

JMU Chemistry and Biochemistry – 2009 Spring Symposium

Poster Session: Thursday April 9 th 1:30 – 3:00 pm (Ph/Ch 3348)	
Marko Andric and Gina MacDonald	Purification and Characterization of Escherichia Coli RecA
Robert E. East, Courtney N. Braxton, and Victoria L. Mariani	Characterization of N-Acylethanolamine-hydrolyzing Acid Amidase Toward a Novel Class of Anti-Inflammatory Agents
Nicholas Dugan and Daniel M. Downey	Inorganic Ions, Trace Elements and Sediment Loading in the South Fork Shenandoah River and Cub Run During Storm Runoff Events
Paris Hamilton, Marilise Hyacinth, Kevin L. Caran, Lin Pu and Michal Sabat	The Effect of Structure Modification on Low-Molecular-Weight Organogelators
Hollins Kitts, Kevin Kindley, Allyson Jones and Kathryn Layman	Characterization of Magnetic Iron Oxide Composites
Puja Mody, Amanda Hoffman, Seth Ensign and Debra L. Mohler	The Synthesis of a Chlorotricarbonylrhenium I Complex of [4, 4'- bis(aminomethyl)-2,2'-bipyridine]
Vanessa Shepperson, John W. Gilje and Donna S. Amenta	Preparation and Spectral Characterization of Ru(CO) ₂ (PPh ₂ CH ₂ CH ₂ P(O)Ph ₂) ₃
Danielle Simpson, Paul Layne, Chelsea Cockburn and Debra L. Mohler	pH Dependence of the Formal Hydrolysis of DNA Phosphodiesterases and the Study of the Location of Cleavage by [CpFe(CO) ₂] ₂ and Hydrogen Peroxide
Jacob Smith and Daniel M. Downey	Analysis of Glyphosate in the South Fork Shenandoah River and Cub Run Following Storm Runoff Events
Dien Tu, Andrew Evangelista, Amanda Hoffman and Debra L. Mohler	The Synthesis of Chlororheniumtricarbonyl Complexes of Substituted and Unsubstituted 2,2'-bipyridine Ligands

Oral Session I: Thursday April 9 th (ISAT 159)	
3:30 – 3:45	David Berry and Thomas C. DeVore Interactions Between Boric Acid and Ammonia
3:45 – 4:00	Stephanie Hall and Daniel M. Downey Analysis of Organic Pesticides in the South Fork Shenandoah River and Cub Run in Storm Runoff Events
4:00 – 4:15	Curtis White and Thomas C. DeVore Proton Chemical Shifts for Alcohols in the Vapor Phase and Dilute Solutions
4:15 – 4:30	William Cannon and Gina MacDonald Ion Induced Effects on RecA Structure, Activity, and Stability During Thermal Unfolding

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Oral Session II: Friday April 10 th (ISAT 159)		
2:00 - 2:15	Adam Colbert and Gina MacDonald	Using Difference Infrared Spectroscopy to Investigate the Effects of pH on PGK-Substrate Complexes
2:15 - 2:30	Alexandra Allen, Brooke Stevens, Cameron Straughn, Nicole Carpenter and Debra L. Mohler	Progress Towards the Synthesis of Stable RNA Analogs
2:30 – 2:45	Nicole Ando, John W. Gilje, Donna S. Amenta and Glen P. Yap	Ruthenium Complexes of Phosphine/Phosphine Oxide Ligands
2:45 – 3:00	Kristina M. Hamill and Kevin L. Caran	Synthesis and Colloidal Properties of Novel Biscationic Bicephalic (Double Headed) Amphiphiles
3:00 – 3:15	Tracy Nichols and Scott Lewis	The Synthesis of 1,2-Disubstituted Cyclobutenes for Study with Difluorocarbene
3:15 – 3:30	Christian R. Schwantes, Devon C. Flaherty, Jenifer L. Banning, Matt H. Becker, Rob M. Brucker, Reid N. Harris, Kevin P. C. Minbiole, and Doug C. Woodhams	Developing a Bacterial Treatment Using <i>Janthinobacterium lividum</i> for Amphibians <i>Rana muscosa</i> and <i>Plethodon cinereus</i> Infected with <i>Batrachochytrium dendrobatidis</i>
3:30 – 3:45	----- break -----	

