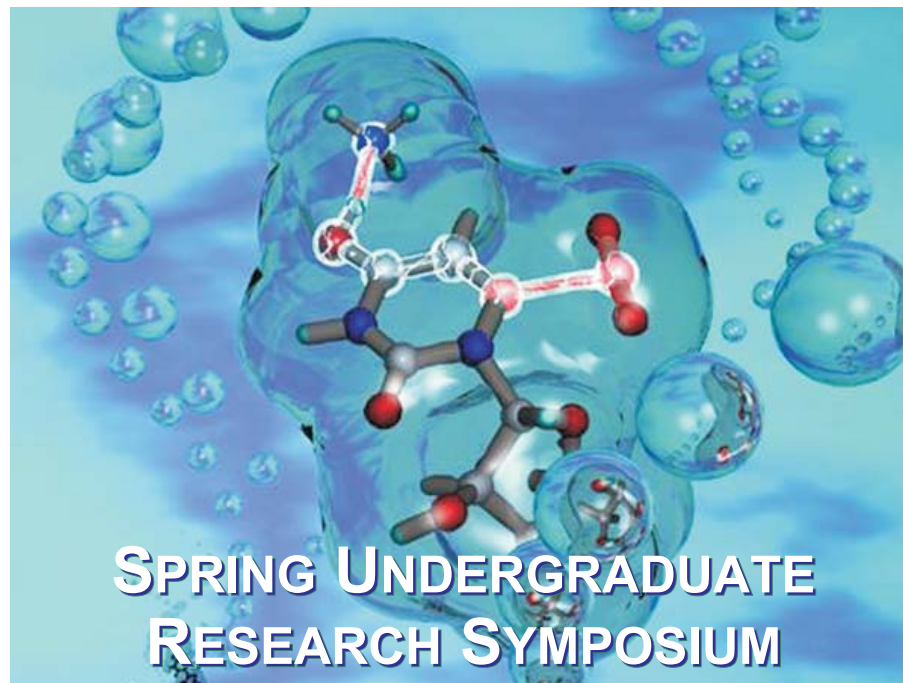


JAMES MADISON UNIVERSITY

DEPARTMENT OF CHEMISTRY

32nd Annual



THURSDAY APRIL 19, 2007

SESSION I: 1:00 - 5:30 PM ISAT 259 (NTELOS ROOM)

FRIDAY APRIL 20, 2007

SESSION II: 1:30 - 3:15 PM ISAT 259 (NTELOS ROOM)

KEYNOTE ADDRESS: 3:30 - 4:30 PM ISAT 259 (NTELOS ROOM)

Computer generated image depicts a molecule reacting to form a DNA base.
This reaction is catalyzed by an enzyme that is an important anti-tumor agent.

Nicholas DeMello and Jeehuin Lee
Rutgers University
(Courtesy: National Science Foundation)

32nd Annual Department of Chemistry Spring Undergraduate Research Symposium Keynote Address

Friday April 20, 2007 at 3:30 pm
ISAT Room 259 (nTelos Room)

“The State of the Union: Education and Healthcare in the US”



*Elizabeth M. Perry, M.D. (Class of 1987)
Partner and Physician
Signature Healthcare, Inc.
Charlotte, NC*

Dr. Perry received her BS degree in chemistry in 1987 from James Madison University graduating *summa cum laude* as an Honors Scholar. She received her M.D. from the Medical College of Virginia in Richmond, followed by residencies in internal medicine at the University of Pennsylvania and emergency medicine at Johns Hopkins University. She has worked as a staff physician as part of the Carolinas Physicians Network and Carolina Emergency Physicians and is currently a partner of Signature Healthcare in Charlotte, NC. Signature Healthcare is the only healthcare provider in the Charlotte region practicing “concierge medicine”—a new philosophy in medical care. Dr. Perry was recently named the 2006 winner of the “Women in Business Award” from the *Charlotte Business Journal*. Dr. Perry is married to her husband, Jon, and is the proud mother of Sydney (8), Carson (6) and Reece (3).

Past Keynote Speakers:

Each year we feature a keynote speaker for the 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	Name and Affiliation
2007	1987	Dr. Elizabeth Perry (M.D.) <i>Signature Healthcare, Inc.</i>
2006	1967	Dr. Carolyn Abitbol (M.D.) <i>University of Miami School of Medicine</i>
	1975	Dr. Daniel Downey <i>James Madison University</i>
2005	1976	Dr. Gary Rice <i>College of William of Mary</i>
2004	1987	Dr. James 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. Katheryn Lam <i>International Business Machines</i>
1999	1987	Dr. Jose Madalengoitia <i>University of Vermont</i>
1997	1986	Dr. Fred Kinder <i>Novartis Research Institute</i>
1996	1976	Dr. Terry Trask <i>DuPont Chemicals</i>
1995	1973	Dr. Carl Lenz <i>Eastman Fine Chemicals</i>
1994	1990	Ms. Michelle Kelly <i>University of Maryland—Baltimore County</i>
1993	1985	Dr. Cynthia Fallon <i>DuPont Chemicals</i>
1992	1983	Dr. Laurie Locascio <i>NIST</i>
1991	1983	Dr. Noreen Naiman <i>NC School of Science and Math</i>
1990	1982	Dr. Matthew Stershic <i>Atomchem North America</i>
1989	1982	Dr. Michael Kinter <i>Cleveland Clinic Lerner Institute</i>
1988	N/A	Dr. Thomas Mayer <i>Los Alamos National Lab</i>
1987		Dr. Steven Davis <i>Naval Research Lab</i>
1986	1980	Dr. Steven Hackney <i>Michigan Technical University</i>
1983		Dr. Richard Lam

Session I: Thursday, April 19 (nTelos Room—ISAT 259)

1:00 - 1:15	<u>Karolina Z. Roszak</u> , Kristen R. Donnelly, David M. Crizer, and Kevin L. Caran	Biscationic Single Chained Amphiphiles with Chiral and Achiral Counterions
1:15 - 1:30	<u>Brent Toland</u> , Christine L. Heinecke, Barbara A. Reisner, and Glenn P. Yap	Reaction Conditions and the Synthesis of 4-Nitrobenzylphosphonate-Zinc Frameworks
1:30 - 1:45	<u>Angela Middleton</u> , Nick Henrich, and Kevin L. Caran	Amphiphilic Catenanes Synthesis
1:45 - 2:00	<u>Christopher Kane</u> and Scott B. Lewis	The Synthesis of 1-Hexylcyclobutene for Synthetic Studies with Difluorocarbene
2:00 - 2:15	<u>Dana M. Edwards</u> , Daniel M. Downey, and James J. Leary	The Analysis of Selenium in Over-the-Counter Dietary Supplements -- A Tour de Force
2:15 - 2:30	<u>Morgan L. Moyer</u> and John W. Gilje	Solution Phase Behavior of Ph₂PCH₂CH₂P(O)Ph₂ with Lanthanide(III) and Late Transition Metal Ions Using Electropray Ionization Mass Spectroscopy
2:30 - 2:45	<u>Diana Gottschalk</u> and Kathryn Layman	ATR – FTIR Characterization of Supported Ruthenium Catalysts
2:45 - 3:00	<u>Matthew Ross</u> and Thomas C. DeVore	Identification and the Thermal Decomposition of the Surface Species Formed from the Reaction Between Acetic Acid and Aluminum Oxide
3:00 - 3:15	<u>Marita C. Lawler</u> and Kevin P. C. Minbiole	Azepine Assembly via Cyclopropanol Fragmentation
3:15 - 3:30	-----	BREAK -----
3:30 - 3:45	<u>Philip Janney</u> and Daniel M. Downey	Otolith Microchemistry Determination by LA-ICP-MS for Heavy Metal Pollution Assessment
3:45 - 4:00	<u>Mike Alvey</u> , <u>Kyle Moler</u> , and Deborah L. Mohler	Varying the Distance of Redox Active Molecules with Respect to Semiconductor Nanoparticle Surfaces
4:00 - 4:15	<u>Allyson Jones</u> and Kathryn Layman	Physiochemical Properties of Magnetic Iron Oxide Composites
4:15 - 4:30	<u>Jaime Campbell</u> and Gina MacDonald	Difference Infrared Studies of Phosphoglycerate Kinase
4:30 - 4:45	<u>Reid Gadziala</u> and Debra L. Mohler	Dependence of Rates of Interfacial Electron Transfer on Anchoring Group and Dye MCLT State Energy
4:45 - 5:00	<u>Meagan Travers</u> and Daniel M. Downey	Ion Chromatography as an Alternative to Titration for the Determination of Alkalinity
5:00 - 5:15	<u>Jeremy Harris</u> and Barbara A. Reisner	Exploration of Ionic Liquid as Solvent and Structure Directing Agent in Aluminophosphate Synthesis
5:15 - 5:30	<u>Cynthia Din</u> , <u>Sarah McDaniel</u> , and Kathryn Layman	P-Cresol Oxidation Catalysts

Session II: Friday, April 20 (nTelos Room—ISAT 259)

