

## Chemistry Oral Presentations Abstracts

### **C1. Predicting Catalytic Parameters of Enantioselective Oxidations by CYP2C19 Using a Chirality Code and Artificial Neural Networks**

Jessica H Hartman, Steven D Cothren, Jerry A Darsey, Grover P Miller

University of Arkansas for Medical Sciences; University of Arkansas at Little Rock

Artificial neural networks incorporating chirality codes have proven to predict chiral reactions; however, their applications have been mainly limited to non-enzymatic reactions. In this study, we identify the most optimal artificial neural network employing chirality codes to predict the Michaelis constant ( $K_m$ ), maximum turnover rate ( $k_{cat}$ ) and efficiency ( $k_{cat}/K_m$ ) of a diverse array of enantioselective reactions catalyzed by CYP2C19. The physicochemical properties and optimized three-dimensional structure were determined using ab initio methods with Gaussian software. The resulting structures and properties were used to generate chirality codes for respective enantiomers. These codes served as inputs to a back propagation neural network. The validity of the architecture of the neural network was validated by a leave-one-out cross-correlation analysis for each network. The best networks are being interrogated by predicting the catalytic parameters for the previously uncharacterized metabolism of (R)- and (S)-naproxen by CYP2C19. Taken together, these findings provide a critical foundation for expanding the application of powerful artificial neural networks to enantiospecific enzymatic reactions. Ab ID: 94

### **C2. Theoretical Justification for Bond Valence - Bond Length Empirical Correlations**

Summer Laffoon, Franklin D Hardcastle

Arkansas Tech University, Russellville, AR

Linus Pauling's electrostatic valence principal, also referred to as the valence sum rule and found to apply to both covalent and ionic bonds, dictates that the sum of the bond valences around an atom is equal to its atomic valence or formal oxidation state (electrons used for bonding). Pauling (1947) was the first to determine the empirical logarithmic dependence of bond order ( $s$ , valence) to bond length,  $R$ , using  $R_0$  as the bond length of unit valence and is an empirical fitting parameter. Since then values were experimentally found to range from 0.32 to 0.42 for many bonds, and as high as 0.7 between soft and hard ions. A common practice, however, is to consider the parameter as a universal constant equal to 0.37. In the present study, we define the bond valence in terms of radial wave-function overlap of hydrogen-like orbitals which allows us to derive Pauling's empirical relationship. We present a theoretical expression for the parameter which allows the systematic determination of bond valence bond length correlations for any chemical bond. Ab ID: 111

### **C3. Design of an Electrospray Ionization (ESI) Source for the Study of Gas-Phase Reactions of Ligated Transition Metal Ions**

Li Chen Chen, William S Taylor

University of Central Arkansas, Conway, AR

Previous studies in our laboratory have shown that reactions involving bare transition metal ions often produce ligated metal products. It is desirable to examine the reactions of these ligated metal ions. However, the current methods of ion production in our reactor are not adequate to produce these species. The primary goal is to extend the versatility of the selected ion drift cell reactor. In order to study reactions with these ligated ions, implantation of an ESI source is necessary to address this deficiency. A hybrid ESI source has been designed specifically to be compatible with our instrument. Unique design details will be discussed. Ab ID: 101

### **C4. State-Specific Reactions of Gas Phase Ni with CH<sub>3</sub>X and CF<sub>3</sub>X (X=Br,I): Evidence of Selective Halogen Abstraction**

Kendall G Fancher, Li C Chen, Ashley J Hicks, Casey A Cameron, William S Taylor

University of Central Arkansas, Conway, AR

The gas-phase reactions of ground and excited state Ni with CH<sub>3</sub>X and CF<sub>3</sub>X (X=Cl, Br, I) were examined in a selected ion drift cell apparatus. Ni was prepared in a sputtering glow discharge utilizing either Ne and Ar to yield different excited state distributions. State-specific product formation was determined using electron state chromatography. The ratio of excited state to ground state Ni ions was deduced using arrival time distribution (ATD) patterns and mass spectrometry. These experiments have revealed that under near-thermal conditions, Ni (2D) (the ground state) produces association products exclusively while Ni excited states can abstract X to form NiX. Excited states of Ni with sufficient energy can also participate in charge-transfer with all four neutrals. State-specific kinetic measurements display a broad range of reaction efficiencies for both ground and excited state metal ions. In general, a Ne discharge was found to produce more excited state ions than an Ar discharge. While several excited Ni states may be present during these reactions, overall energetic and spin requirements limit production of NiX to excited doublet states. In combination with the kinetic results, this suggests the presence of one or more unreactive excited states. Ab ID: 103