Keynote Address: Friday April 10 th (ISAT 159)		
3:45 – 4:45	Dr. Chris E. Holmes (Class of 1988)	“Platelet Modulation: A New Approach to Cancer and Angiogenesis Control”

Platelet Modulation: A New Approach to Cancer and Angiogenesis Control

Dr. Chris E. Holmes, M.D., Ph.D.
The University of Vermont College of Medicine

In addition to their role in hemostasis, platelets serve as a circulating reservoir of over 30 key angiogenic and metastatic proteins. The platelet protein storage pool represents the largest available reservoir of proteins that can stimulate or inhibit tumor growth. These proteins are released during the process of platelet activation and platelet activation and deposition is seen in the tumor microenvironment. Studies conducted in Dr. Holmes' laboratory as well as others suggest pro-angiogenic and anti-angiogenic protein release from platelets can be selectively regulated. Dr. Holmes will discuss the influence of key platelet activation pathways on platelet protein release and the processes of angiogenesis and metastasis using cellular models. In addition, she will present data from her recent clinical studies in patients with breast cancer that suggest anti-platelet therapy may play a pivotal role in both the cancer prevention and treatment setting.

STUDENT ABSTRACTS

Progress Towards the Synthesis of Stable RNA Analogs

Alexandra Allen, Brooke Stevens, Cameron Straughn, Nicole Carpenter and Debra L. Mohler
Department of Chemistry and Biochemistry, James Madison University

Emerging research has shown that short RNA strands known as siRNAs, that bind to DNA to inhibit the transcription of mRNA, a method with much therapeutic potential. However, RNA is a relatively unstable compound in the cell, because the 2'-OH group on the ribose sugar allows the easy and quick degradation of the macromolecule. Therefore, an expedient synthesis of stable RNA mimics designed to bind RNA and/or DNA is under development, and preliminary work in this area will be described.

Ruthenium Complexes of Phosphine/Phosphine Oxide Ligands

Nicole Ando,¹ John W. Gilje,¹ Donna S. Amenta¹ and Glen P. Yap²

¹Department of Chemistry and Biochemistry, James Madison University

²University of Delaware

The reactions of $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ with 1 equivalent $\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ and 1 or 2 equivalents of $\text{PPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ were run in toluene at room temperature. From the first reaction $\text{Cl}_2\text{Ru}(\text{PPh}_3)_2(\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)$ was characterized by ^{31}P NMR spectroscopy and by a crystal structure. When the reaction is run in acetonitrile, $\text{Cl}_2\text{Ru}(\text{PPh}_3)_2(\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)$ is observed. The chemical shifts of the PPh_2 and $\text{P}(\text{O})$ moieties indicate that both the phosphino phosphorus and phosphoryl oxygen are bonded to the Ru. We postulate that the acetonitrile facilitates the dissociation of the second PPh_3 and that acetonitrile may be coordinated to the Ru. The ^{31}P NMR spectra of the products from the reactions between $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ with either 1 or 2 equivalents of $\text{PPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ are not well defined at room temperature. Upon cooling the spectra undergo changes, but the peaks are still not well resolved.

Purification and Characterization of Escherichia Coli RecA

Marko Andric and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

The Escherichia Coli protein RecA is a multifunctional protein that is required for homologous recombination, DNA repair, and the induction of the SOS response. RecA plays a vital role in maintaining genetic information while also having the opposing effect of introducing genome variation. Numerous studies on the RecA protein have been carried out in order to obtain a better understanding of these biological processes. Several purification procedures of RecA have been published. We have utilized and modified one rapid large scale purification that was previously published. (Singleton, S.F., Simonette, R.A., Sharma, N.C., Roca, A.I. (2002) Protein Expression and Purification 26, 476-488). RecA protein with a modified C-terminus containing a chitin binding domain and a splicing contributor, intein, was purified using one-step affinity chromatography procedure. Fractions containing RecA protein have purities greater than 95% and have ATP hydrolysis activity in the presence of single stranded DNA. Purified RecA protein was used in Fourier Transform Infrared spectroscopic studies that enabled further characterization of RecA's structure and aggregation states. Thermal unfolding of RecA was monitored in the presence of various salts. FT-IR spectroscopic studies should provide new evidence of secondary structural changes of RecA protein in absence of DNA during thermal denaturation.