1:30 - 1:45	<u>Diego Ramallo</u> , <u>Beth Hochreiter</u> , Gina MacDonald, and Jeffrey Molloy	Quantitation of Blood Neurotransmitters and Metabolites by Means of High Performance Liquid Chromatography Investigation of Epimerization in Cyclopropane Fragmentation Approach to Oxepane Synthesis with Applications to Natural Products
1:45 - 2:00	<u>R. Stephen Andrews</u> and Kevin Minbiole	Identification and the Thermal Decomposition of the Surface Species Formed from the Reaction Between Acetic Acid and Copper Acetate/Aluminum Oxide
2:00 - 2:15	<u>John DeJarnette</u> and Thomas C. DeVore	Supramolecular Studies on Aromatic Propargylic Alcohols Modified With Aliphatic Chains
2:15 - 2:30	<u>Ashleigh Borges</u> , Michelle Lum, Marilise Hyacinth, Kevin Caran, Michal Sabat, and Lin Pu	Surface Modification and Characterization of POSS-based Acrylic Thin Films
2:30 - 2:45	<u>Kathryn Zimmermann</u> , Ashley Fueigero, Wm. Christopher Hughes, Brian H. Augustine	Study of Novel Deep Eutectic Solvents as Reaction Media for the Synthesis of Inorganic Materials
2:45 - 3:00	<u>Jaime Mirowsky</u> and Barbara A. Reisner	Development of Colloid Chemistry Experiments for Organic and Nanoscience Laboratory Courses
3:00 - 3:15	<u>Stephanie Torcivia</u> and Kevin L. Caran	
3:15 - 3:30	-----	BREAK -----

KEYNOTE ADDRESS: Friday, April 20 (nTelos Room—ISAT 259)

3:30 - 4:30	Dr. Elizabeth Perry (Class of 1987) Partner and Physician Signature Healthcare, Inc. Charlotte, NC	“The State of the Union: Education and Healthcare in the US”
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STUDENT ABSTRACTS:

Varying the Distance of Redox Active Molecules with Respect to Semiconductor Nanoparticle Surfaces

Mike Alvey, Kyle Moler, and Deborah L. Mohler
Department of Chemistry, James Madison University

Interfacial electron transfer (ET) is an important process to such applications as photocatalysis, solar energy conversion, and photography. An increased understanding of ET will aid in developing and improving applications whose efficiencies rely on ET. The Mohler group is currently studying long distance electron transfer across molecule-nanocrystalline semiconductor interfaces. The general idea is to use a tripod-based organic molecule as an anchor for a redox active molecule. The distance of the redox active molecule from the surface of a semiconductor nanoparticle can be varied by changing the size of the tripod-based organic molecule. The redox active molecule, known as the sensitizer, previously used to study electron transfer rates is Ru(Ad-Ph-E-phen)(bpy)₂(PF₆)₂. Previous studies have shown that the length of the linker that connects the redox active molecule to the tripod-shaped organic molecule has shown no effects on electron transfer rates when this ruthenium compound is used. It is believed that the charge on the ruthenium compound pulls the molecule toward the surface of the semiconductor nanoparticle, causing the molecule to lie flat on the surface. Employing a neutral metal complex should prevent this behavior, positioning the linker perpendicularly to the surface and allowing the distance dependence of ET rates to be studied. Progress towards the synthesis of such molecules will be discussed.

Investigation of Epimerization in Cyclopropane Fragmentation Approach to Oxepane Synthesis with Applications to Natural Products

R. Stephen Andrews and Kevin Minbiole
Department of Chemistry, James Madison University

Oxepanes are oxygen-containing seven-membered heterocycles. Oxepanes with various functional groups have been synthesized using an endo cyclization mediated by a cyclopropanol, which demonstrates the potential of this method in the synthesis of oxepane containing natural products. Preliminary steps have been taken to explore a model system to synthesize isolaurepinnacin. The epimerization of cis- and trans-oxepanes has been investigated. Cis-oxepanes can be readily converted to trans-oxepanes in the presence of an excess of Lewis acid, while epimerization of trans-oxepanes to cis-oxepanes has been unsuccessful. A possible mechanism has been investigated and proposed.

Supramolecular Studies on Aromatic Propargylic Alcohols Modified With Aliphatic Chains

Ashleigh Borges¹, Michelle Lum¹, Marilise Hyacinth², Kevin Caran¹, Michal Sabat², and Lin Pu²

¹Department of Chemistry, James Madison University

²Department of Chemistry, University of Virginia

A number of chiral aromatic propargylic alcohols have recently been found to display interesting supramolecular interactions in the solid state based on three intermolecular interactions: OH...O hydrogen bonds, aromatic-fluoroaromatic pi stacking, and weak CH...F hydrogen bonds. Several derivatives display hexameric aggregates that stack into columns containing pseudo-infinite channels a few angstroms wide. Our current efforts include modifying these structures with aliphatic hydrocarbons of different chain lengths and investigating the supramolecular behavior of these structures in various environments. Such modifications may promote the formation of fibrous aggregates with a high aspect ratio by suppressing aggregation lateral to the direction of fiber growth. Synthesis and colloidal studies of these molecules will be presented.