### **C5. CYP2C19-catalyzed metabolism of R- and S-warfarin and potential inhibition by hydroxywarfarin metabolites**

Sun-ha Park, So-Young Kim, Drew R Jones, Jessica H Hartman, Chul-Ho Yun, Grover P Miller  
Chonnam National University, Gwangju, South Korea, University of Arkansas for Medical Sciences

The clinical importance of CYP2C19 in Coumadin (R/S-warfarin) metabolism and the corresponding effects on patient response to anticoagulant therapy is controversial because of conflicting findings from genetic studies and reported drug-drug interactions. A mechanistic basis for these observations is not possible due to limited details on CYP2C19 metabolism of warfarin by others. To address this gap in knowledge, we investigated the metabolic efficiency of recombinant CYP2C19 toward R- and S-warfarin under steady-state conditions and the inhibitory potential of hydroxywarfarin metabolites that accumulate in patients undergoing warfarin therapy. CYP2C19 metabolized R-warfarin to R-6-, 7-, and 8-hydroxywarfarin as major metabolites, while producing R-4-hydroxywarfarin as a minor metabolite. These differences manifested in variations in V<sub>max</sub> and not K<sub>m</sub>, which were similar among the reaction pathways. For the reaction with S-warfarin, CYP2C19 generated the same relative products, although less efficiently. When compared to R-warfarin parameters, V<sub>max</sub> and K<sub>m</sub> values for S-warfarin were about 50% lower and 10- to 20-fold higher, respectively. The corresponding catalytic efficiencies (V<sub>max</sub>/K<sub>m</sub>) suggest CYP2C19 is likely a major metabolizer of R-warfarin but a minor one for S-warfarin. Our findings contrast with previous studies using human liver microsomes that implicated a much less important role for CYP2C19 in R- and S-warfarin metabolism. Nevertheless, the analysis of data from that work was complicated by the contributions of other metabolizing enzymes, which is not the case in our studies with the recombinant enzyme. CYP2C19 activity was also susceptible to inhibition by hydroxywarfarin metabolites. The corresponding K<sub>i</sub> values indicated hydroxylation of warfarin has variable but relatively minor effect on binding and hence inhibition of CYP2C19 activity. Collectively, our findings suggest that the biological relevance of CYP2C19 during anticoagulant therapy most likely manifests in its role in R-warfarin and not S-warfarin metabolism, and possibly depends on levels of hydroxywarfarin metabolites. Ab ID: 168

### **C6. Electrodeposition of Copper Indium Disulfide Films Using Photovoltammetry and Rest Potentials**

M. Jason Newell, Robert Engelken, Maqsood Ali Mughal, John Hall, Joshua Vangilder, Frederick Felizco, David McNew, Shyam Thapa, Elizabeth Hundley, Bruce Johnson, Ross Carroll  
Arkansas State University-Jonesboro, AR

We report research on the electrodeposition of CuInS<sub>2</sub> from ethylene glycol baths in a three electrode setup with graphite anode and Ag/AgCl reference electrode. CuInS<sub>2</sub> has attracted attention as a solar cell material less toxic than CdTe or CuInSe<sub>2</sub> often used as absorber layers in thin film solar cells. Solutes included CuCl, InCl<sub>3</sub>, elemental sulfur, NaCl as a conductivity salt, and KI as a complexing/reducing agent in case of

formation of Cu (II) ions. Cyclic photovoltammetry and open-circuit voltage transient measurements over a range of deposition voltages were analyzed in order to understand the processes involved, including compound formation. Cyclic photovoltammetry was conducted with both indium tin oxide (ITO)-coated glass and Mo-coated glass substrates. ITO-coated glass allowed for the analysis of photoactivity at different applied voltages. Open-circuit transients were measured on Mo-coated glass. Cyclic voltammetry and open-circuit transient measurements were first performed with a solution of only sulfur and NaCl in ethylene glycol. Then  $\text{InCl}_3$  was added, and cyclic voltammetry and open-circuit transients repeated. Finally, CuCl and KI were added and the measurements repeated again. Analyses of data from these individual steps were compared to determine which processes were important for the formation of  $\text{CuInS}_2$ . This work is jointly sponsored by EPSCoR grants from both NASA/Arkansas Space Grant Consortium (# NNX09AW22A) and the National Science Foundation/Arkansas Science and Technology Authority (# EPS-1003970). Ab ID: 170