Interactions Between Boric Acid and Ammonia

David Berry and Thomas C. DeVore

Department of Chemistry and Biochemistry, James Madison University

Evaporating a solution of boric acid, $\text{B}(\text{OH})_3$, and ammonia yields only solid boric acid. However, FT-IR indicated the reaction of boric acid with ammonia vapor resulted in a complex by the presence of amine bands in the 3000-3500 cm^{-1} region. The thermal analysis of the solid boric acid amine complex was studied using EGA-FTIR, DSC, and TGA analysis. The decomposition of the complex begins with dehydration followed by ammonia loss with an activation energy, E_a , of 78.1 J/mol. Investigation of boric acid and ammonia in solution was studied using ^{11}B NMR. Boric acid has a characteristic chemical shift at 19.7 ppm. As the concentration of ammonia increases and boric acid remains constant, the B-OH peak shifts upfield. In addition, ^{11}B NMR showed peaks at 13.01 ppm, 6.64 ppm, and 1.12 ppm indicating the formation of a boric acid amine complex. Density Functional Theory calculations were performed to understand the shifts that occur in the ^{11}B NMR spectrum of a solution of boric acid in ammonia and to attempt to better characterize these species.

Ion Induced Effects on RecA Structure, Activity, and Stability During Thermal Unfolding

William Cannon and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

The *Escherichia coli* protein, RecA, is critical for maintaining genetic integrity. RecA catalyzes DNA pairing and strand exchange reactions that are utilized in DNA recombination and DNA repair. Buffer and salt conditions influence the aggregation and activity of RecA. In low salt conditions, RecA is a DNA-dependent ATPase. However, prior research demonstrated that high salt concentrations allow RecA to hydrolyze ATP in the absence of DNA and at levels comparable to those obtained in the presence of DNA [Pugh, B. F. and Cox, M. M. (1988) *Journal of Biological Chemistry* 263, 76-83]. We have used circular dichroism (CD) and fluorescence spectroscopies to better understand the salt-induced effects on RecA structure and function. CD and fluorescence studies were performed in order to monitor the thermally induced unfolding of RecA in the presence of a variety of salts. We found that different salts had unique effects on RecA unfolding transitions and stability. Unfolding studies performed under salt conditions known to activate RecA's ATPase activity showed unique, thermally stable RecA structures. A comparison of the influences of different ions on RecA unfolding will be presented. These studies may help to elucidate how different ions influence RecA activity, structure, aggregation, and stability.

Using Difference Infrared Spectroscopy to Investigate the Effects of pH on PGK-Substrate Complexes

Adam Colbert and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

Yeast phosphoglycerate kinase catalyzes the reversible phosphate transfer in the reaction: $\text{ADP} + 1,3\text{-bis-phosphoglycerate} \leftrightarrow \text{ATP} + 3\text{-phosphoglycerate}$. Prior research indicates a hinge-bending mechanism occurs during catalysis to bring the substrates into closer proximity. Domain closure is only initiated in ternary complexes, in which both substrates are simultaneously bound to the enzyme. The activity and conformation of PGK is directly influenced by substrate and salt concentrations as well as pH. For example, activity assays confirm that PGK activity increases from pH 6.5 to 7.5. To determine the effects of pH on the conformational changes of PGK, we used difference Fourier transform infrared spectroscopy (FTIR) in conjunction with caged nucleotides. Difference infrared data associated with nucleotide (ATP or ADP) binding to PGK or PGK-3PG complexes was compared at pH 5.5, 6.5 and pH 7.5. Circular dichroism was also used to study PGK secondary structure at the aforementioned pH conditions. Comparison of the difference FTIR data allowed the isolation of pH dependent vibrations that arise from protein conformational changes induced by substrate binding. We have identified multiple vibrations that are associated with the PGK ternary complex and are influenced by pH. Difference FTIR studies resulted in the identification of specific changes within amino acid side chains and protein secondary structures that are altered by pH and associated with ternary complex formation.