Difference Infrared Studies of Phosphoglycerate Kinase

Jaime Campbell and Gina MacDonald
Department of Chemistry, James Madison University

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

Identification and the Thermal Decomposition of the Surface Species Formed from the Reaction Between Acetic Acid and Copper Acetate/Aluminum Oxide

John DeJarnette and Thomas C. DeVore
Department of Chemistry, James Madison University

Copper oxides are used in industry to catalyze the decomposition and dehydrogenation of organic compounds, the formation of methanol from the reaction between CO₂ and H₂ in the Fisher-Tropsch process, and the catalytic combustion of volatile organic hydrocarbons in waste gas streams. Investigations of the interactions between the catalytic surface and the reactant molecule provide insight into the catalytic mechanism and may offer insight that can be used to generate more efficient catalysts. We are investigating the interaction between pyrolyzed copper acetate aluminum oxide and acetic acid. The compound was shown to produce weak acetate bands in the infrared spectrum. EGA (Evolved Gas Analysis) FT-IR, however, did not produce any detectable organic compounds besides CO₂. During EGA FT-IR though, the compound turned black after heating in vacuum. Heating the residue in air returned the compound to its original green color indicating the removal of surface carbon. By comparing the infrared spectrum and X-ray diffraction patterns to those obtained for known copper and aluminum acetate compounds, we should be able to identify the chemical species formed on the surface from this interaction.

P-Cresol Oxidation Catalysts

Cynthia Din, Sarah McDaniel, and Kathryn Layman
Department of Chemistry, James Madison University

The desired product of the oxidation of *p*-cresol is *p*-hydroxybenzaldehyde (PHBA), which is an important intermediate in the synthesis of many pharmaceuticals, perfumes, flavoring agents, and agricultural chemicals. Cu, Co, Mg, and Mn are frequently employed for oxidation reactions. Therefore, the oxidation of *p*-cresol by metal oxides of Cu, Co, Mg, and/or Mn supported on aluminum oxide was investigated. Each metal oxide catalyst was calcined at temperatures between 400 and 900°C. The oxidation of *p*-cresol was monitored using high performance liquid chromatography (HPLC). It was found that both the *p*-cresol conversion and selectivity to *p*-hydroxybenzaldehyde increases by increasing the catalyst loading on the Al₂O₃ support. The % *p*-cresol conversion and catalytic selectivity depend on the calcination temperature of the supported metal oxide catalyst. X-ray diffraction (XRD) characterization indicates that the dependence of *p*-cresol conversion on calcination temperature results from the formation of a less active metal aluminum oxide (e.g., CoAl₂O₄) phase at the higher calcination temperatures. The CoO/Al₂O₃ (30 wt% Co) catalyst has shown to be the most active and selective (95.7% *p*-cresol conversion and 92.4% selectivity to *p*-hydroxybenzaldehyde).

The Analysis of Selenium in Over-the-Counter Dietary Supplements -- A Tour de Force

Dana M. Edwards¹, Daniel M. Downey², and James J. Leary²
¹Department of Health Sciences, James Madison University
²Department of Chemistry, James Madison University

Students in Instrumental Analysis at JMU routinely analyze over-the-counter (OTC) dietary supplements using an inductively coupled plasma mass spectrometer (ICP-MS). Of the elements analyzed in these OTC supplements selenium has been the most challenging. The first attempt to determine the selenium content of OTC supplements used a simple calibration curve; serious accuracy and precision problems were encountered. The next step in the evolution of this project was the use of tellurium as an internal standard; the precision of the results improved, but accuracy problems persisted. The final analytical method utilized a standard addition protocol in addition to using tellurium as an internal standard. The quality of the achievable results is documented in terms of the accuracy with which "spiked" samples can be analyzed. The nonlinearity of standard addition calibration curves will be briefly discussed. Insights will be offered about the selection of where points should be placed along the independent axis. The precision of the method will be described, and three factors influencing the achievable precision will be mentioned. Finally, results will be presented for the analysis of selenium in eight OTC supplements.

Dependence of Rates of Interfacial Electron Transfer on Anchoring Group and Dye MLCT State Energy

Reid Gadziala and Debra L. Mohler
Department of Chemistry, James Madison University

A series of chlorotricarbonylrhenium compounds have been synthesized to measure their effects on ultrafast electron transport systems. These compounds are hypothesized to affect interfacial ET in two ways. First, the properties of attached anchoring groups will bring the bipyridine ligand in direct contact with a nanoparticle making electron transport more efficient. A second hypothesis is to attach energy modulators to the chlorotricarbonylrhenium's bipyridine ligand in an effort to better hybridize the molecular orbitals between it and the nanoparticle. A molecule of chlorotricarbonylrhenium complexed with a sulfonic acid functionalized bipyridine ligand has been synthesized. Characterization of the complex was accomplished by ¹H and ¹³C NMR, IR, UV-vis, and high-res mass spec. A second approach to attaching a nitro compound to the bipyridine ligand is being explored as a way of modulating the energy level of the MLCT state.