### **C7. Optimization and Characterization of the Electrodeposition Process for CdTe for Potential Solar Cell Applications**

Joshua Vangilder, Robert Engelken, Maqsood Ali Mughal, M. Jason Newell, David McNew, John Hall, Shyam Thapa, Elizabeth Hundley, Bruce Johnson, Ross Carroll  
Arkansas State University-Jonesboro, AR

We report on the continuation of research into electrodepositing semiconducting CdTe films. Electrodeposition is a low-cost, easily maintainable method for depositing thin films for solar cells, and can easily be scaled-up for mass production. Experimentation and characterization of the electrodeposition process for CdTe will be reported, along with the different factors that have been varied. These factors include the substrate, deposition temperature, and deposition voltage. Cyclic photovoltammetry was used to characterize the electrodeposition process, and examples of the photovoltammograms produced will be shown. This work is jointly funded by National Science Foundation Grant EPS 1003970 and NASA Grant NNX09AW22A, respectively administered by the Arkansas Science and Technology Authority (Dr. Gail McClure, Cathy Ma, and Marta Collier) and the Arkansas Space Grant Consortium (Dr. Keith Hudson and Laura Holland). The authors also thank the Principal Investigators on the projects, respectively Dr. Alan Mantooth and assistant Kathy Kirk (University of Arkansas-Fayetteville), and Dr. Tansel Karabacak (University of Arkansas-Little Rock). Ab ID: 171

### **C8. Taguchi Analysis and Characterization of Electrodeposited Indium (III) Sulfide ( $\text{In}_2\text{S}_3$ ) Films for use as Potential Buffer Layers in Solar Cells**

Maqsood Ali Mughal, Robert Engelken, M. Jason Newell, John Hall, Joshua Vangilder, Frederick Felizco, David McNew, Shyam Thapa, Elizabeth Hundley, Bruce Johnson, Ross Carroll  
Arkansas State University-Jonesboro, AR

We report continuing progress in electrodeposition of  $\text{In}_2\text{S}_3$  films from organic baths (ethylene glycol-based) containing indium salts,  $\text{InCl}_3$ , sodium chloride, NaCl, and sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , the latter used as an additional sulfur source along with elemental sulfur. Our initial task was to deposit material of good uniformity and adherence onto the substrate (indium tin oxide (ITO)-coated glass or molybdenum (Mo)-coated glass) with correct stoichiometric ratios for indium and sulfur (2:3). Experimental procedures were designed using Taguchi Orthogonal Arrays (TOA) based upon the Degree of Freedom (DOF) method. The measured performance characteristic (molar ratio of In:S) for all the  $\text{In}_2\text{S}_3$  films was used to analyze the effect of different factors (deposition voltage, deposition temperature, composition of solution, and deposition time) involved in the electrodeposition process by calculating the sensitivity (signal to noise,  $S/N$ , ratios). We performed characterization of  $\text{In}_2\text{S}_3$  films with a UV-VIS-NIR spectrophotometer to obtain reflectance and absorbance spectra, calculate the optical bandgap, and estimate the thickness of the deposited films. Scanning electron microscope (SEM) characterization helped us to study the surface morphology of the films and perform elemental analysis with energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) has

characterized the crystal structure of  $\text{In}_2\text{S}_3$  films that exhibited a  $\beta\text{-In}_2\text{S}_3$  structure without any post deposition annealing. Taguchi Orthogonal Regression Analysis (*TORA*) revealed that a cathode-to-reference electrode voltage of -0.685 V and a temperature of 150 °C yield the best adherence, uniformity, and stoichiometry (2 indium : 3 sulfur). A major problem to-date is the thickness of the films, currently around 400-500 nm, that needs to be increased in order to form a reliable p-n junction. Our ultimate goal is to couple n- $\text{In}_2\text{S}_3$  films with p-CuInS<sub>2</sub> or p-CdTe films to form heterojunction solar cells. This work is jointly sponsored by EPSCoR grants from both NASA/Arkansas Space Grant Consortium (# NNX09AW22A) and the National Science Foundation/Arkansas Science and Technology Authority (# EPS-1003970). Ab ID: 172