Inorganic Ions, Trace Elements and Sediment Loading in the South Fork Shenandoah River and Cub Run During Storm Runoff Events

Nicholas Dugan and Daniel M. Downey

Department of Chemistry and Biochemistry, James Madison University

Since 2004 large numbers of fish have been killed in the Shenandoah River and its major tributaries following storm runoff events during the months of April and May each year. In order to establish the importance of water chemistry in these kills, concentrations of common inorganic ions (sodium ion, ammonia/ammonium-nitrogen, potassium ion, magnesium ion, calcium ion, chloride ion, nitrate-nitrogen and sulfate) and trace elements (Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Th, and U) were determined in samples collected during Spring 2008 runoff events. Samples were taken over a period of six weeks from the South Fork of the Shenandoah River (SFSR) and Cub Run. Major ions and trace elements were determined by Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry, respectively. Measurements made at the time of collection included pH, conductivity, water temperature, turbidity and discharge. It has been suggested that elevated ammonia concentrations from land application of fertilizer and animal waste could be a contributor to the fish mortality. We found no samples that contained ammonia-nitrogen more than 22.1% of the VADEQ acute criterion. All of the other ions and trace metals were found at concentration values significantly below VADEQ criteria. However, turbidity and suspended sediment values were large during storm runoff events. At the SFSR sampling location, a single storm at the end of April transported 2,900 metric tons of suspended solids down the river during an eight day period. We believe loading of suspended solids in the SFSR is a significant stress factor and may be a contributing factor in the fish kills.

Characterization of *N*-Acylethanolamine-hydrolyzing Acid Amidase Toward a Novel Class of Anti-Inflammatory Agents

Robert E. East, Courtney N. Braxton, and Victoria L. Mariani

Department of Chemistry and Biochemistry, James Madison University

Fatty acid derivatives where the carboxylate function is amidated by the primary amine of ethanolamine form a class of bioactive lipids referred to as *N*-acylethanolamines (NAEs). These NAEs possess a variety of biological activity. However, NAEs are hydrolyzed to their free fatty acids and ethanolamine by amidohydrolases. *N*-Palmitoylethanolamine (PEA), a saturated NAE which exhibits anti-inflammatory, immunosuppressive, anti-nociceptive, antioxidant and neuroprotective effects, is the most active substrate of *N*-acylethanolamine-hydrolyzing acid amidase (NAAA), a lysosomal amidohydrolase. NAAA has sequence homology and functional similarity to acid ceramidase (AC), a lysosomal amidohydrolase responsible for the degradation of ceramide into sphingosine and fatty acid. The recombinant enzyme of NAAA was cloned and purified. Cloning of recombinant AC has thus far been attempted. A fluorophore-coupled PEA analog was synthesized as a substrate in order to functionally characterize NAAA to its potential as a target for inhibitory drug design

Analysis of Organic Pesticides in the South Fork Shenandoah River and Cub Run in Storm Runoff Events

Stephanie Hall and Daniel M. Downey

Department of Chemistry and Biochemistry, James Madison University

Water samples were taken during April/May 2008 storm events from the South Fork of the Shenandoah River (SFSR) and Cub Run (SFSR tributary). This study was conducted as part of an effort to identify and quantify contaminants that may be contributing to mysterious fish kills in the river system. A total of 166 storm event water samples were collected, processed and analyzed by standard methods. One liter of each water sample was extracted by solid phase extraction, desorbed, concentrated to one mL, and injected into a gas chromatograph - electron capture detector (GC-ECD) or gas chromatograph - mass spectrometer (GC-MS). The organochlorine group that was analyzed on the GC-ECD included 35 compounds in widespread use in the Shenandoah Valley including heptachlor, chlorpyrifos, and dieldrin.

The GC-MS was used for the analysis of 9 compounds of the triazine group including atrazine and simazine. For the majority of samples, no pesticides were found above method detection limits. Two pesticides, heptachlor exo-epoxide and alpha BHC, have been found in the majority of samples. The concentration of heptachlor exo-epoxide was not more than 54.2% and 42.7% of the VADEQ acute criterion in the Shenandoah River and Cub Run, respectively. These results were compared to passive sampler results from the Virginia Department of Environmental Quality. Heptachlor exo-epoxide was the only contaminant that increased with stream discharge increase following a storm. Sediment analysis also performed on the samples showed increased concentration of heptachlor exo-epoxide with increased sediment. The literature shows that heptachlor exo-epoxide adheres to sediment, which suggests the pesticide travels in the river with the sediment.