ATR – FTIR Characterization of Supported Ruthenium Catalysts

Diana Gottschalk and Kathryn Layman
Department of Chemistry, James Madison University

Heterogeneous catalysis at solid-gas interfaces plays an important role in many industrial applications. For example, silica-supported metal (e.g. Ru) catalysts are used in the oxidation of aqueous organic contaminants, water-gas shift of CO to CO₂, Fisher-Tropsch synthesis of alkanes, and fuel cell applications. Although chemical reactions at the solid-gas interfaces are important in several catalytic processes, few *in-situ* studies have focused on investigating them in the presence of water. Our research efforts focus on using *in-situ* attenuated reflection Fourier transform infrared (ATR-FTIR) spectroscopy to characterize the surface properties of silica-, alumina-, and NaY zeolite-supported ruthenium (Ru) catalysts in the presence of co-adsorbed water. Specifically, we are studying the adsorption of CO on these catalysts as a function of time, catalyst loading, and treatment. We observe three ν_{CO} absorbances at 2048, 1992, and 1927 cm⁻¹. Our results indicate that these absorbance features are uncorrelated. Furthermore, the band positions and intensities depend on the amount of co-adsorbed water. Therefore, we have tentatively assigned the ν_{CO} absorbances at 1927, 1992, and 2048 cm⁻¹ to Ru(CO)_n (n ≥ 1), Ru(CO)X_m, and Ru(CO)_nX_m, respectively, where X represents co-adsorbed H₂O, OH, O, Cl, and S species.

Exploration of Ionic Liquid as Solvent and Structure Directing Agent in Aluminophosphate Synthesis

Jeremy Harris and Barbara A. Reisner
Department of Chemistry, James Madison University

Due to their large pore sizes, open-framework aluminophosphates (AIPO) have many uses in catalysis, molecular transport, molecular separation, and sorption. AIPO synthesis has been extensively investigated hydrothermally and solvothermally, but little is known about producing AIPOs with ionic liquids (IL) as the solvent. IL have received much attention for properties such as low vapor pressures, recyclability, high thermal stability, and its ability to dissolve metal salts and organic compounds. Several experiments have been performed to produce AIPOs ionothermally. AIPO-11, 41, 5 and other AIPOs have been successfully synthesized by varying temperature, heating duration, heat source, and structure-directing agents (SDAs). Reactions were conducted in Teflon-lined autoclaves or microwave test tubes for heating. X-ray Diffraction (XRD) was used to identify these compounds and document the trends that occurred upon changing reaction conditions; and scanning electron microscopy (SEM) to analyze samples on the micrometer scale.

Otolith Microchemistry Determination by LA-ICP-MS for Heavy Metal Pollution Assessment

Philip Janney and Daniel M. Downey
Department of Chemistry, James Madison University

The elemental microchemistry of fish otoliths (ear bones) can be used to determine the uptake of heavy metals, and other pollutants in the aquatic environment. An otolith is an aragonitic calcium carbonate (CaCO_3) structure that grows continually throughout the life of a fish. The continual deposition of new CaCO_3 layers produces growth annuli, similar to those found in trees, which may be biologically inert records of the water chemistry surrounding the fish. Currently, inductively coupled plasma mass spectrometry (ICP-MS) is one of the most sensitive means of conducting trace elemental analysis. Previous studies have determined the bulk contaminant concentrations in otoliths with solution based ICP-MS following an acid digestion of the otolith. The acid digestion leads to a further dilution of trace analytes as well as a failure to utilize the temporal nature of the otolith. Coupling ICP-MS with a laser ablation (LA) sample introduction system, it is possible to directly analyze solid samples with little preparation. Utilizing LA-ICP-MS, it is possible to analyze the individual growth annuli within the otolith in an attempt to develop a temporal record of contaminant uptake throughout the lifetime of a fish. In order to quantitatively report the concentrations of metals within the growth annuli, standards were first produced. To match the otolith matrix, pressed CaCO_3 pellets spiked with selected metals were produced by coprecipitation of the analytes in the CaCO_3 matrix. Four standards were produced containing between 0 and 200 ng/g of the analytes and the analyte concentrations within the CaCO_3 standards were verified by solution mode ICP-MS. Ablation parameters were determined in order to optimize the analysis of otoliths using the standards produced. LA-ICP-MS was used to examine microchemistry of smallmouth bass (*Micropterus dolomieu*) otoliths to develop a temporal record of exposure to heavy metal pollutants.