## **Chemistry Poster Presentations Abstracts**

### **C-1. Investigation of Contamination Levels in Southwest Arkansas Lake Water**

Katherine S Dockter, Tim S Schroeder  
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Lake Columbia, the drinking water reservoir for Columbia County in Southwest Arkansas, was recently notified of rising levels of ethylbenzene and xylenes by state testing agencies: the Arkansas Department of Environmental Quality (ADEQ) and the Arkansas Department of Health (ADH). At the request of local water officials, investigations were conducted to independently confirm or refute these reports and to locate the source(s) of any possible contaminations. Care was taken to collect samples from the same sources and locations, both at Lake Columbia and at the local water treatment facility, as those taken by the state agencies and to test them in a timely manner. Water samples were analyzed for organics by GC-MS with purge and trap sample introduction. Funding was provided through a SURF grant by the Arkansas Department of Higher Education. Ab ID: 87

### **C-2. Synthesis and Characterization of Pyrazolyl Methane Nickel Thiocyanate Complex**

Hee Kyung Jeon<sup>1</sup>, <sup>1</sup>Ganna Lyubartseva,<sup>1</sup>Uma Prasad Mallik<sup>1</sup> and Sean Parkin<sup>2</sup>

<sup>1</sup>Southern Arkansas University, Magnolia, AR, <sup>2</sup>University of Kentucky, Lexington, KY

Tripodal ligands with three pyrazolyl groups are increasingly being used in small-molecule modeling of the active sites of metallo-enzymes in which the metal is coordinated to two or three imidazole groups from histidine. In this work we synthesized and characterized nickel thiocyanate complex, bis[tris(1H-pyrazol-1-yl- $\kappa\text{N}^2$ )methane]nickel(II)bis{[tris(1H-pyrazol-1-yl $\kappa\text{N}^2$ )methane]tris (thiocyanato  $\kappa\text{N}$ )nickelate(II)} methanol disolvate. The nickel complex, [(tpm)<sub>2</sub>Ni<sup>II</sup>][[(tpm)Ni<sup>II</sup> (NCS)<sub>3</sub>]<sub>2</sub> · 2CH<sub>3</sub>OH where tpm= tris(pyrazol-1-yl)methane, is the asymmetric unit which consists of half a centrosymmetric bis[tris(1H-pyrazol-1-yl)methane]- nickel(II) cation and an octahedral nickelate(II) anion bound to one tpm and three thiocyanate ligands, and a methanol solvent molecule. There are O—H····S interactions between the methanol and the disordered thiocyanate anion, and a weak C—H····O hydrogen bond between the cation and the methanol oxygen atom. Ab ID: 89

### **C-3. Influence of Audience Response System Technology on Student Performance in Organic Chemistry Lecture Class**

Ganna Lyubartseva  
Southern Arkansas University, Magnolia, AR

The use of audience response system (commonly known as clickers) supports communication and interactivity in class by allowing the instructor to ask thought-provoking questions and encouraging students to articulate and reflect their thinking, reveal misconceptions, probe the knowledge and follow their progress in the course. Recent studies on the use of clickers in chemistry and physics courses indicate positive student attitudes, and several educators (Crouch & Mazur, 2001; Pollock, 2005; Gaddis et. al., 2006; Lin et. al., 2011) reported research on their effectiveness. Although there have been many reports which describe use of clickers in introductory science courses, there have been virtually no studies describing the effect of clicker use in advanced chemistry classes. In the present study we collected and analyzed student feedback on using clickers in Organic Chemistry courses and investigated the relationship between the use of clickers and student performance. Ab ID: 90