Synthesis and Colloidal Properties of Novel Biscationic Bicephalic (Double Headed) Amphiphiles

Kristina M. Hamill and Kevin L. Caran

Department of Chemistry and Biochemistry, James Madison University

The synthesis of a family of novel amphiphiles with two cationic headgroups and a single hydrocarbon chain connected to a central benzene ring has been prepared. The series of amphiphiles were synthesized (in three steps each) with the two trimethylammonium headgroups in different positions relative to a tetradecyloxy chain. The headgroups are in the 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5- positions. Furthermore, the dependence of the colloidal properties on chain length was assessed by studying 2,5-derivatives with chain lengths ranging from 10-18 carbons. A monocationic derivative with the same aromatic ring and 14 carbon chain was also prepared for comparison. The Kraft temperatures of the final products were determined using differential scanning calorimetry (DSC) and conductivity. The critical micelle concentrations (cmc) were determined using conductivity and confirmed using ¹H NMR. Results show that the addition of a second headgroup increases the hydrophilicity of the amphiphile and results in an increase in cmc and a decrease of Kraft temperature and ionization degree (α). The decrease in α is attributed to partial dehydration of the headgroups due to greater exposure of the hydrophobic arene to water than the arene of the single-headed derivative at the micelle surface. Preliminary data on the antibacterial properties of these novel amphiphiles will also be presented.

The Effect of Structure Modification on Low-Molecular-Weight Organogelators

Paris Hamilton,¹ Marilise Hyacinth,² Kevin L. Caran,¹ Lin Pu² and Michal Sabat²

¹ Department of Chemistry and Biochemistry, James Madison University

² Department of Chemistry, University of Virginia

A family of multifunctional alcohols was synthesized and tested to determine their capacity to form gels in a variety of solvents. Each of these alcohols has a pentafluorophenyl ring and a second aromatic ring (phenyl, 1-naphthyl, 2-naphthyl, 9-anthracenyl, or tetrathiafulvalene) connected either directly or with an alkyne spacer, to the alcohol carbon. For those compounds that formed stable gels, concentration studies were performed to determine the lowest concentration necessary for gel formation. Furthermore, the thermostability of the gels was determined using the ball-drop method. To develop an aggregation model, ATR-IR was used to detect the presence of OH...O hydrogen bonding between molecules. Also, diffraction data from the gels were compared to simulated powder patterns of the analogous single crystal X-ray structures to determine whether the molecular organization in the gel was related to that of the solid state. The affects of chirality on the gel formation ability will also be discussed.

Characterization of Magnetic Iron Oxide Composites

Hollins Kitts, Kevin Kindley, Allyson Jones and Kathryn Layman

Department of Chemistry and Biochemistry, James Madison University

In order to remove metal cations from contaminated ground water, magnetic iron oxide composites are being investigated. These composites can be supported on various ratios of NaY zeolites, aluminum oxide, and silica. A previously published procedure to synthesize these composites was varied in order to create a more effective and practical adsorbent. The composites were then characterized using IR spectroscopy, the magnetic susceptibility balance, and the x-ray power diffractometer (XRD). In order to determine the amount of Cu²⁺ uptake by the composite, atomic absorption (AA) was used. Prior research has shown that 25°C is the optimal temperature for the synthesis of these composites. The amount of Cu²⁺ uptake and the magnetic susceptibility were influenced by six factors: 1) whether or not the support was added prior to the formation of the iron oxide particles; 2) the support to iron oxide mass ratio; 3) the type support used; 4) the source of iron; 5) the stirring time; and 6) the amount of time it took to add the NaOH. The type of support used determines the degree of correlation between the amount of Cu²⁺ uptake and the magnetic susceptibility. XRD data shows that the zeolite support with the SiO₂: Al₂O₃ ratio equal to 4.9 was best able to maintain its structure. These metal composites have also shown unselective reactivity in the oxidation of *p*-cresol.

The Synthesis of a Chlorotricarbonylrhenium I Complex of [4, 4'- bis(aminomethyl)-2,2'-bipyridine]

Puja Mody, Amanda Hoffman, Seth Ensign and Debra L. Mohler

Department of Chemistry and Biochemistry, James Madison University

In order to elucidate the fundamental factors that influence the efficiency in solar cells, a variety of functionalized bipyridine ligands are being tested to determine the anchoring group's influence on interfacial electron transfer between the rhenium complexes of the ligands and semiconductor nanoparticles. Specifically, the effect of anchoring amino groups is being examined. The synthesis and properties of the chlorotricarbonylrhenium(I) complex of [4, 4'- bis(aminomethyl)-2,2'-bipyridine] will be discussed.