Physiochemical Properties of Magnetic Iron Oxide Composites

Allyson Jones and Kathryn Layman
Department of Chemistry, James Madison University

Magnetic iron oxide composites supported on NaY zeolite, aluminum oxide, and silica are being investigated as an environmental application for removing metal cations from ground water. Magnetic iron oxide composites were synthesized by varying a previously published procedure to create a more efficient and practical adsorbent. The composite's properties were then characterized using the magnetic susceptibility balance, X-ray powder diffractometer (XRD), and scanning electron microscope (SEM). Atomic absorption (AA) was used to analyze the composite's ability to uptake Cu^{2+} ions. The results indicate that the composite's magnetic susceptibility and Cu^{2+} uptake capacity is dependent upon: 1.) the temperature at which the composite is synthesized; 2.) the support to iron oxide mass ratio; and 3) the order of the procedure. When synthesized at 25°C, the composite with an equal mass ratio of NaY zeolite to iron oxide has the best magnetic susceptibility and Cu^{2+} uptake capacity.

The Synthesis of 1-Hexylcyclobutene for Synthetic Studies with Difluorocarbene

Christopher Kane and Scott B. Lewis
Department of Chemistry, James Madison University

Organofluorine compounds are prevalent in pharmacological applications worldwide and are a source of constant research. Fluorinated aromatics provide unique properties, beneficial for use for in vivo functions. Lack of steric effects and high biological activity are among several contributions fluorine can make. Because of fluorine's ortho/para directing capability, the meta arrangement is not easily observed. Through the use of a substituted cyclobutene and difluorocarbene, this motif can be more easily synthesized. The synthesis of 1,3-difluoro-2-hexylbenzene has been accomplished in a multi-step synthesis from 1-hexylcyclobutene using a difluorocarbene precursor. Characterization of intermediates have been made using Bruker 400 and 600 MHz NMR, GC-MS, and HR-MS.

Azepine Assembly via Cyclopropanol Fragmentation

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

The ring strain of cyclopropanols can be exploited for the stereocontrolled formation of oxygenated heterocycles such as oxepanes. Progress has been made toward the synthesis of nitrogenous heterocycles, particularly azepines, via analogous fragmentation/recondensation strategies. This method condenses a β -amino alcohol with an aldehyde or an alkyne, producing an amina. Under Lewis acid promotion, the amina is expected to rearrange to an azepine. Different protecting groups have been explored for the starting amino ester, in order to allow for Kulinkovich cyclopropanation as well as to enhance iminium electrophilicity during cyclization. The protecting groups Boc, Troc, Fmoc, and benzophenone imine were attempted. The Fmoc group has allowed for cyclopropanation and *in-situ* protecting group removal, allowing for successful amina formation. The subsequent azepine formation will be explored utilizing various Lewis acids.

Amphiphilic Catenanes Synthesis

Angela Middleton, Nick Henrich, and Kevin L. Caran
Department of Chemistry, James Madison University

We have prepared an amphiphilic catenane, composed of two interlocked macrocyclic rings serving as a hydrophilic (polar) head and two covalently bound hydrophobic (non-polar) tail. We have used an organic-templated method based on the cyclophane-crown ether complex first prepared by Stoddart and co-workers in 1989. To synthesize our catenane, we reacted a biscationic cyclophane precursor bearing a long hydrophobic chain and two nucleophilic nitrogens with a bis-electrophile (also bearing a long chain) to close the ring, thus forming the electron poor cyclophane unit. This is accomplished in the presence of an electron-rich crown ether to form the amphiphilic catenane. Through aromatic stacking interactions, the cyclophane unit is closed around the crown ether in a one-step synthesis. We are currently investigating supramolecular interactions of this catenane. All intermediates were characterized using ^1H NMR and mass spectroscopy. Synthetic details, preliminary colloidal studies, and future work will be presented.

Study of Novel Deep Eutectic Solvents as Reaction Media for the Synthesis of Inorganic Materials

Jaime Mirowsky and Barbara A. Reisner
Department of Chemistry, James Madison University

Several deep eutectic solvents (DES) have been explored as reaction media for the synthesis of coordination polymers, metal phosphates and metal-organic frameworks (MOF). Binary DES composed of choline chloride with either urea, malonic acid, oxalic acid or 1,3-dimethylurea and ternary DES containing choline chloride and urea with either malonic or oxalic acid were studied by thermal analysis and investigated for their utility as solvents. Synthesis of metal carboxylates and metal phosphates using Li, Zn, Ni, Mn, and Co with 1,3,5-benzenetricarboxylic acid, phosphonoacetic acid, phosphoric acid, and tetraethyl-1,1,2,2-ethane tetracarboxylate ligands in the presence of binary DES and structure directing agents were unsuccessful. Thermal analysis of the binary DES showed that above 120°C, the choline chloride:urea eutectic gives off CO_2 , HNCO , H_2O , and NH_3 gases and above 140°C CO was released. Above 120°C, the choline chloride:malonic acid eutectic gives off an unknown gas observed in the FT-IR at 1723 cm^{-1} . Above 120°C, the choline chloride:oxalic acid eutectic gives off CO and CO_2 . The solvent system comprising of urea shows promise for the synthesis of isocyanates because the decomposition products of NH_4^+ and NCO^- can act as a structure directing agent and ligand, respectively.