#### **C-4. A Study of Nutrient and Sediment Input in the Cache River Watershed**

Alisha Gilmer, Carlos Rosado Berrios, Jennifer L Bouldin

Arkansas State University-Jonesboro, AR

Contaminants in our watersheds have been a problem since land use changes were made by humans. Clearing the land for agricultural uses is needed to support our population; however, agricultural input is cited as the greatest input of suspended solids and nutrients to our waterways. Measuring various contaminants in our surface water and the quantity of them is useful in determining their origin, thus aiding in their elimination. Our study is focused in the Cache River watershed. In particular, we are measuring pH, dissolved oxygen, conductivity, turbidity, and suspended solids (TSS), NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and PO<sub>4</sub><sup>-</sup>, in this specific river's subwatersheds. In order to measure nutrients, we are using an OI Analytical Model DA3500 nutrient analyzer. Using this instrument, we determined that in this river, at particular sites, TSS NO<sub>3</sub>, NO<sub>2</sub>, and PO<sub>4</sub> concentrations differ due to varying sources of agricultural input. In the future, we hope to also measure seasonal total and dissolved nitrogen and phosphorus to determine the seasonal changes affecting the values. Ab ID: 138

#### **C-5. Synthesis and Characterization of Ruthenium Complex with Phenanthroline and chlorophenanthroline**

Anwar A. Bhuiyan, Jaehwan J. Lee, Albert R. Del Carmen

Arkansas Tech University, Russellville, AR

The study of the photophysical and photochemical properties of Ruthenium polypyridine complexes have been of great interest for a variety of fundamental and practical reasons. These complexes have been investigated for use in artificial photosynthesis and many biological electron transfer processes because of suitable redox properties, excited state reactivity, luminescent emission, and excited state lifetimes. It had been documented that ruthenium polypyridine complexes have potential use as efficient photoinitiators in biological electron transfer studies. This has prompted us to investigate the properties of such complexes. In this work Ru(phen)<sub>2</sub>(Cl-phen)(PF<sub>6</sub>)<sub>2</sub> (where Cl-phen = 5-chloro 1,10 phenanthroline and phen = 1,10 phenanthroline) complex was synthesized in a two step procedure. In the first step, cis-Ru(phen)<sub>2</sub>Cl<sub>2</sub> was prepared from one equivalent of RuCl<sub>3</sub>·3H<sub>2</sub>O and two equivalents of phenanthroline (phen) ligand. Then Ru(phen)<sub>2</sub>(Cl-phen)(PF<sub>6</sub>)<sub>2</sub> was prepared by the reaction of one equivalent of cis-Ru(phen)<sub>2</sub>Cl<sub>2</sub> and two equivalent of Cl-phenanthroline ligand. The compound was purified by column chromatography. The identity of the complex was confirmed by UV/Vis absorption, emission spectroscopic method, and cyclic voltammetric method. Ab ID: 151

#### **C-6. Comparisons of Sample Introduction Methods: Limits of Detection and Analytical Sensitivities in Inductively Coupled Plasmas**

Justin R May, Tim S Schroeder

Southern Arkansas University, Magnolia, AR

In atomic spectroscopy, it is widely accepted that sample introduction method variations have a significant impact on analytical signal. Typical sample introduction methods vary in their nebulization process and in their analyte transport efficiency, resulting in different analytical sensitivities during atomic emission or atomic absorption analysis. Under typical conditions, ultrasonic nebulization (USN) results in increased sensitivities and improved detection limits when compared to conventional pneumatic nebulization. When comparing the two techniques, most literature sources do not specify the extent to which analytical figures of merit are improved for individual elements, only that USN sample introduction offers better performance than conventional nebulization. This work is being done to quantify the differences in these nebulization techniques in our own laboratory and on our own instrument. Our study centers around determinations of the analytical sensitivities and the limits of detection for over 30 commonly analyzed elements ranging from main group metals, transition metals, and even some nonmetals such as sulfur and phosphorus. The instrument being used to perform this investigation is a Shimadzu ICPE-9000 inductively coupled plasma (ICP) with a conventional Meinhard-style pneumatic nebulizer and cyclonic spray chamber and for comparison, a Cetac U5000AT ultrasonic nebulizer. A series of standard solutions are prepared for each element of interest in order to determine calibration curve linearity, analytical sensitivity, and limit of detection values for each sample introduction method. The collected data will be summarized in this poster for easy comparison between the two techniques and will greatly benefit future atomic analysis in our laboratory. Ab ID: 162