The Synthesis of 1,2-Disubstituted Cyclobutenes for Study with Difluorocarbene

Tracy Nichols and Scott Lewis

Department of Chemistry and Biochemistry, James Madison University

The synthesis of 1,2-disubstituted cyclobutenes was undertaken in order to study their chemistry with difluorocarbene. The compounds 1-methyl-2-pentylcyclobutene and 1-hexylcyclobutene were prepared by using a modified version of the Negishi procedure. Scale-up of 1-methyl-2-pentylcyclobutene and 1-hexylcyclobutene are currently in progress. Details of their synthesis as well as plans for future studies will be discussed.

Developing a Bacterial Treatment Using *Janthinobacterium lividum* for Amphibians *Rana muscosa* and *Plethodon cinereus* Infected with *Batrachochytrium dendrobatidis*

Christian R. Schwantes,¹ Devon C. Flaherty,² Jenifer L. Banning,² Matt H. Becker,² Rob M. Brucker,² Reid N. Harris,² Kevin P. C. Minbiole,¹ and Doug C. Woodhams²

¹ Department of Chemistry and Biochemistry, James Madison University

² Department of Biology, James Madison University

Chytridiomycosis, an amphibian disease caused by the fungus *Batrachochytrium dendrobatidis*, can be fought by metabolites produced by bacteria that live on amphibian skin. We have investigated a particular bacterium, *Janthinobacterium lividum*, and its ability to protect the mountain yellow-legged frog, *Rana muscosa*, and the red-backed salamander, *Plethodon cinereus* from *B. dendrobatidis*. Previous research has shown that *J. lividum* produces indole-3-carboxaldehyde and violacein, two antifungal compounds. In two separate experiments, frogs and salamanders received both the pathogen and the bacterium to determine if *J. lividum* is an adequate way of protecting the species. In the *R. muscosa* experiment, the group given *J. lividum* as well as *B. dendrobatidis* had 100% survival, however only one of the six frogs given the fungus alone survived. Similar survival rates were seen in the *P. cinereus* experiment, with 75% survival in the group given *J. lividum* and *B. dendrobatidis*, and 53% survival in the group given only *B. dendrobatidis*. Violacein concentrations on each individual were measured by HPLC analysis of skin samples. Violacein was present on most individuals; however, in groups with *B. dendrobatidis* and *J. lividum*, the average concentration was higher than groups with just *B. dendrobatidis* or just *J. lividum*, suggesting the bacterium is fighting the fungal infection via production of violacein. These results indicate that bioaugmentation with *J. lividum* may be a successful protective strategy for amphibians that are susceptible to chytridiomycosis in captivity or even in the wild.

Preparation and Spectral Characterization of $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$

Vanessa Shepperson, John W. Gilje and Donna S. Amenta

Department of Chemistry and Biochemistry, James Madison University

In solution Roper's Complexes, $\text{Ru}(\text{CO})_2(\text{PR}_3)_3$, readily dissociates a phosphine ligand to generate an unsaturated, reactive species that binds small molecules including alkynes, alkenes, and dihydrogen. Roper's Complexes have important uses in the catalysis of organic reactions, including the Murai olefin coupling reaction. We are interested in preparing analogs of the traditional Roper's Complexes that contain $\text{R}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{R}_2$ ligands. These ligands can potentially coordinate through both the phosphino phosphorus and the phosphoryl oxygen atoms. Such chelate formation might stabilize the species that forms after ligand dissociation and allow new chemistry to be developed. Reaction of $\text{Cl}_2\text{Ru}(\text{CO})_3\text{thf}$ dissolved in acetonitrile at -5°C with one equivalent of methanolic NET_4OH followed by the rapid, sequential addition of three equivalents of $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ in methylene chloride at -5°C and three equivalents of methanolic NET_4OH yielded an orange solid. This solid showed IR bands at 1889 and 1834 cm^{-1} , which can be compared to 1898 and 1845 cm^{-1} in $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{Me})_3$. Additionally, the ^{31}P NMR chemical shifts indicate that the PR_2 groups are coordinated to Ru, while the $\text{P}(\text{O})\text{Ph}_2$ moieties are not. The ^{31}P spectrum can be interpreted in terms of a second order $\text{AA}'\text{A}''\text{XX}'\text{X}''$ spin system with 60 Hz coupling between phosphorus atoms in the three PR_2 groups. This data is consistent with the complex being $\text{Ru}(\text{CO})_2(\text{PPh}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$. Additionally, preliminary data for the reaction of $\text{Ru}(\text{CO})_3(\text{PPh}_2)_2$ with $\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$ have been obtained.