Solution Phase Behavior of Ph₂PCH₂CH₂P(O)Ph₂ with Lanthanide(III) and Late Transition Metal Ions Using Electrospray Ionization Mass Spectroscopy

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

We are interested in the coordination of Ph₂PCH₂CH₂P(O)Ph₂ to lanthanide ions. Previously, we have crystallized and determined the structure of [Ph₂PCH₂CH₂P(O)Ph₂]₃Ln(NO₃)₃, Ln = Ce, Tb, and Yb, from the reaction of Ph₂PCH₂CH₂P(O)Ph₂ with Ln(NO₃)₃. Electrospray Ionization Mass Spectra (ESI-MS) of methanolic solutions of these lanthanide complexes indicate complex solution equilibria. Complexes containing two, three, and four ligands have been observed. Addition of Ni³⁺, Co³⁺, Pt²⁺, and Pd²⁺ to these solutions appears to favor formation of transition metal/ligand complexes at the expense of lanthanide/ligand complexes. When Ce³⁺ is added to solutions of Cl₂Pt[Ph₂PCH₂CH₂P(O)Ph₂]₂, a complex containing the Pt²⁺ and Ce³⁺ is detected. This NMR data is consistent with this result.

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

Diego Ramallo, Beth Hochreiter, Gina MacDonald, and Jeffrey Molloy
Department of Chemistry, James Madison University

Neurotransmitters play important and diverse roles in mood and behavior regulation. We are interested in improving methodologies to determine the concentrations of dopamine, serotonin, and their metabolites in blood. 3,4-dihydroxy phenyl acetic acid (DOPAC), 4-hydroxy-3-methoxyphenylacetic acid (HVA), 5-hydroxy-3-indole acetic acid (5-HIAA), and 4-hydroxy-3-methoxyphenylglycol hemipiperazinium salt (MHPG) are found in blood and are metabolites of dopamine, serotonin, and norepinephrine, respectively. Our goal is to find a highly-sensitive, reproducible method for quantitating the concentrations of these compounds in whole blood samples. Our initial studies have focused on trying to implement published procedures and use various standards in conjunction with HPLC to determine the best approach for quantitating the neurotransmitters and their metabolites. We have begun to use HPLC with coulometric detection in order to monitor their concentrations. A second method involving fluorescence detection is under development to verify our results from the coulometric detection. Specific fluorescent labels attached to neurotransmitters and their metabolites can facilitate their identification and quantitation. Benzylamine HCl was used to label 5-HIAA while fluorescein isothiocyanate isomer I (FITC) was used to label 5-HT and DA. Fluorescence spectra of the labeled compounds were obtained to ascertain if concentrations were proportional to the fluorescence intensity. All compounds showed fluorescence yet only the 5-HT samples' fluorescence intensity was proportional to concentration. Preliminary studies on the purification of the neurotransmitters and metabolites from blood have commenced. The methods for electrochemical and fluorescence detection will eventually be used to simultaneously quantitate the metabolite concentrations of blood samples in our laboratory.

Identification and the Thermal Decomposition of the Surface Species Formed from the Reaction Between Acetic Acid and Aluminum Oxide

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

Aluminum oxide is used in industry to dehydrate alcohols to make alkenes and as a support in several catalytic formulation that are used in a wide variety of other industrial processes. Investigations of the interactions between the catalytic surface and the reactant molecule provide insight into the catalytic mechanism and may offer insight that can be used to generate more efficient catalysts. We are investigating the interaction between aluminum oxide and acetic acid to try to establish the mechanism for the decarboxylation of this compound to produce acetone. By comparing the infrared spectrum and X-ray diffraction patterns to those obtained for known aluminum acetate compounds, we were able to identify that aluminum hydroxyacetate was the principle chemical species formed on the surface from this interaction. TGA-Mass Spectroscopy, FT-IR, and Differential Scanning Calorimetry (DSC) have found that acetic acid, ketene and acetone desorb from the coated surface as the sample is heated. The apparent activation energy for the formation of acetone is ~ 80 kJ/ mol.

Biscationic Single Chained Amphiphiles with Chiral and Achiral Counterions

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While a broad diversity of amphiphiles is readily available, there remains the need to continue to explore new systems that will expand the utility and specificity of colloidal aggregation. We have thus prepared several novel amphiphiles with two cationic headgroups and a single aliphatic chain. The amphiphiles have been synthesized via a three-step procedure. The first step consists of a Williamson ether synthesis, which is subsequently followed by a benzylic bromination, and then a Menshutkin reaction. Three final products have been successfully synthesized. The products vary in the length of the hydrophobic chain. They are eighteen, fourteen, and ten carbons in length. Currently aggregation studies of the final products are being undertaken. When added to water, the amphiphile tends to aggregate in such a way as to place hydrophobic groups away from the polar water while placing the hydrophilic groups facing water. The major cause for this associated behavior is the 'competition' between the attractive interactions between the alkyl chains and the repulsive interactions between the polar heads. The aggregation of these molecules is being studied using several techniques including DOSY-NMR, fluorescence, surface tension and conductivity.