### **C-7. Accuracy and Efficiency of the Hybrid Algorithm: Modeling AP-ESI Simulation**

Kenichiro Saito, Hideya Koizumi

Arkansas State University-Jonesboro, AR

Electrospray ionization (ESI) generates highly charged droplets through process of producing the gas phase ion from charged droplets at high pressure. Despite its importance and usefulness, its mechanism has not been completely understood due to a variety of phenomena such as evaporation, fission and aerodynamic drag affects that complicate simulations. We studied the process by a computer simulation for which may provide insight into the process mechanism and contribution to potential development of new designs and future mass spectrometry technology. The droplets undergo fission process several times during the drying stage. Smaller droplets should be located near the plume surface due to their small inertia, and our results agreed on that also. Simulation of each individual ten million particles is over the computational capacity of the system in our lab; hence, we defined a charge diffused cloud of many particles. The total charge in a cloud was defined as the number of particles times the average particle charge. We then tracked clouds' dynamics during the entire ESI process. This approach does calculations of both explicit two-body Columbic interactions in the cloud and ion-cloud interactions using only ~100 independent clouds instead of 10 million individual particles. This hybrid algorithm contributes on saving computational time while providing approximate results in few days. Ab ID: 157

### **C-8. Theoretical Investigation of M Vorinostat-18c6 and its Partition Coefficient (M=K & Na )**

Elizabeth G. Tyner, Eiko Koizumi, Hideya Koizumi

Arkansas State University-Jonesboro, AR

Recent studies support potential use of 18-crown-6 or 18c6 [1,4,7,10,13,16-hexaoxacyclooctadecane] in cancer treatment in which 18c6 and some in its derivative forms play a role as an ionophore transporter that carries Na ions across cell membranes. Some argue that Na imbalance may inhibit the cell replication process; however, there is not enough evidence to support if either 18c6 or its derivatives can cause enough K imbalance to work as effective antitumor agents. To address this issue and start a pilot study with a known antitumor agent of our interest, we have selected a supramolecular system of Vorinostat [N-hydroxy-N-phenyl-octanediamide] -18c6 and conducted a computational investigation of the structure and properties of the system, and that with K and Na . Presence of local dipole and interaction with solvent heavily influence the structure. To study such effects, we have calculated Na Vorionstat-18c6 in gas phase and two solution phases, in water, and octanol. Our analyses found a few statistically significant conformational isomers including tightly chelated geometries in

each case. In addition to geometrical results, we also calculated Log P values, generally used as a measure of lipophilicity, to discuss the effectiveness of Vorinostat-18c6 as an ionophore transporter and the Na imbalance issue. Ab ID: 158

### **C-9. Predicting Catalytic Parameters of Enantioselective Oxidations by CYP2C19 Using a Chirality Code and Artificial Neural Networks**

Jessica H Hartman, Steven D Cothren, Jerry A Darsey, Grover P Miller

University of Arkansas for Medical Sciences; University of Arkansas at Little Rock

Artificial neural networks incorporating chirality codes have proven to predict chiral reactions; however, their applications have been mainly limited to non-enzymatic reactions. In this study, we identify the most optimal artificial neural network employing chirality codes to predict the Michaelis constant ( $K_m$ ), maximum turnover rate ( $k_{cat}$ ) and efficiency ( $k_{cat}/K_m$ ) of a diverse array of enantioselective reactions catalyzed by CYP2C19. The physiochemical properties and optimized three-dimensional structure were determined using ab initio methods with Gaussian software. The resulting structures and properties were used to generate chirality codes for respective enantiomers. These codes served as inputs to a back propagation neural network. The validity of the architecture of the neural network was validated by a leave-one-out cross-correlation analysis for each network. The best networks are being interrogated by predicting the catalytic parameters for the previously uncharacterized metabolism of (R)- and (S)-naproxen by CYP2C19. Taken together, these findings provide a critical foundation for expanding the application of powerful artificial neural networks to enantiospecific enzymatic reactions. Ab ID: 94