pH Dependence of the Formal Hydrolysis of DNA Phosphodiester and the Study of the Location of Cleavage by $[\text{CpFe}(\text{CO})_2]_2$ and Hydrogen Peroxide

Danielle Simpson, Paul Layne, Chelsea Cockburn and Debra L. Mohler

Department of Chemistry and Biochemistry, James Madison University

Cleaving DNA in a hydrolytic manner with synthetic agents is becoming very important in molecular biology, either by serving as models for restriction enzymes or by targeting specific DNA sequences to block gene expression. The organometallic compound $[\text{CpFe}(\text{CO})_2]_2$ in the presence of peroxide performs the formal hydrolysis of plasmid DNA. To determine the mechanistic details of this DNA cleavage, its kinetics, temperature dependence, pH dependence, and sequence selectivity are being examined. Here, the outcome of the pH dependence studies of this process will be described, as will preliminary work towards developing Southern blotting as a method for determining the sequence selectivity of strand scission.

Analysis of Glyphosate in the South Fork Shenandoah River and Cub Run Following Storm Runoff Events

Jacob Smith and Daniel M. Downey

Department of Chemistry and Biochemistry, James Madison University

From 2004 through 2007 fish kills occurred in Virginia's Shenandoah River in April and early May. Although lesions and parasites were cited as the cause of mortality, they are thought to be the result of elevated stress levels in the fish population. Previous studies of the Shenandoah River Fish Kills have focused on physical and environmental factors such as water temperature and discharge. Chemical contaminants may also be stress contributing factors. Conservation farming, widely used in the Shenandoah Valley, employs various herbicides for weed removal rather than plowing. An herbicide commonly known as RoundUp™ which contains the active ingredient glyphosate (or one of its salts) is used extensively in the Shenandoah River watershed. Glyphosate has acid-base properties and cannot be extracted or concentrated by the same methods used for the analysis of other pesticides, nor can it be determined at low levels by GC-MS or GC-ECD, which are the main analysis methods used for other pesticides. We have developed an alternative method of analysis for glyphosate that uses evaporation concentration followed by anion exchange chromatography. A strong anion eluent of pH 11.6 resolved the glyphosate anion ($R > 1.25$) from common anions present in the water samples. The detection limit for our method was $1.2\text{ }\mu\text{g/L}$, which compares favorably to the LC-fluorescence detection limit. We have used this method to determine the concentrations of glyphosate in the South Fork Shenandoah River and Cub Run, a tributary, during April and May of 2008. The highest concentration of glyphosate found in any sample was $44.8\text{ }\mu\text{g/L}$, 6.39% of the EPA maximum concentration level of $700\text{ }\mu\text{g/L}$.

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

Dien Tu, Andrew Evangelista, Amanda Hoffman and Debra L. Mohler

Department of Chemistry and Biochemistry, James Madison University

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

Proton Chemical Shifts for Alcohols in the Vapor Phase and Dilute Solutions

Curtis White and Thomas C. DeVore

Department of Chemistry and Biochemistry, James Madison University

Alcohol molecules form hydrogen bonded clusters in solution and the chemical shift observed for the OH proton is known to depend on the concentration of the alcohol and provides an indication of the amount of cluster formation. Quantitative information can be obtained if the chemical shifts for the pure species can be established, for instance by using high level Hartree-Fock or density functional theory calculations. Calculations at various levels of theory are compared to the measured chemical shifts in the proton NMR spectrum of methanol, ethanol, 2-propanol, and 2-methyl 2-propanol in the vapor phase and 2-methyl 2-propanol in dilute toluene, chloroform, and acetone solutions. While the relative chemical shifts agree well with the measurements made for the vapor molecules, the absolute chemical shifts differ by ~ 2 ppm, suggesting that the air introduces an absolute shift to the spectrum. The high level calculations for methanol are fast enough for use in a laboratory.