Reaction Conditions and the Synthesis of 4-Nitrobenzylphosphonate-Zinc Frameworks

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The ligand diethyl(4-nitrobenzyl)phosphonate has been used to synthesize two new zinc phosphonate framework materials. Reaction temperature affects the nature of the framework. ZnO₃PCH₂C₆H₄NO₂·H₂O (**HT**) was synthesized at reaction temperatures greater than 130°C. **HT** consists of 1-D ladders composed of [Zn₂P₂O₄] 4-rings that are connected to adjacent ladders by hydrogen bonding to form an inorganic layer. The layers are separated by nitrobenzyl groups that are oriented in a herringbone configuration. A related low temperature phase (**LT**) has been synthesized; it is believed to be Zn[O₂P(OC₂H₅)CH₂C₆H₄NO₂]₂. FT-IR experiments indicate that compounds **HT** and **LT** have similar structural features. Both materials appear to exhibit disorder depending on synthesis temperature.

Development of Colloid Chemistry Experiments for Organic and Nanoscience Laboratory Courses

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In an effort to integrate nanoscience concepts throughout the chemistry curriculum at JMU, several new laboratory experiments have been designed. The synthesis of the Gemini surfactant, ethanediyl--bis(dodecyldimethylammonium) dibromide, also referred to as 12-2-12, was optimized and a critical micelle concentration (CMC) study was completed. Formation of the ~2 nanometer wide worm-like micelles was studied using several indirect techniques: surface tension, conductivity, and diffusion rate (using DOSY) of a series of aqueous solutions were measured over a range of concentrations. In addition, pyrene was used as a fluorescent probe to measure the CMC. DCM dye was also used in solution to visualize the change in polarity with a change in surfactant concentration. Various aspects of the synthesis and colloidal analysis of 12-2-12 will be implemented in several labs at JMU including the Organic labs (Chem221L and Chem346L), Physical Chemistry lab (438L), and the new "Science of the Small" course (Chem480P). Future studies will include the preparation of a Gemini surfactant with chiral counterions, which will allow fine-tuned control of the pitch of a twisted membrane on the nano scale.

Ion Chromatography as an Alternative to Titration for the Determination of Alkalinity

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Alkalinity is a useful water-quality parameter that can be used for describing the effect of acid deposition on stream water and other aquatic systems. It is defined as the sum of all titratable bases in a water sample, expressed as mg CaCO₃ per liter. Although other bases may occur in some waters of unusual geology carbonate, bicarbonate, and hydroxide are the most common alkaline species. The standard method of alkalinity determination is by titration of standardized HCl to a pH 4.5 endpoint. For samples of low alkalinity a two endpoint titration method must be used. The titration methods can be tedious, time-consuming and labor intensive. A computational method based on charge balance has been studied as an alternate approach to alkalinity determination. In this approach all ions except bicarbonate and carbonate are determined by ion chromatography, which is automated. The bases are then calculated from the difference between cations and anions. Results for low, medium and high alkalinity water samples determined by both methods will be presented and compared statistically.

Surface Modification and Characterization of POSS-based Acrylic Thin Films

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Poly(methacrylisobutyl)POSS-co-methylmethacrylate (POSS-MA) is a nanocomposite copolymer consisting of a poly(methylmethacrylate) backbone with attached polyhedral oligomeric silsesquioxane (POSS) cages. The combination of the acrylic backbone and nanoscale glasslike POSS cages is being investigated for possible use in microfluidic devices. The effect of remote oxygen plasma on POSS-MA has been investigated using advancing contact angle, variable angle spectroscopic ellipsometry (VASE), and X-ray photoelectron spectroscopy (XPS). Solutions of 2.0 mg/mL PMMA-POSS (10%, 20%, and 45% POSS by weight) in CHCl₃ were spuncast onto 4" thermally oxidized silicon wafers. Exposure to remote oxygen plasma was found to alter the PMMA-POSS surface from hydrophobic to hydrophilic, with a positive correlation between plasma exposure time and increasing hydrophilicity. A control of 100% nitrogen plasma treatment showed a less significant change in hydrophilicity, suggesting that the presence of oxygen is responsible for the change in wettability of the surface. VASE data showed that an increase in the weight percent of POSS in the copolymer resulted in a significantly slower degradation of the surface by remote oxygen plasma. XPS data showed that upon plasma treatment of the PMMA-POSS film, the percentages of silicon and oxygen in the surface regions increased, while that of carbon decreased. From this data, a model has been created suggesting that plasma treatment with oxygen removes the isobutyl groups from the POSS cages, leaving behind a SiO₂-rich surface.